

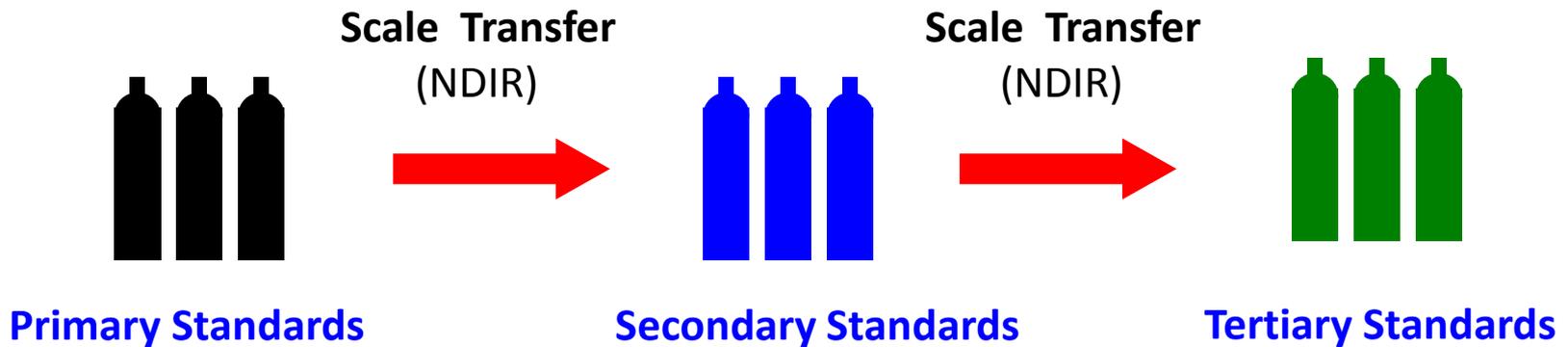
Recent Analysis of the WMO CO₂ Primary Standards

Brad Hall, Duane Kitzis, Pieter Tans



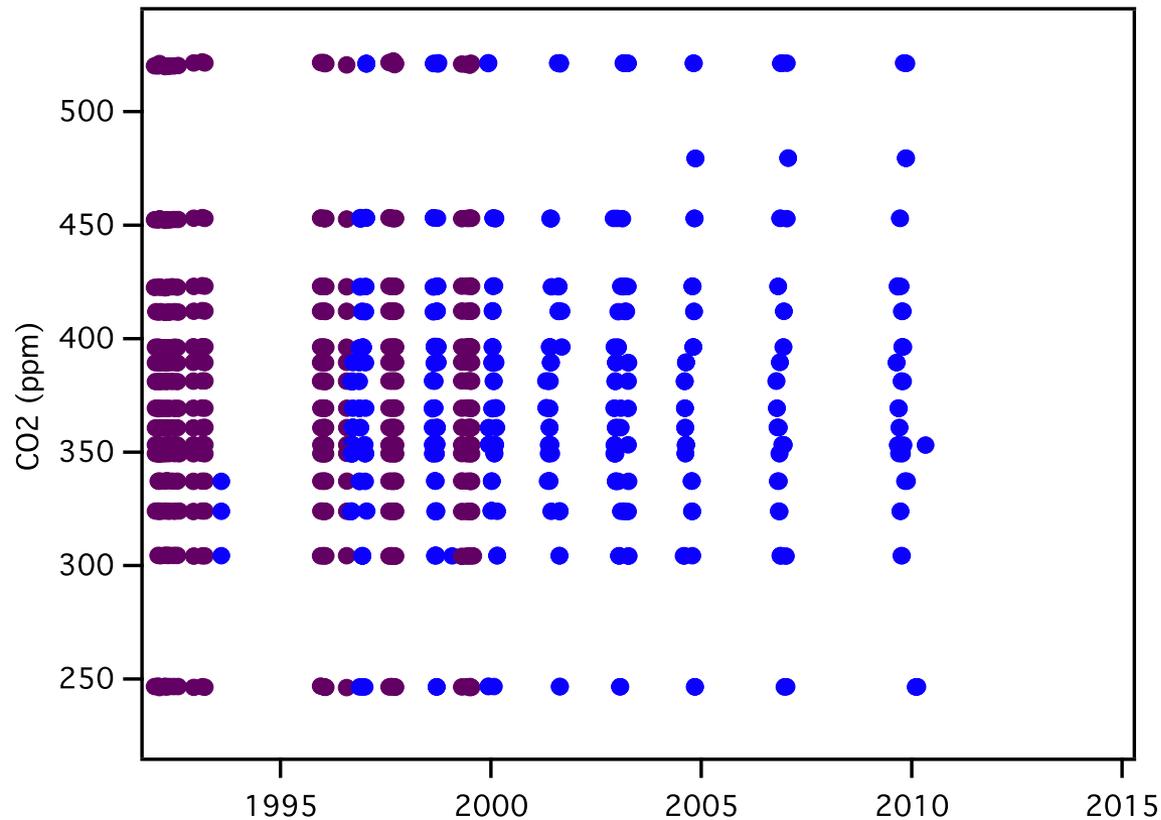
WMO CO₂ scale

- Reference scale for CO₂ in dry air, maintained by NOAA/GMD
- Defined by 15 primary standards (~250 – 520 ppm)



