Offline preparation of carbonates for $\delta^{13}C$ and $\delta^{18}O$ analysis via Gasbech-IRMS

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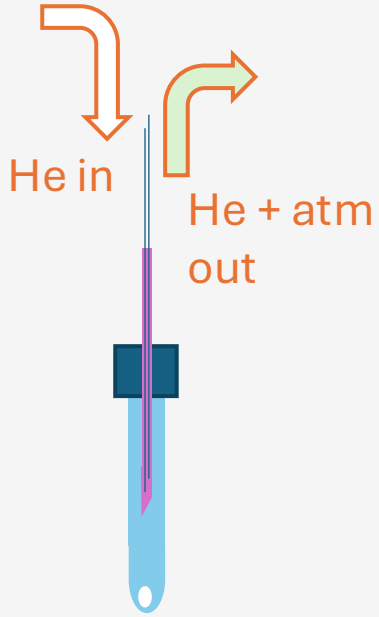
Why prep offline?

Overview of standard method



Flush 8 mins

1
Flush With He online using autosampler

Add 0.1 mL phosphoric acid

2
Manual injection of phosphoric acid to each vial

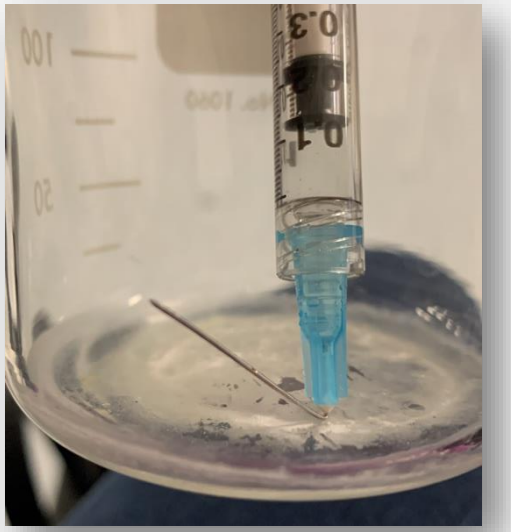
Gasbench + GCPal + IRMS system

3
Analysis

Why prep offline?

Potential issues with this method

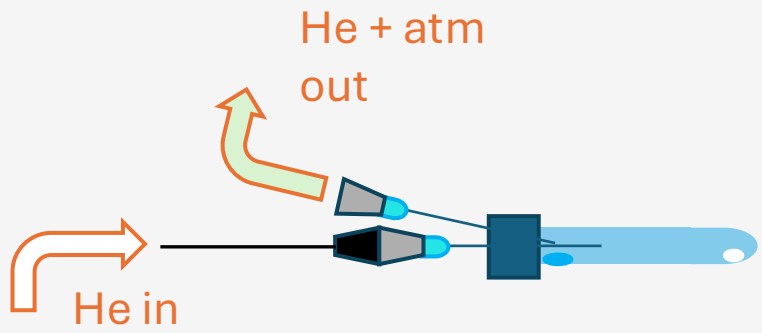
- **Use of concentrated acid outside a fumehood**
- Loss of sample through user error in acid delivery
- He consumption (minimal, but non-negligible)
- **Story time: the hazards of handling acid-filled syringes!**



Alternative Methods

Acid can be added before atmosphere is replaced with He:

1. Add acid and flush with He offline
- Samples weighed into vials
- Acid added via pipette to horizontal vials
- Capped and flushed with He while remaining horizontal
- Tipped upright and loaded into autosampler to react at set temperature



2. Add acid, evacuate under vacuum, pressurize with He
- Samples weighed into vials
- Acid added via pipette to horizontal vials
- Capped and evacuated under vacuum
- Slowly pressurized to slightly more than 1 atm
- Vials tipped upright and loaded into autosampler to react at set temperature

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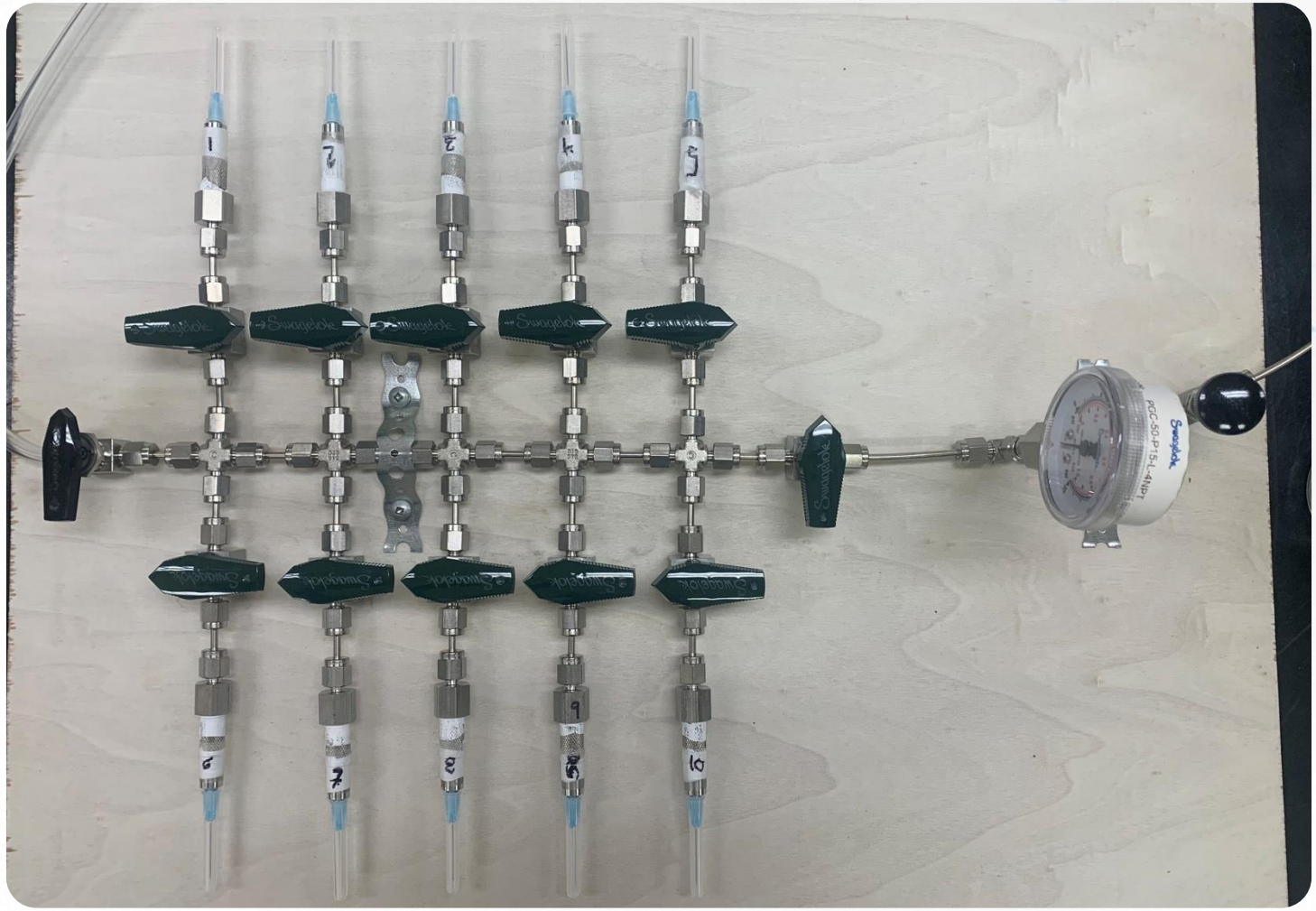
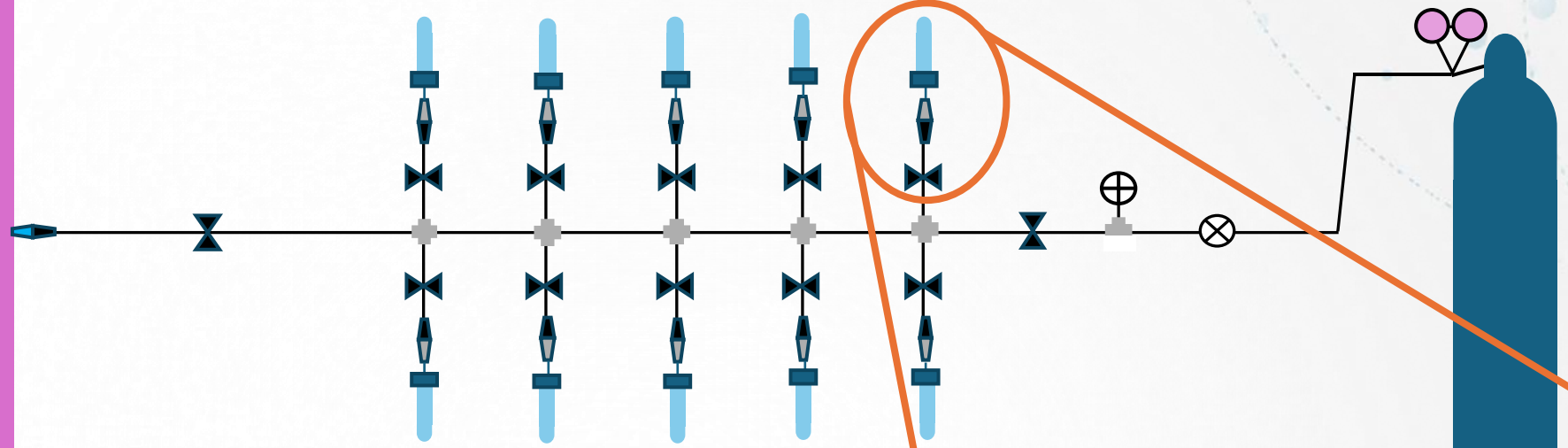
Possible benefits:
- Safety
- He consumption
- More precise + accurate $\delta^{18}O$ values?