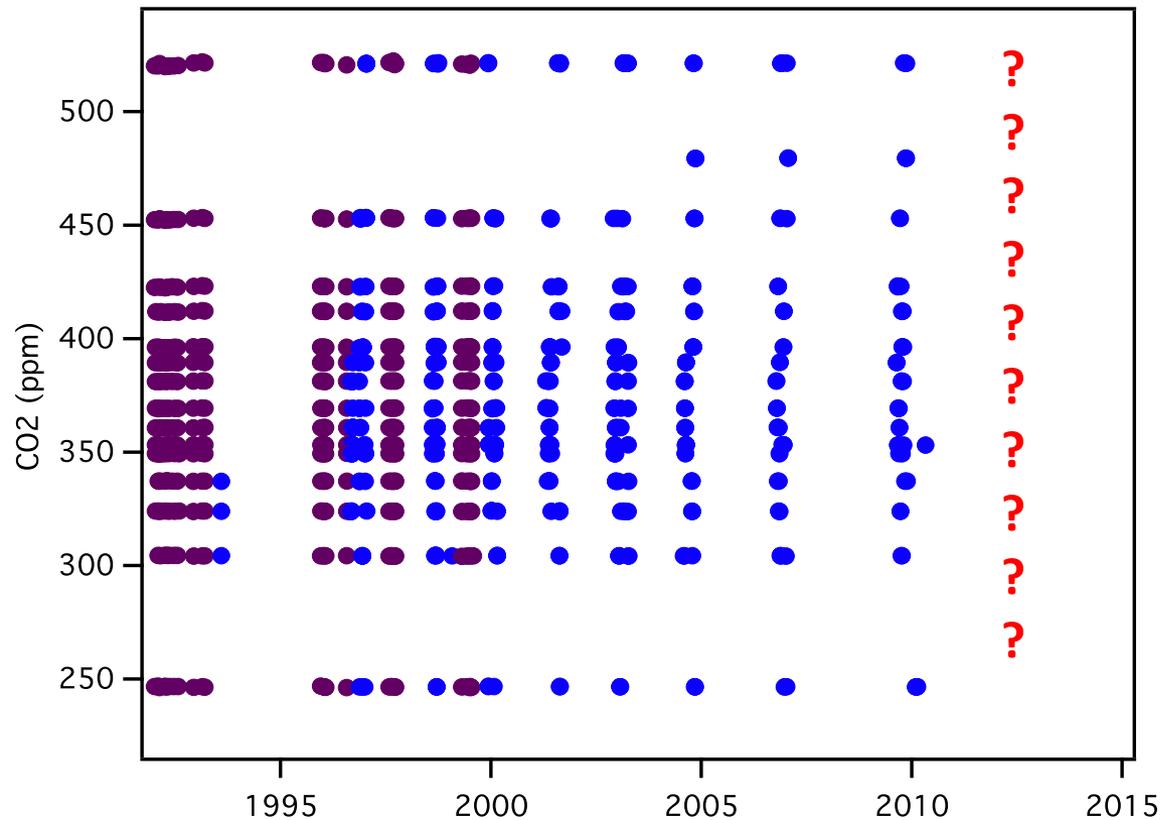
WMO CO₂ scale

- PS analyzed for CO₂ approx. every 2 years: calibration episodes
- Maintained by Cong Long Zhao, 1995-2010



WMO CO₂ scale

- PS analyzed for CO₂ approx. every 2 years: calibration episodes



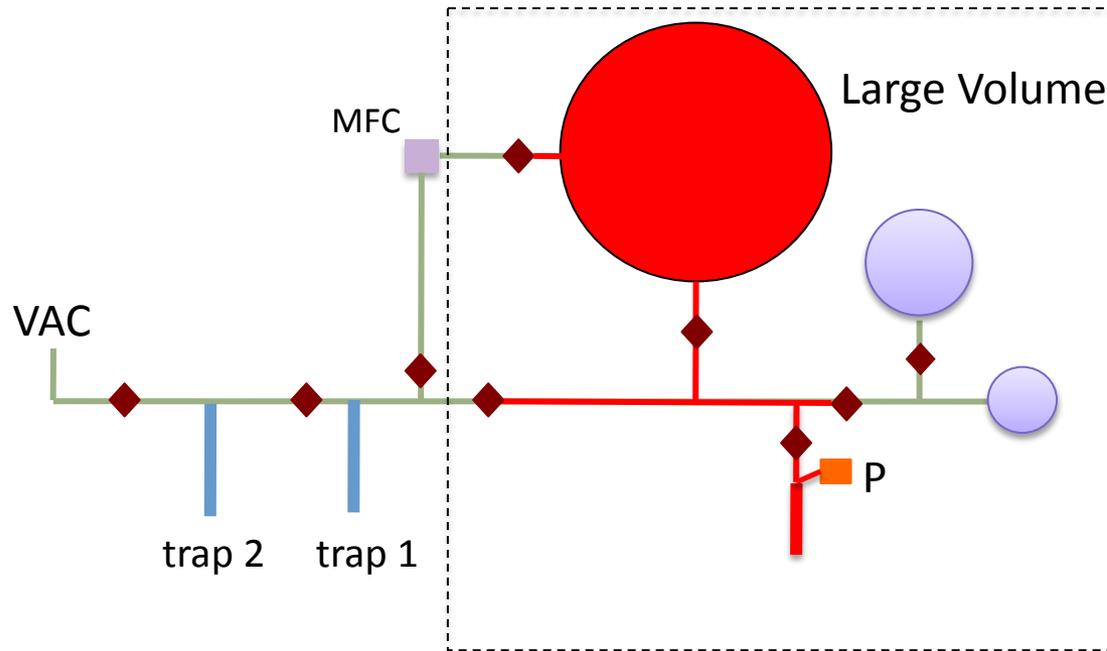
What is the manometer?

-Device used to determine the mole fraction of CO_2 in dry air (absolute).