Physical setup of vacuum/manifold system



Schematic of vacuum/manifold system

Vacuum line



Sample loaded into very bottom of vials.

With vials on their sides, 0.1ml acid is added to the shoulder of the vial.

Vials, still horizontal, are capped and the septa carefully pierced with a luer lok needle that has been twisted into place on the luer “plug” on the manifold.

Legend

- 1/8 female NPT to 1/8 swage (11)
- “socket” luer insert to 1/8 male NPT (1)
- Ball valve, 1/8” (11) (closed / open)
- “plug” luer port to 1/8 male NPT (10)
- Union cross, 1/8” (5)
- Union T, 1/8 swage + ¼ female NPT” (1)
- Inline P gauge (male ¼” NPT threads)
- Needle valve for P regulation, 1/8

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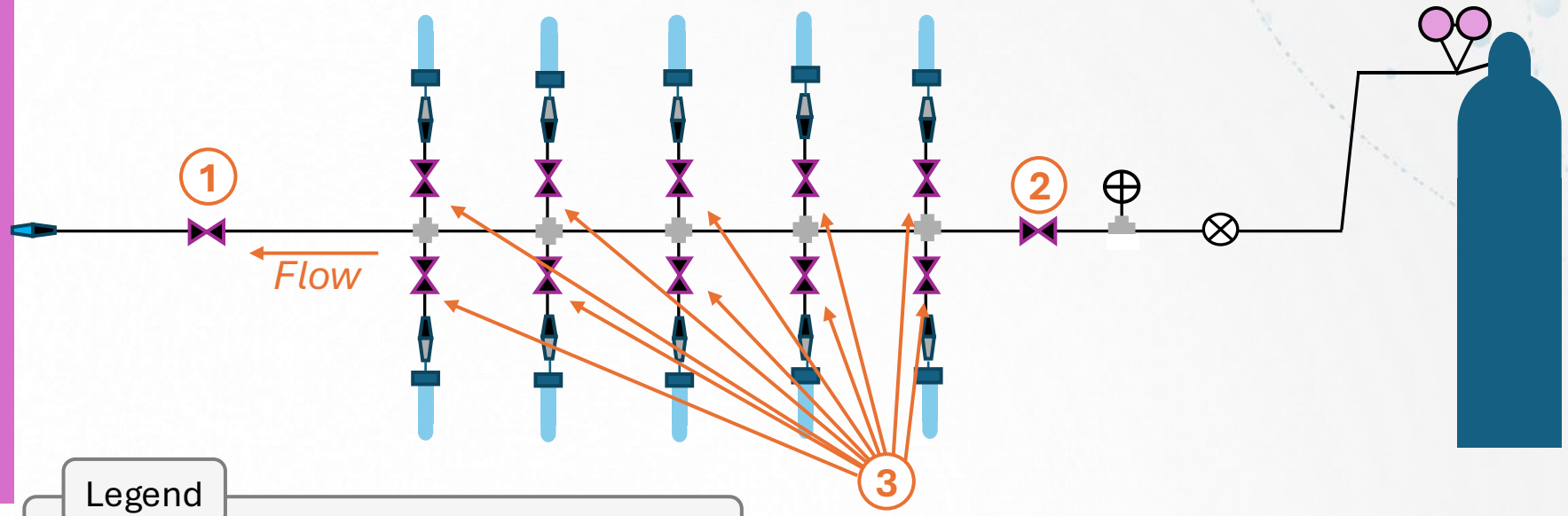

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Once ten vials are in place the line is evacuated.

Valves to vials must be opened **SLOWLY**.

It can take up to 15 minutes to reach baseline.