Start with ~ 6 L air

$P = 85$ kPa

$T = 37$ deg C

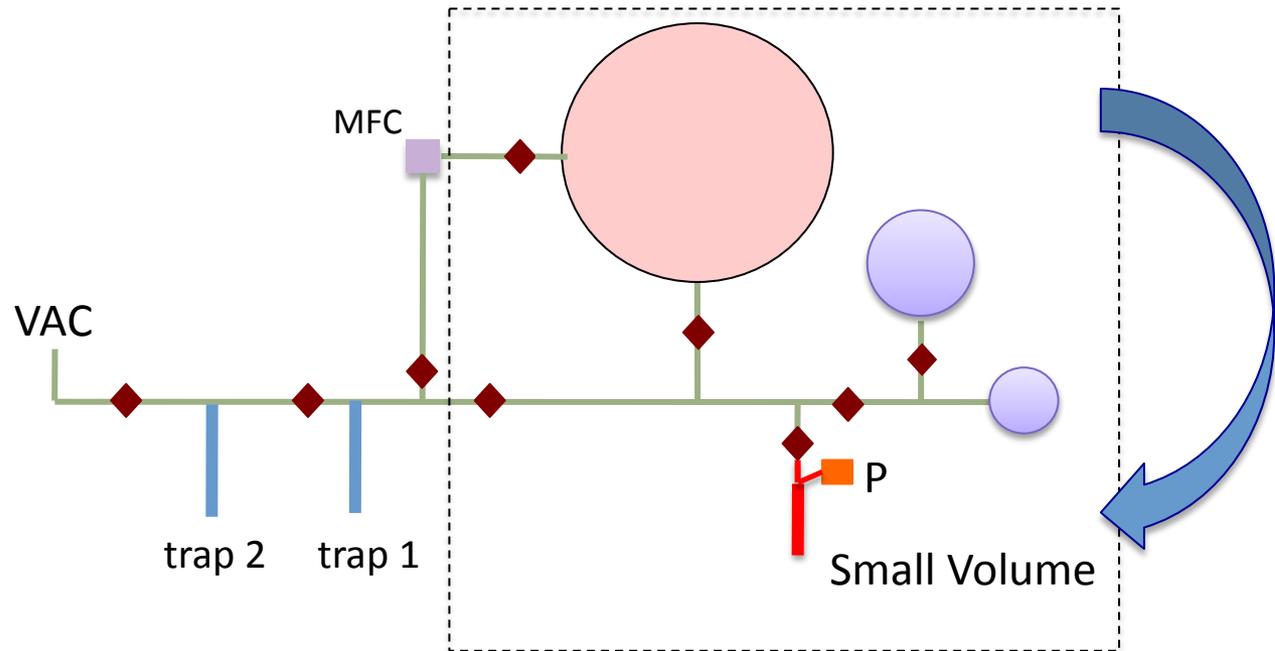


What is the manometer?

-Device used to determine the mole fraction of CO₂ in dry air (absolute).

Extract CO₂ (and N₂O)

P = 20-90 kPa
T = 37 deg C



for ideal gases

$$\text{mole fraction } \{\text{CO}_2 + \text{N}_2\text{O}\} = \frac{P_{\text{CO}_2}/T_{\text{CO}_2}}{P_{\text{air}}/T_{\text{air}}} \frac{1}{\text{VR}}$$

VR = Volume Ratio

Uncertainty: ~0.07 ppm (~1 part in 5000, 1-sigma)

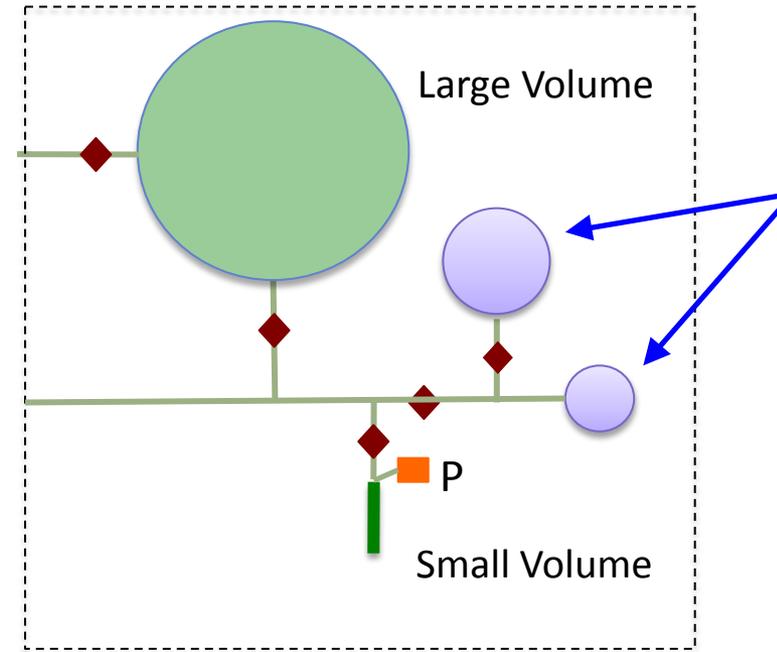
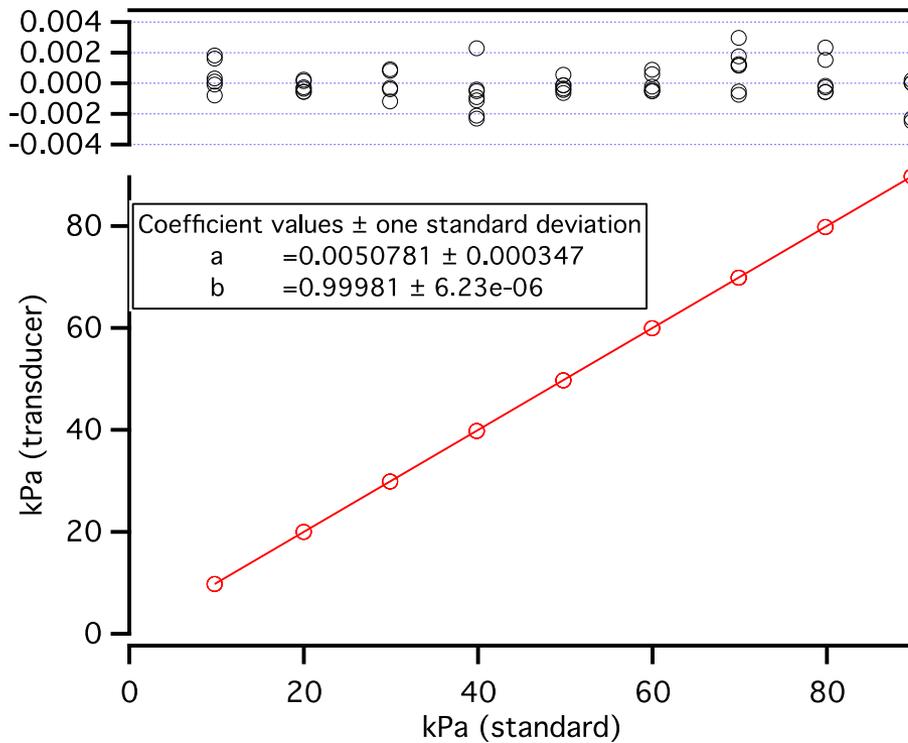
Zhao and Tans, 2006