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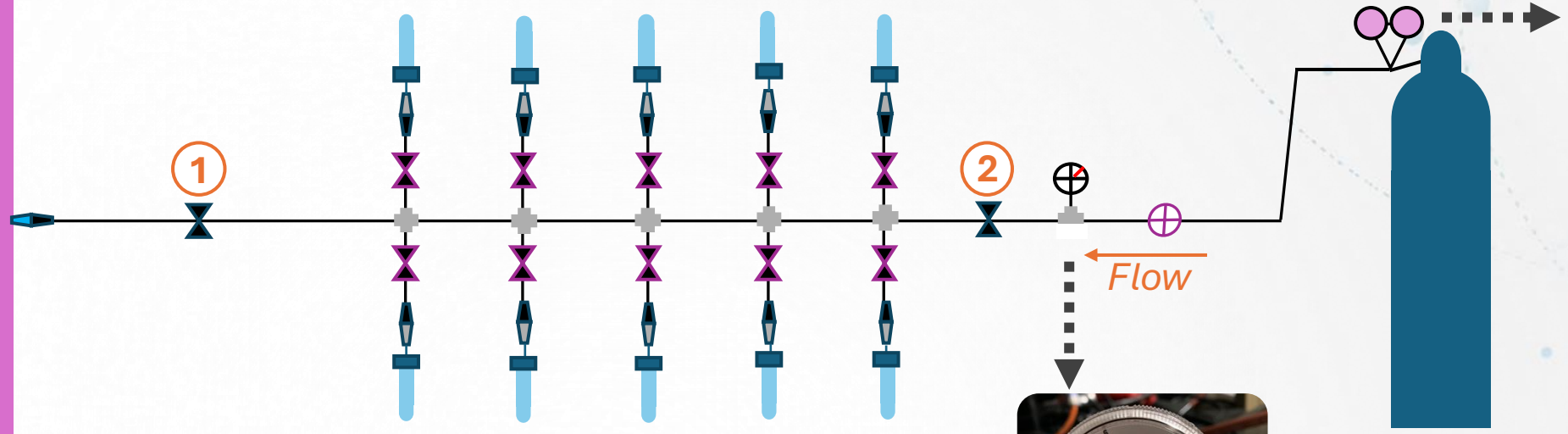
Vacuum line



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After closing to the vacuum, He is slowly released into the line (and vials) to ~1atm

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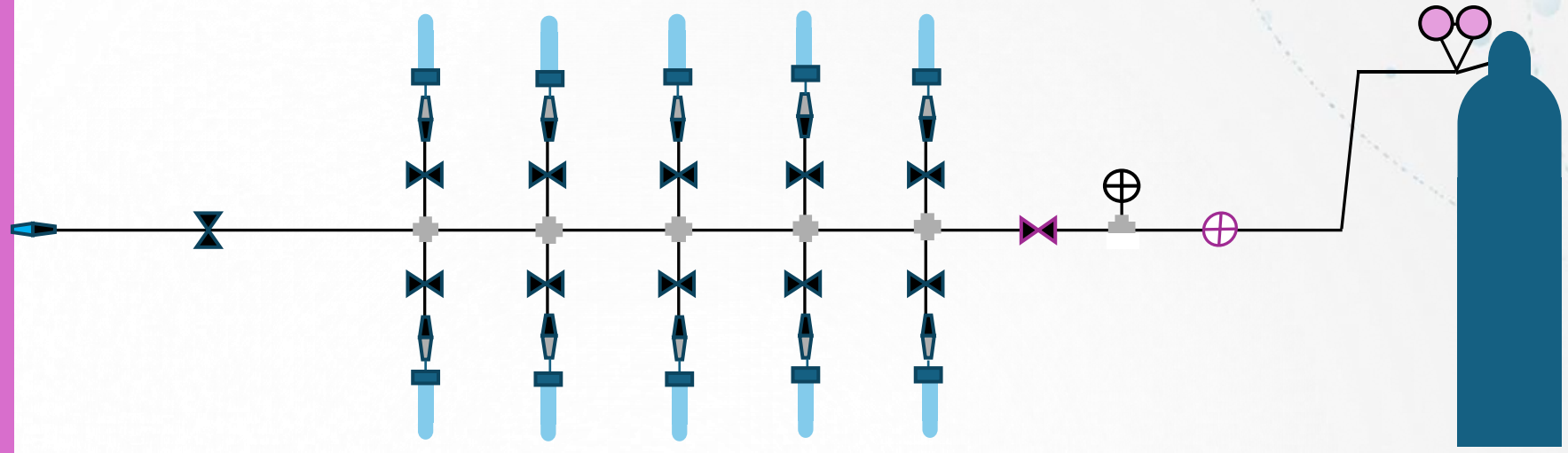

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The ball valves are closed and each vial is pulled off the needle

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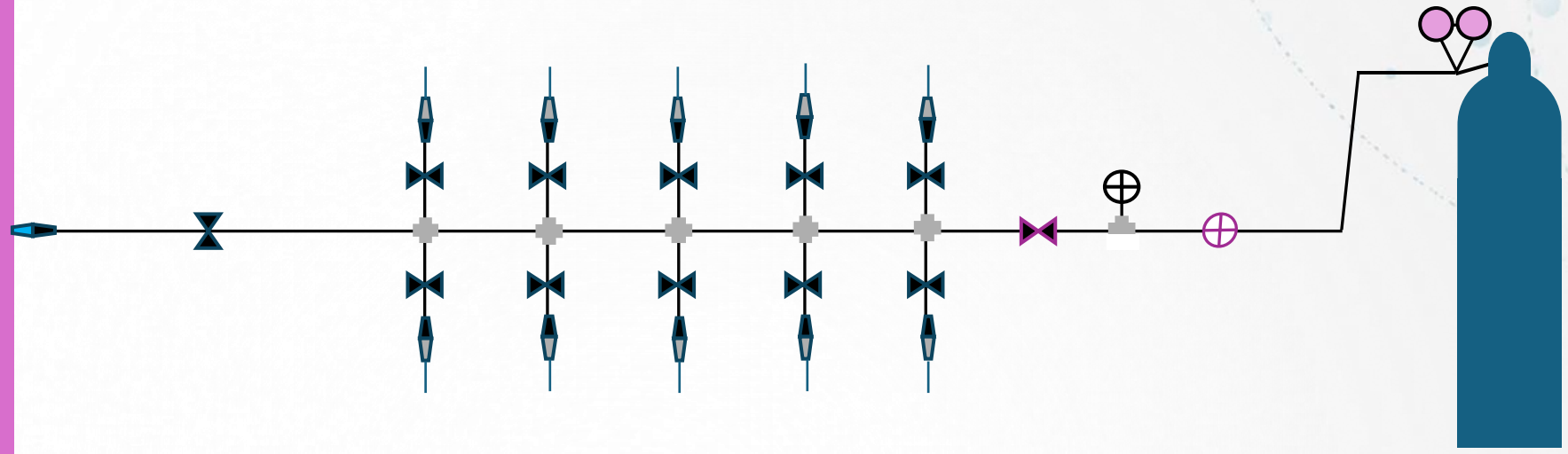

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Vials are then turned vertical to let the acid drip down to meet the sample, and immediately placed in the autosampler at 50°C.