Manometer Calibration: establish traceability

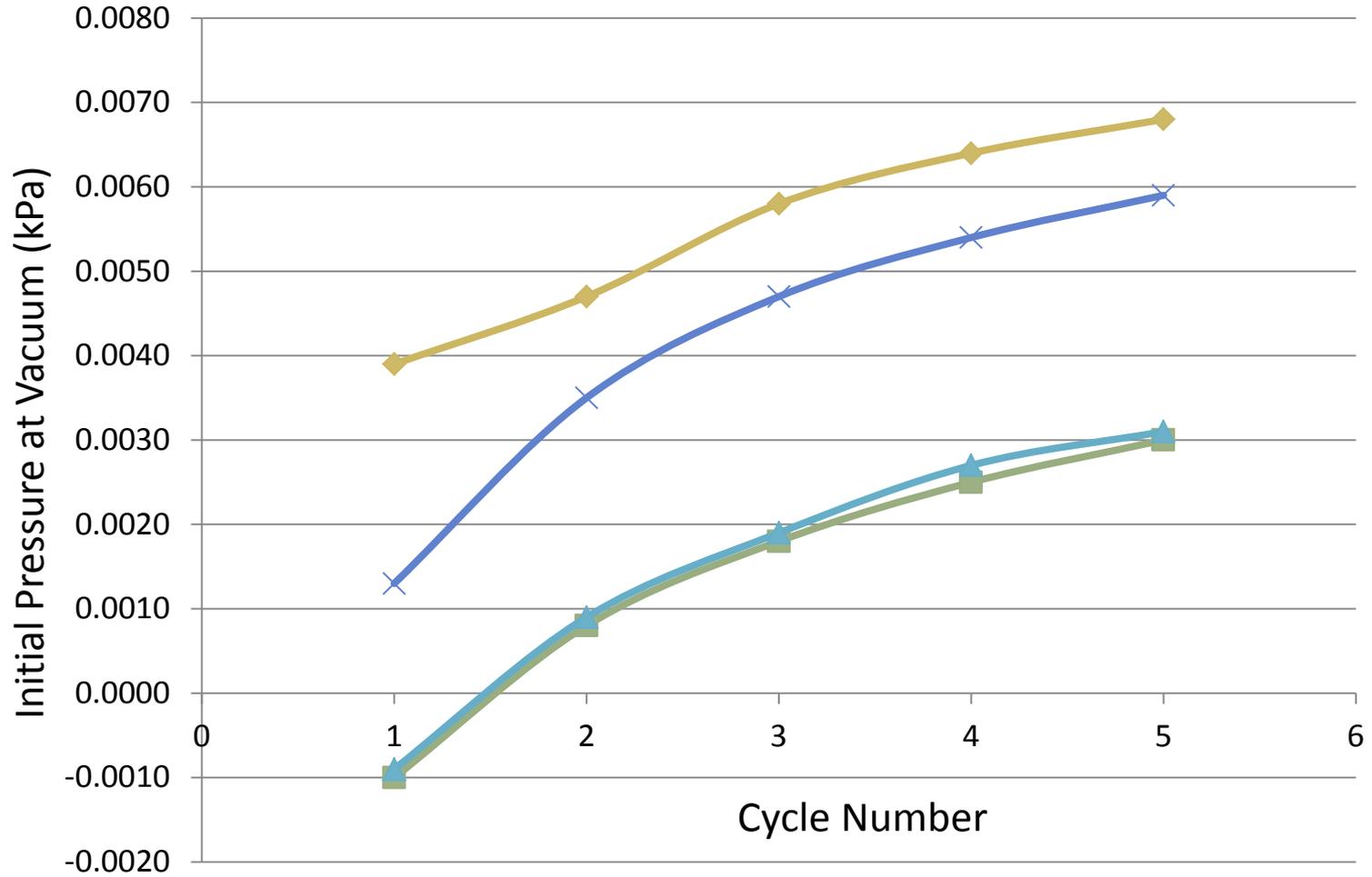
Pressure: in-house using piston gauge (NIST traceable)

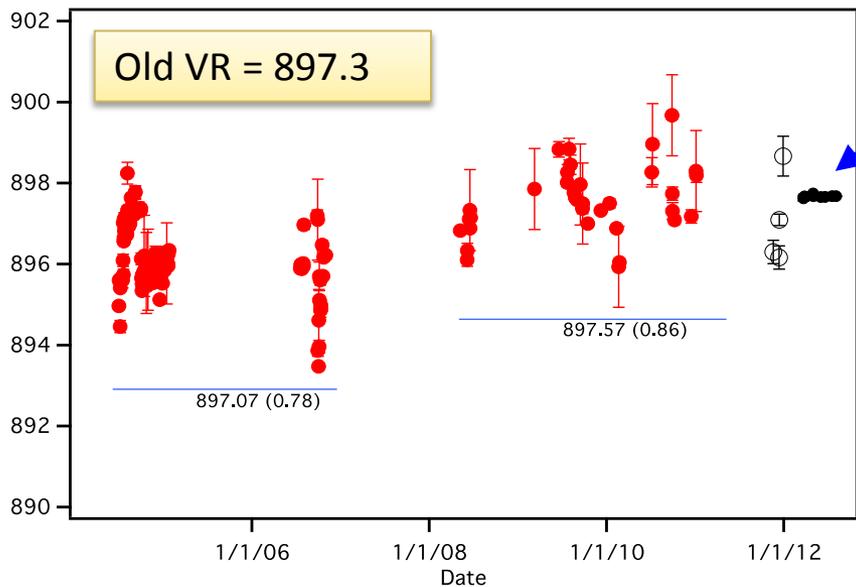
Temperature: outside laboratory (NIST traceable)