Testing Setup

- Four reference materials commonly used in every run:
  - C7 = NBS-18
  - C6 = NBS-19
  - C132 = SPEX internal $CaCO_3$ standard
  - C5 = CBM internal $CaCO_3$ standard

$\delta^{18}O$ calibration: C7 = NBS-18, C6 = NBS-19

$\delta^{13}C$ calibration: C6 = NBS-19, C132 = SPEX internal $CaCO_3$ standard

- Each test condition included 5 replicates of each reference material
- Five test conditions
- All reference materials from all tests were analysed in the same run

Test Conditions

1. Whole line (10 vials) evacuation and fill, room temperature
   - Vacuum baseline 45uHg
   - Evacuation time ~15 min = ~1.5 min per vial

2. Single vial (port 1) evacuation and fill, room temperature

3. Whole line (10 vials) evacuation and fill, heat gun
   - Vacuum baseline 50uHg
   - Evacuation time ~18 min = ~1.8 min per vial

4. Single vial (port 1) evacuation and fill, heat gun

5. “old method” of flushing online with acid addition via syringe

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   - Vacuum baseline 45uHg
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2. Single vial (port 1) evacuation and fill, room temperature
   - Vacuum baseline ~27uHg
   - Evacuation time = ~3 min per vial

3. Whole line (10 vials) evacuation and fill, heat gun
   - Vacuum baseline 50uHg
   - Evacuation time ~18 min = ~1.8 min per vial

4. Single vial (port 1) evacuation and fill, heat gun
   - Vacuum baseline ~27uHg
   - Evacuation time = ~4 min

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1. Whole line (10 vials) evacuation and fill, room temperature
2. Single vial (port 1) evacuation and fill, room temperature
3. Whole line (10 vials) evacuation and fill, heat gun
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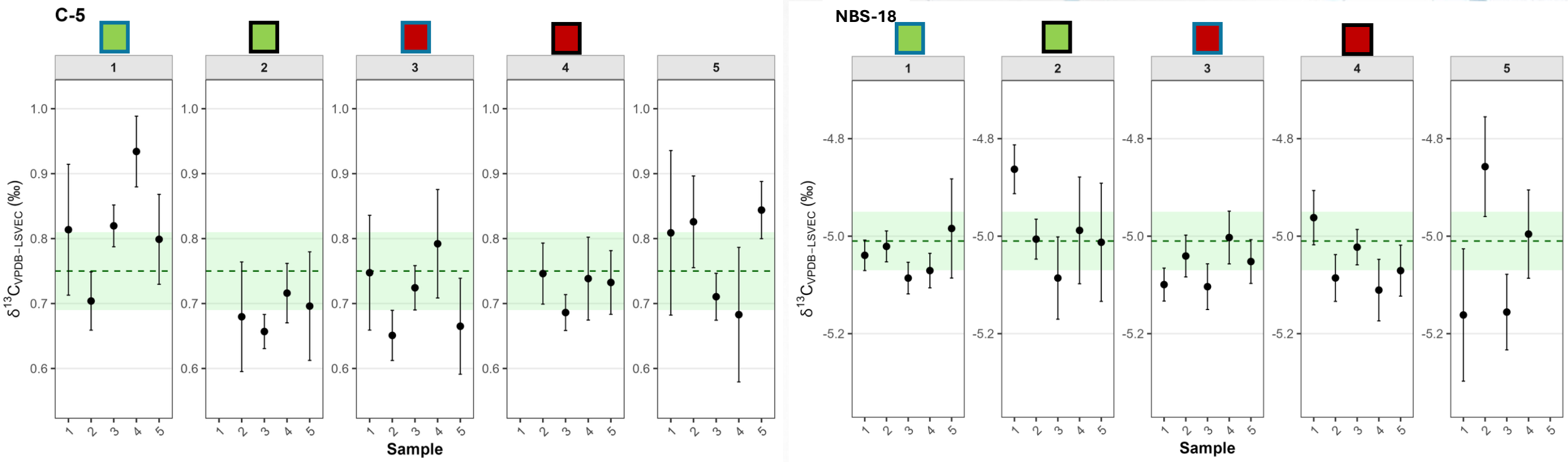
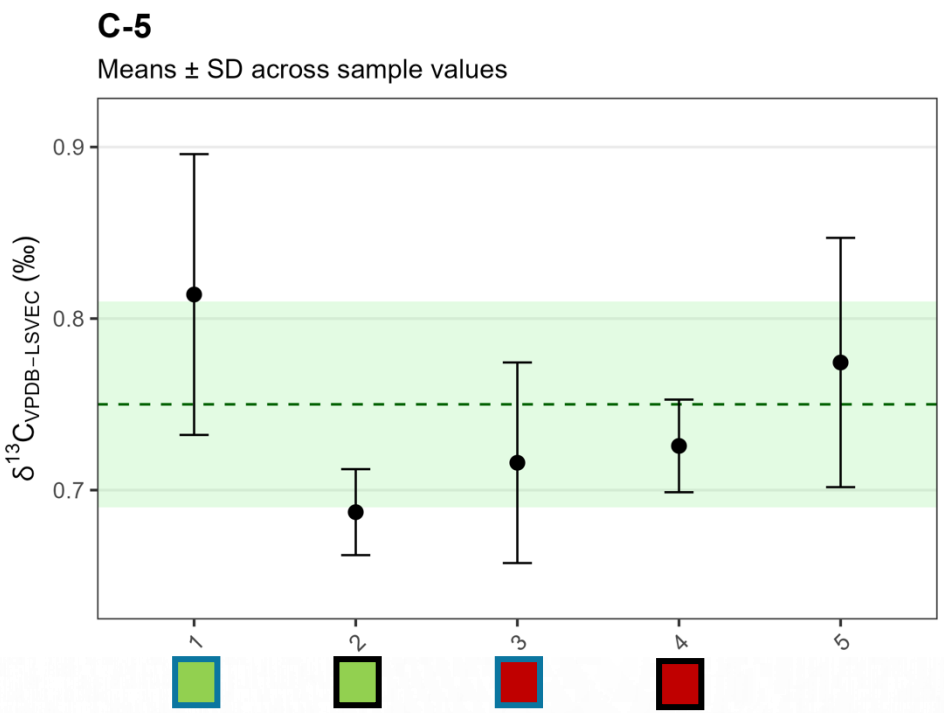
$\delta^{13}C$ values of check standards