Volume Ratio: series of volume expansions

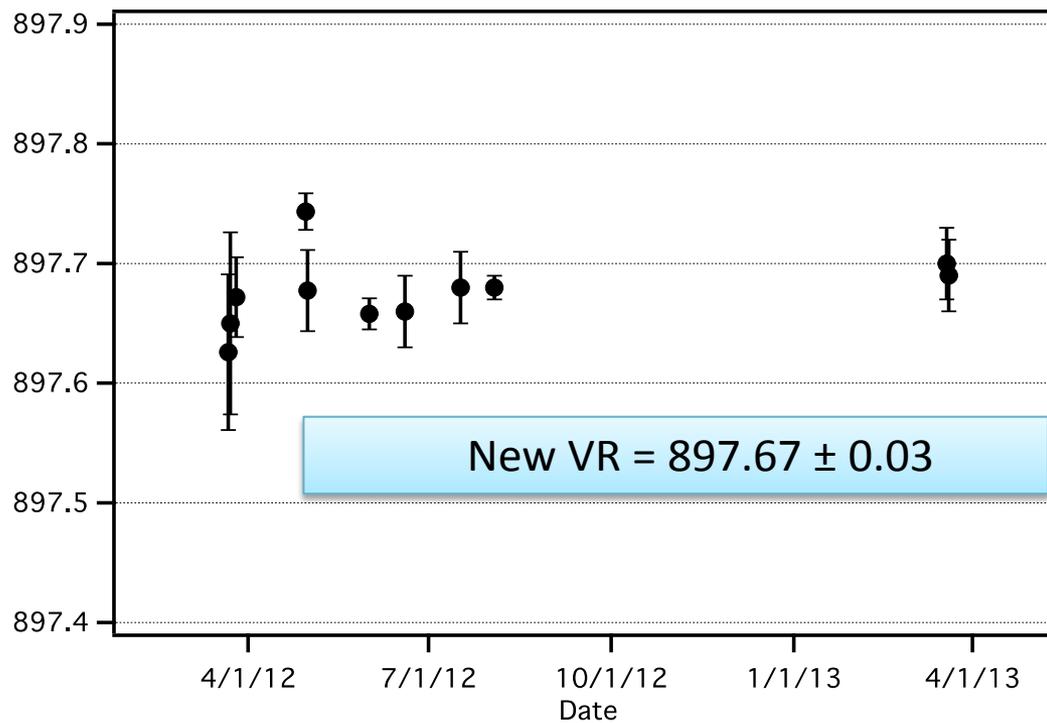


Variation of P_0 with pump-down cycle on different days

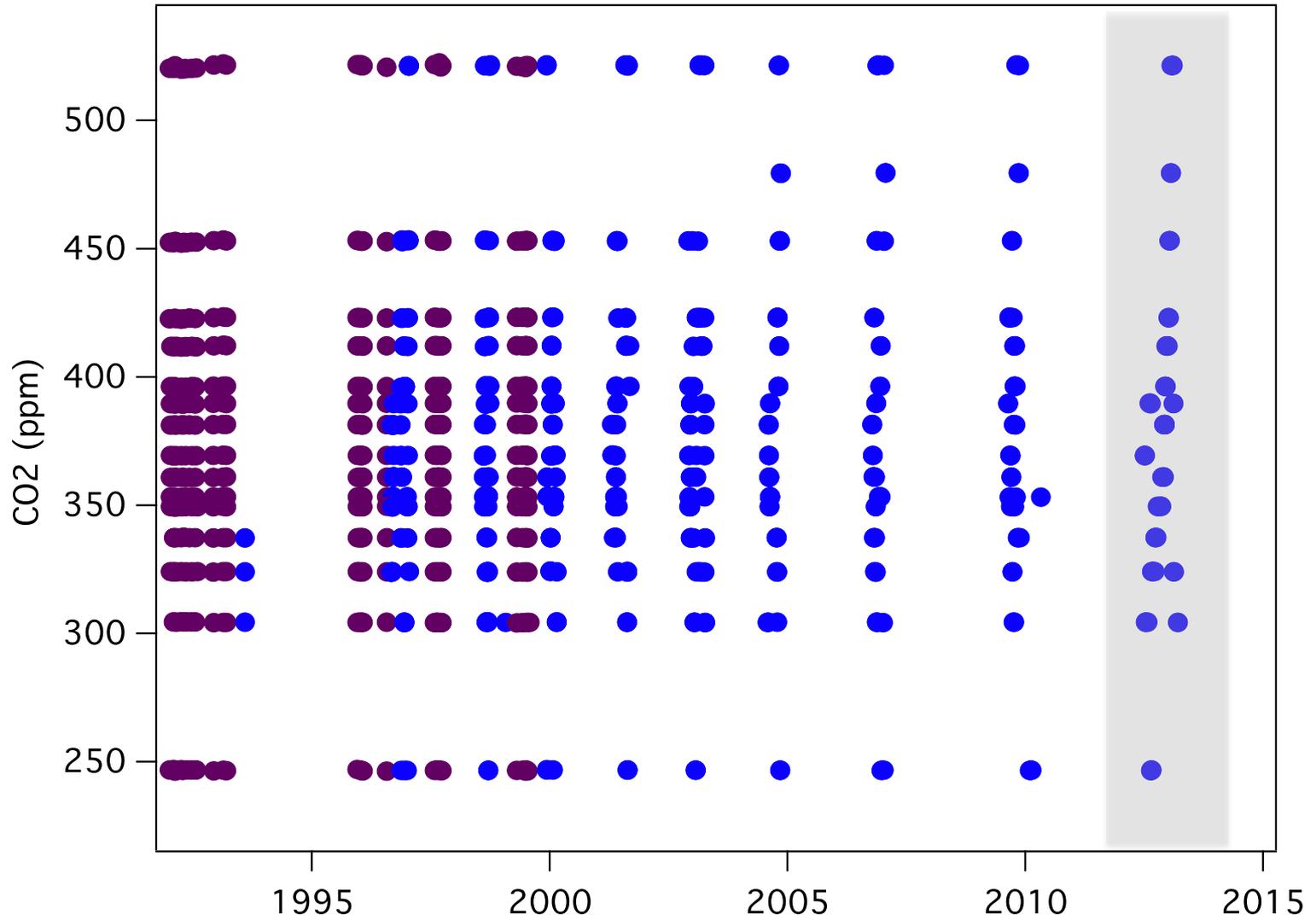