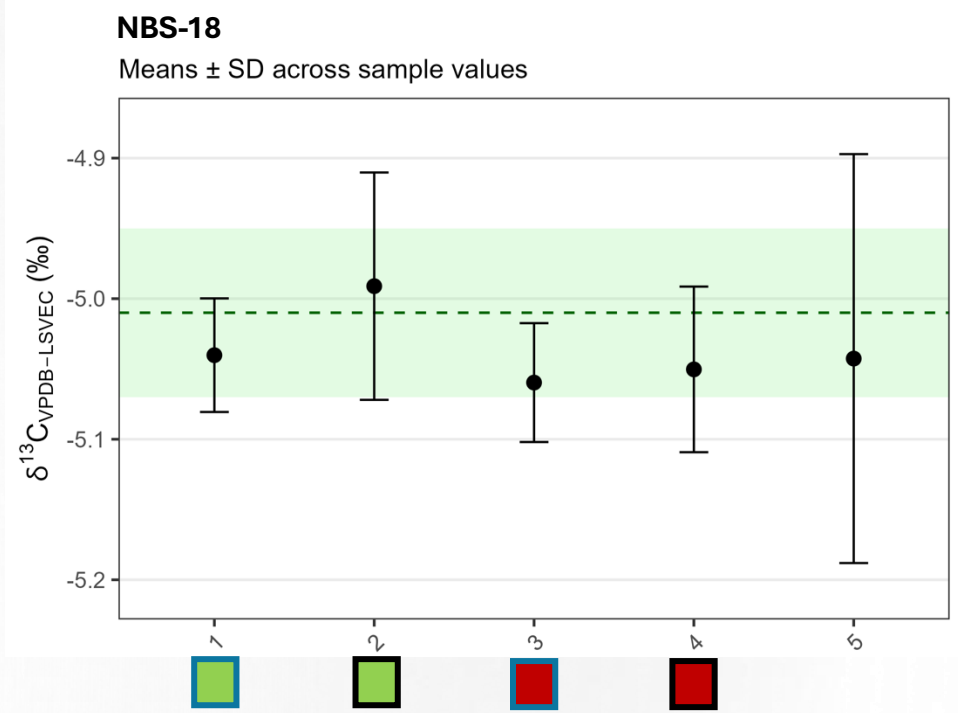


Legend

- Multi-vial evacuation/fill
- Single-vial evacuation/fill
- Heated
- Room temperature

$\delta^{13}C$ values of check standards

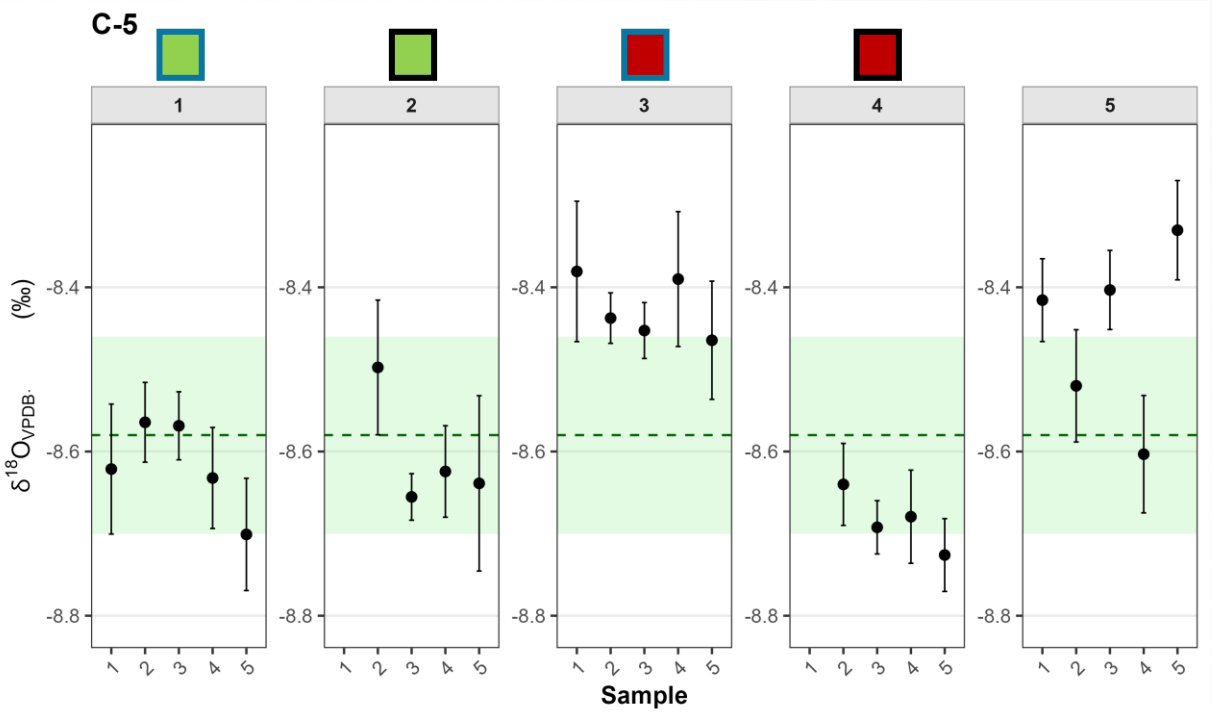


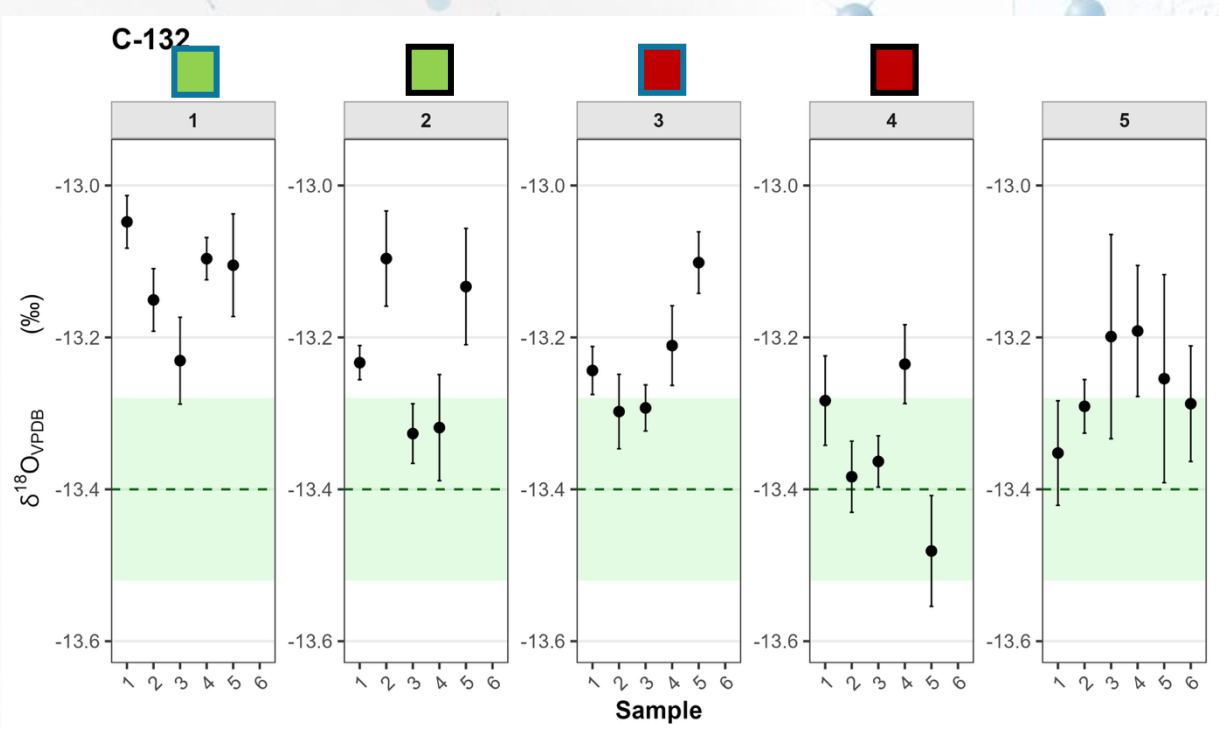


Legend

- Multi-vial evacuation/fill
- Single-vial evacuation/fill
- Heated
- Room temperature

$\delta^{18}O$ values of check standards





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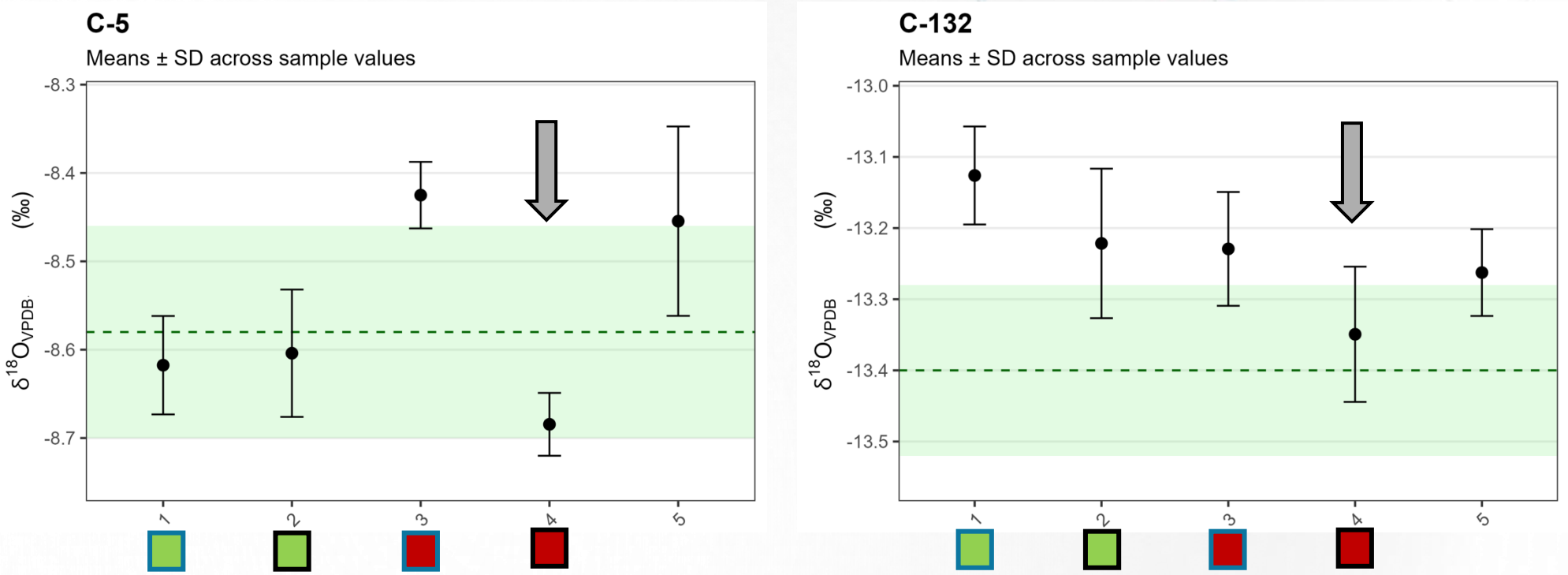
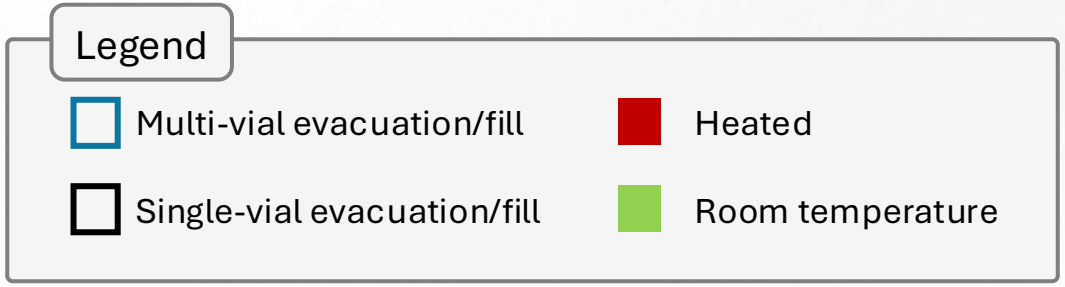
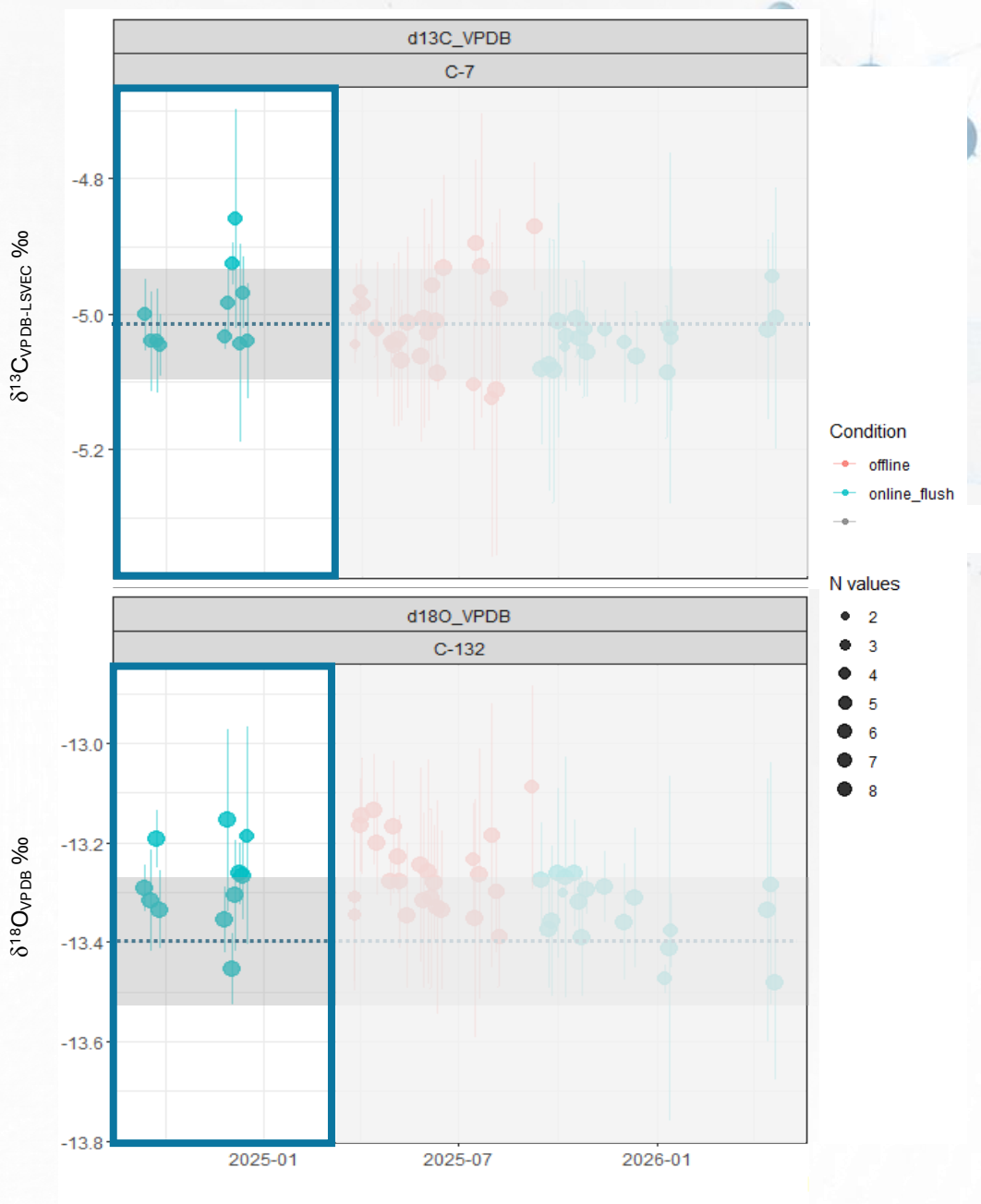