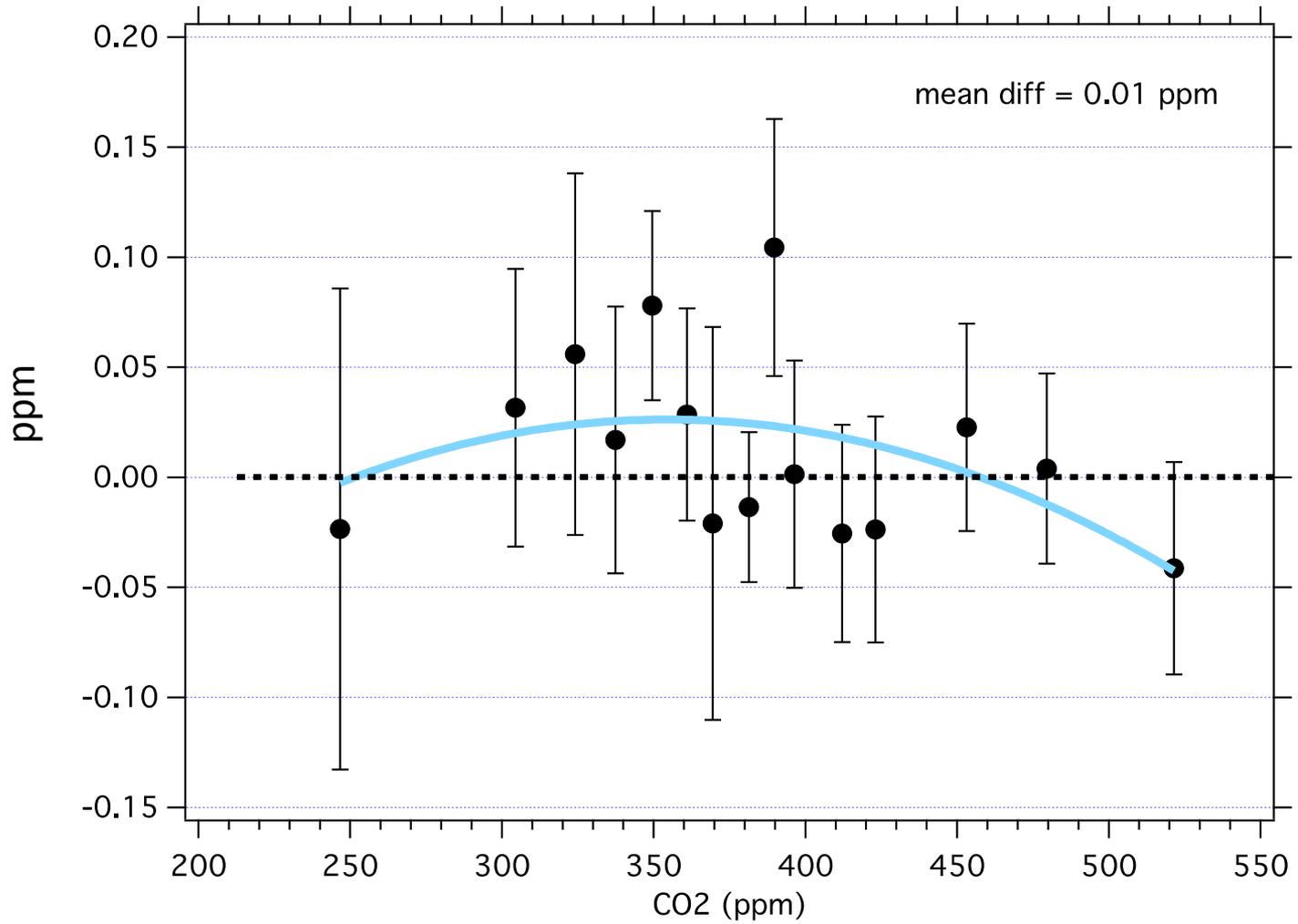
Stable VR during 2012-2013 experiment



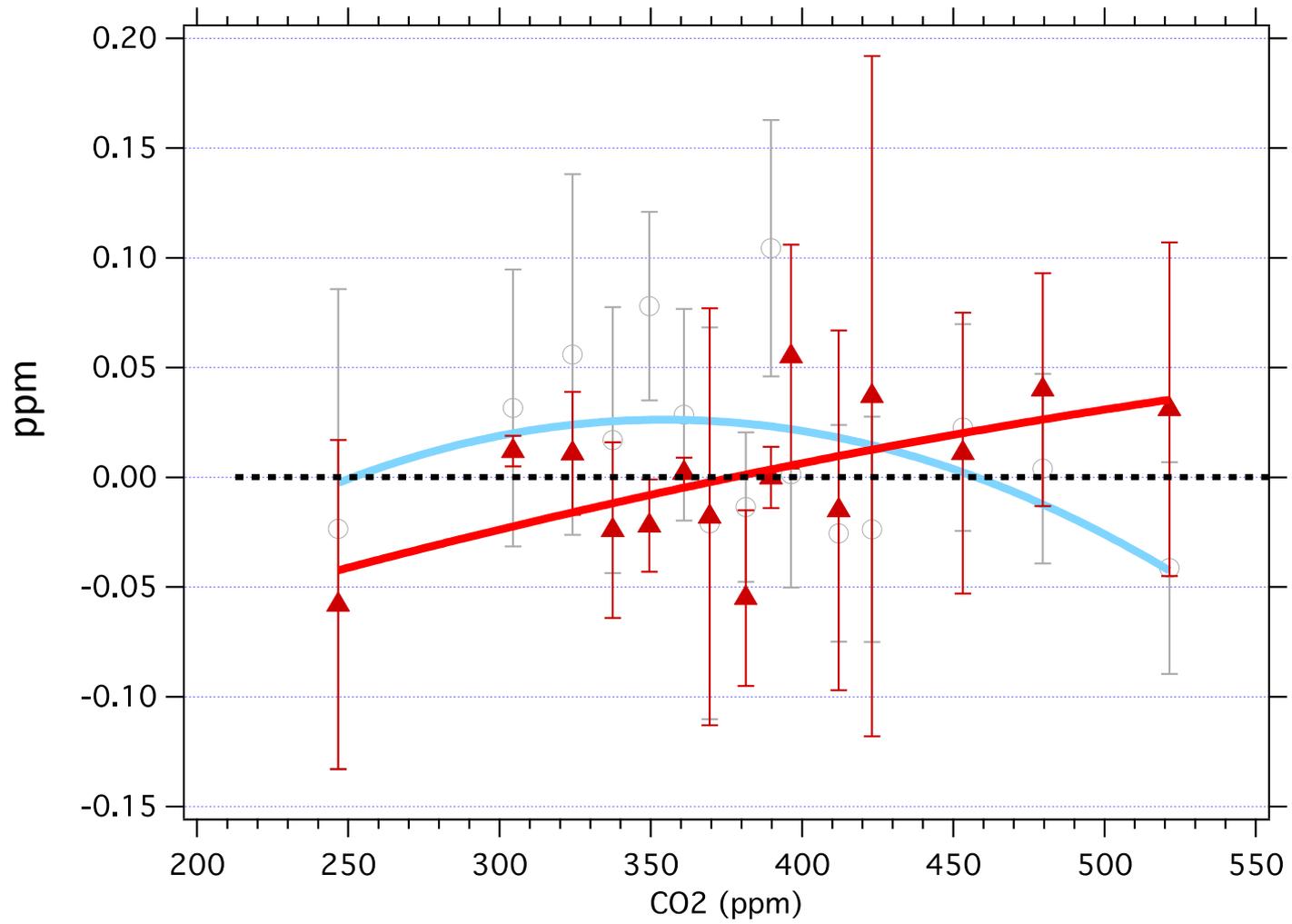
All measurements of WMO Primary Standards