What now?

Carbon check standard

Oxygen check standard



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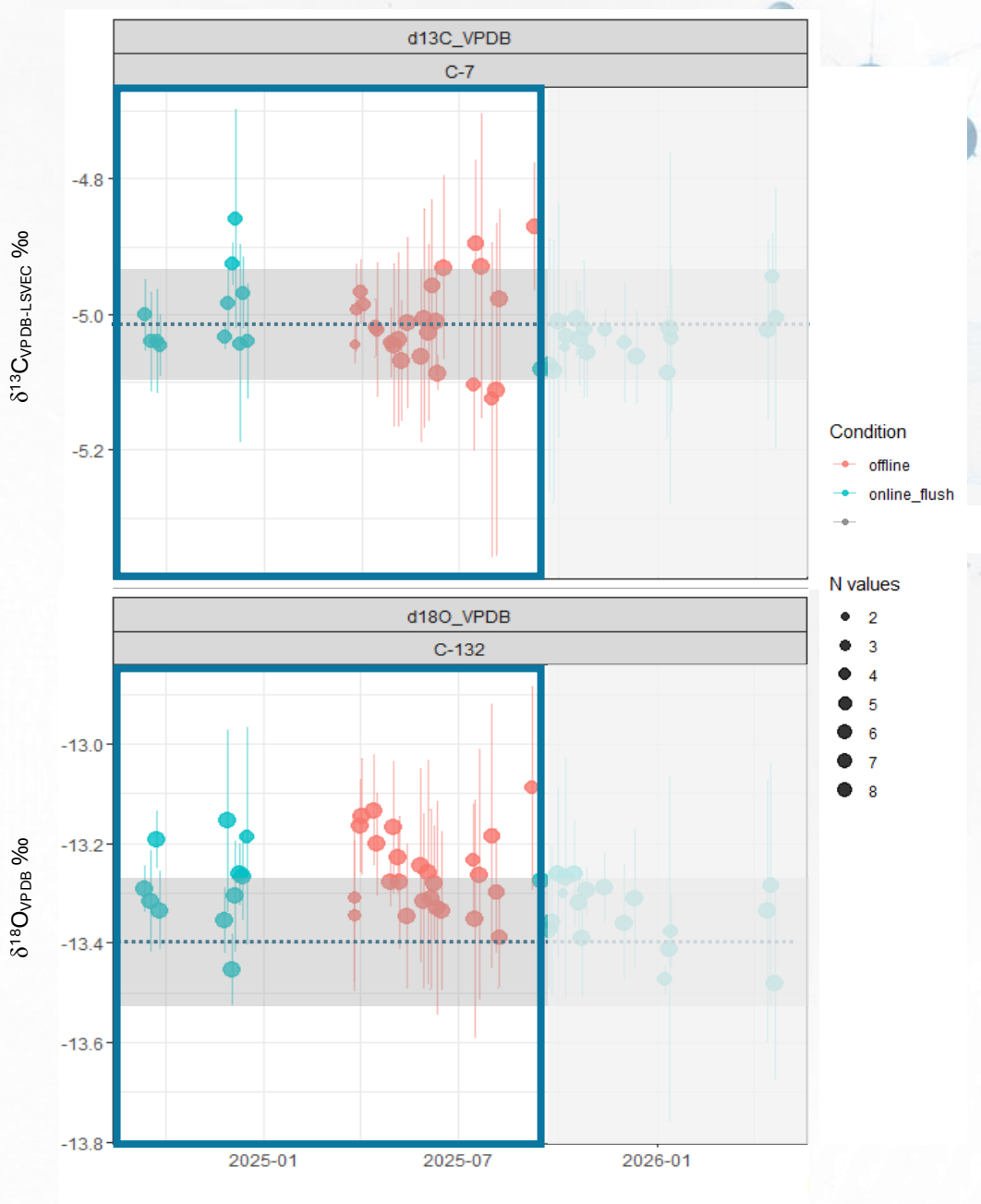

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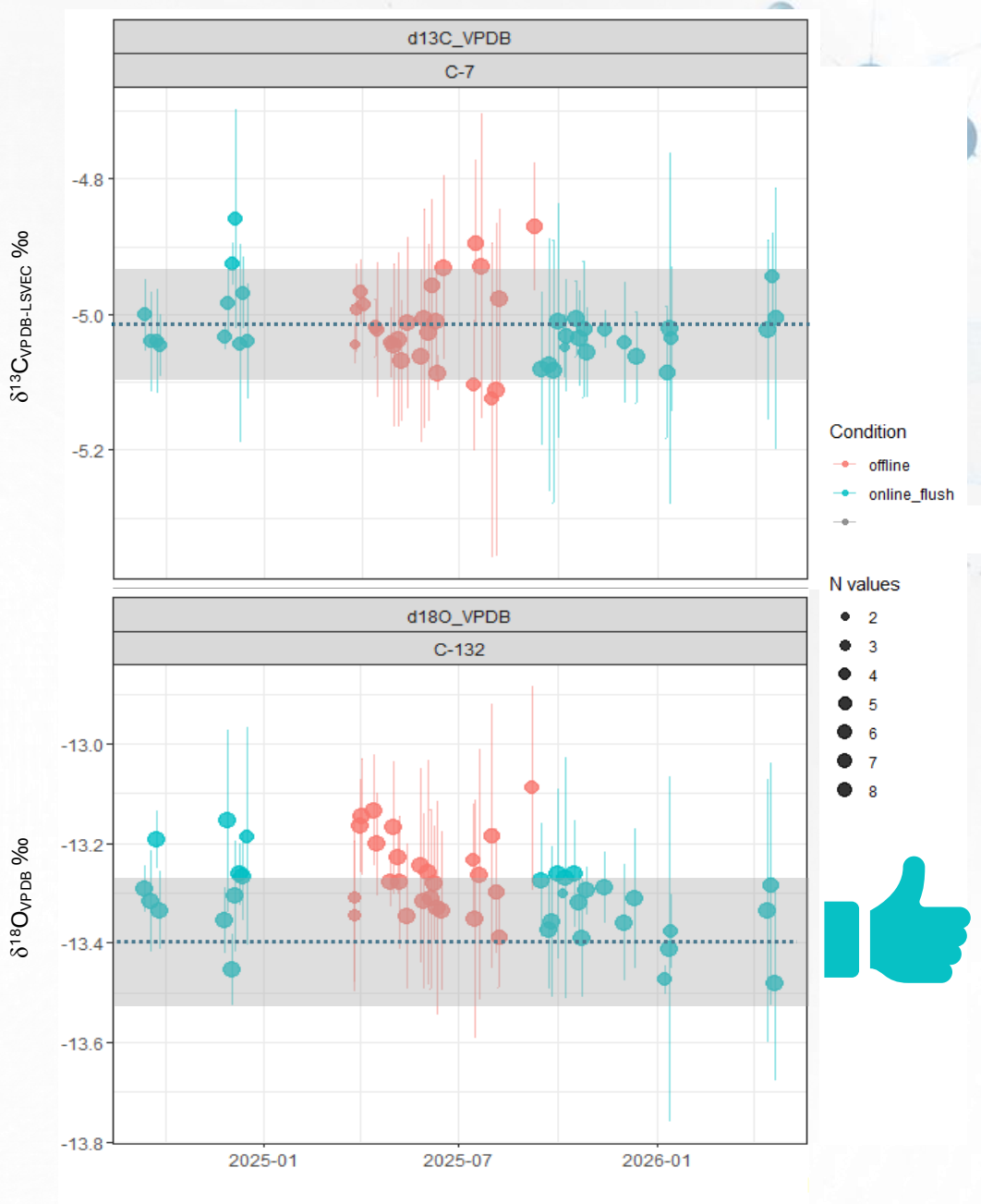
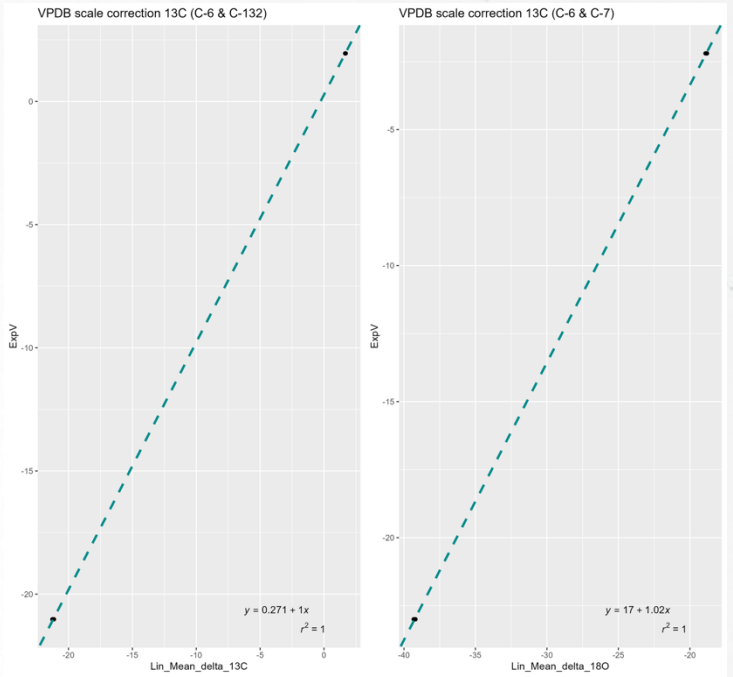


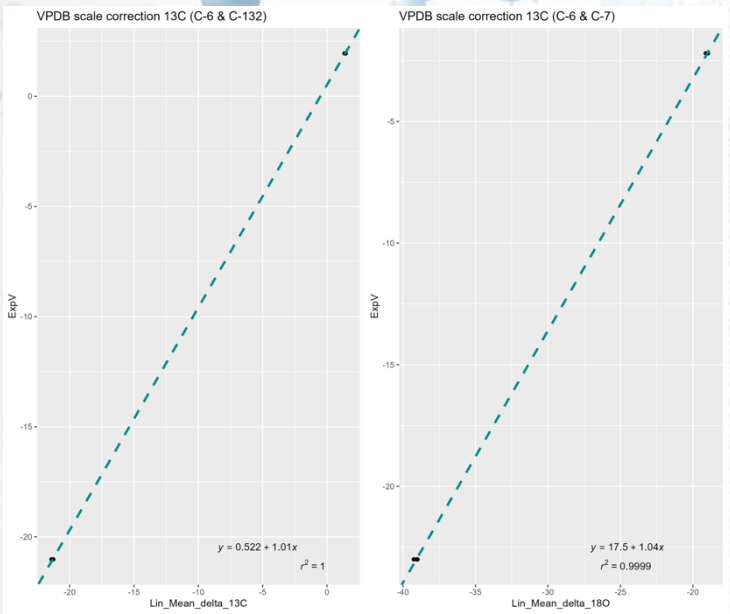
In summary…

- Carbonates are not for the clumsy
- Vacuum evacuation is an acceptable alternative for safety-conscious labs
- Monitoring of the system for leaks is important
- Can be converted for offline flushing
- Warm acid is best

ASITA 2027 @ MUN!

Calibration Curves





Test	$\delta^{13}C$ slope	$\delta^{13}C$ intercept	$\delta^{18}O$ slope	$\delta^{18}O$ intercept
1	1.01	0.52	1.04	17.5
2	1.00	0.37	1.03	17.2
3	1.01	0.49	1.04	17.7
4	1.00	0.59	1.03	17.3
5	1.00	0.27	1.02	17.0