Difference between mean 2012 results and WMO-CO2-X2007 scale

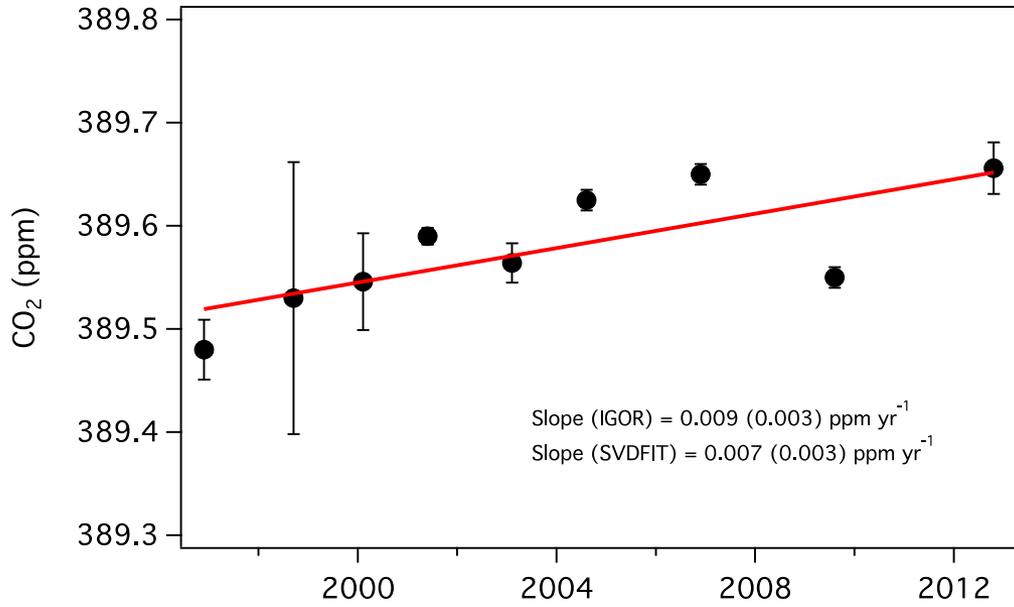


Difference between mean 2010 results and WMO-CO2-X2007 scale

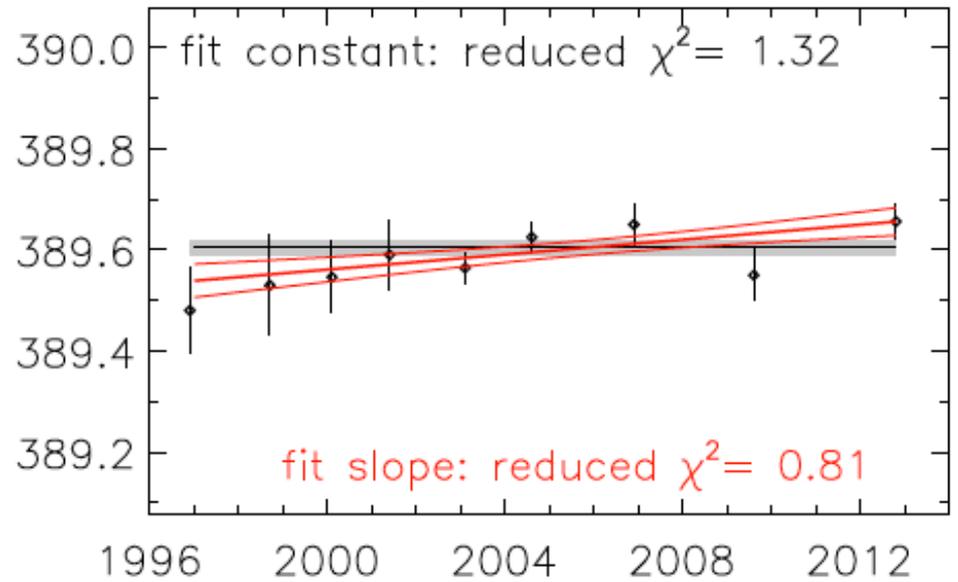


AL47-146

One primary standard is drifting

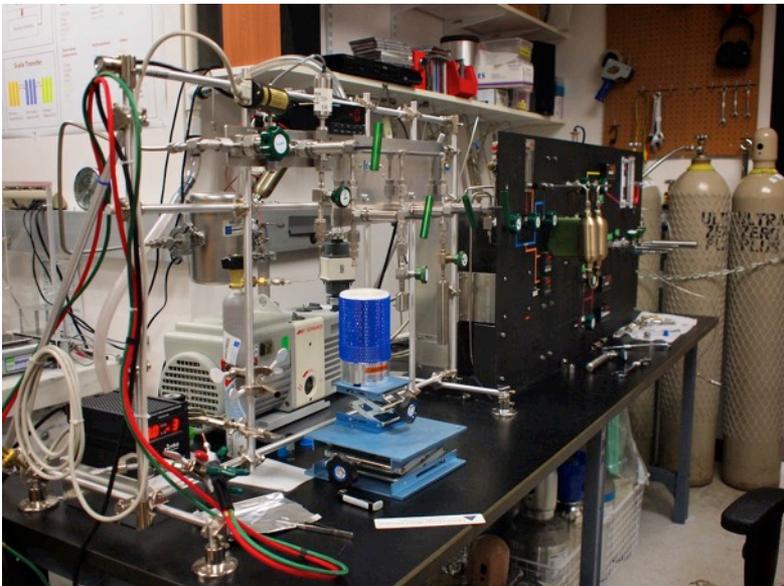


cylinder 146



Can we verify CO₂ scale independently?

- Gravimetric capability
- CO₂ transfer through stainless steel (pure CO₂ can be “sticky”)
- Loss of CO₂ on introduction to evacuated cylinders
- weighing precision



Gravimetric CO₂ standards

Cylinder	Prepared	Analyzed	Difference
FB03439	391.17 ± 0.06	391.17 ± 0.07	0.00 ppm
FB03442	391.09 ± 0.06	390.97 ± 0.07	0.12 ppm

mean diff = 0.06 ppm

Summary and future work

- Transitioned into the post - Cong Long era
- 2012-2013 experiment completed
- No change in WMO CO₂ scale (X2007), however, one standard is drifting
- Minor issues with respect to accuracy need to be addressed
- Need to plan for next set of Primary Standards and backup set
 - extend CO₂ mole fraction range (in progress)
- Independent method for scale verification

extra slides

What would cause errors in measured CO?

- 1) H₂O
- 2) leak in system
- 3) loss or carry-over of CO₂
- 4) errors in T, P (last calibrated in 2007, 2012)
- 5) change in physical parameters (VR)

Use P_0 measured at start of run (span = constant)

