

**A new CO<sub>2</sub> calibration scale based on  
gravimetric one-step dilution cylinders  
in National Institute for Environmental Studies  
– NIES 09 CO<sub>2</sub> Scale –**

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# NIES 95 CO<sub>2</sub> Scale

## Gravimetric 3-step dilution

320, 330, 340, 350, 360, 370, 380, 390 ppm  
for atmospheric CO<sub>2</sub>

250, 470 ppm

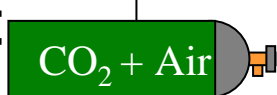
for oceanic pCO<sub>2</sub>

(Machida et al. [2009], WMO report 186.)

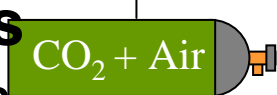
Pure CO<sub>2</sub>



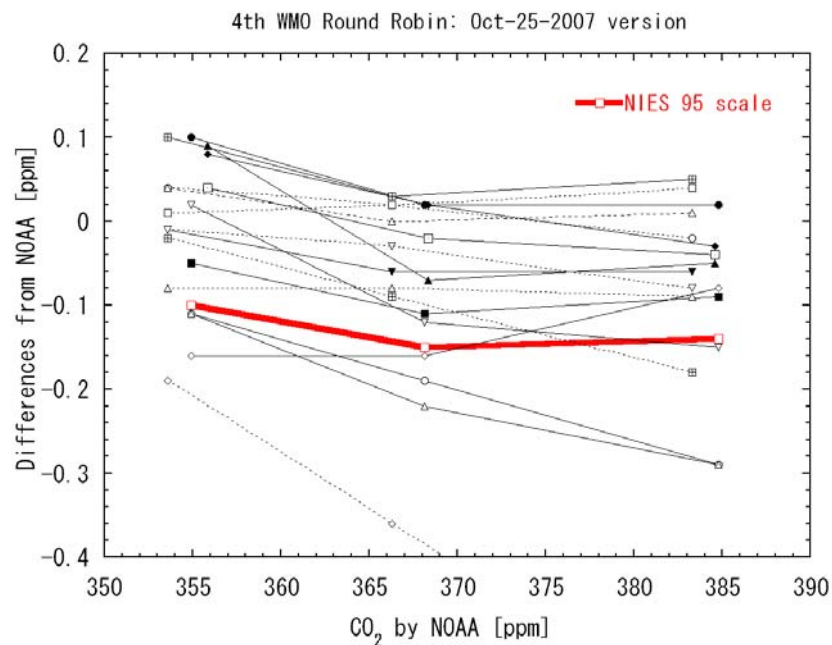
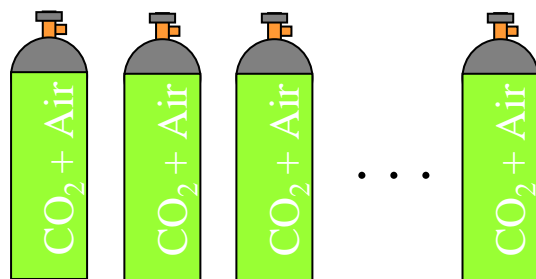
Parent  
~7 %



Daughters  
~5000 ppm

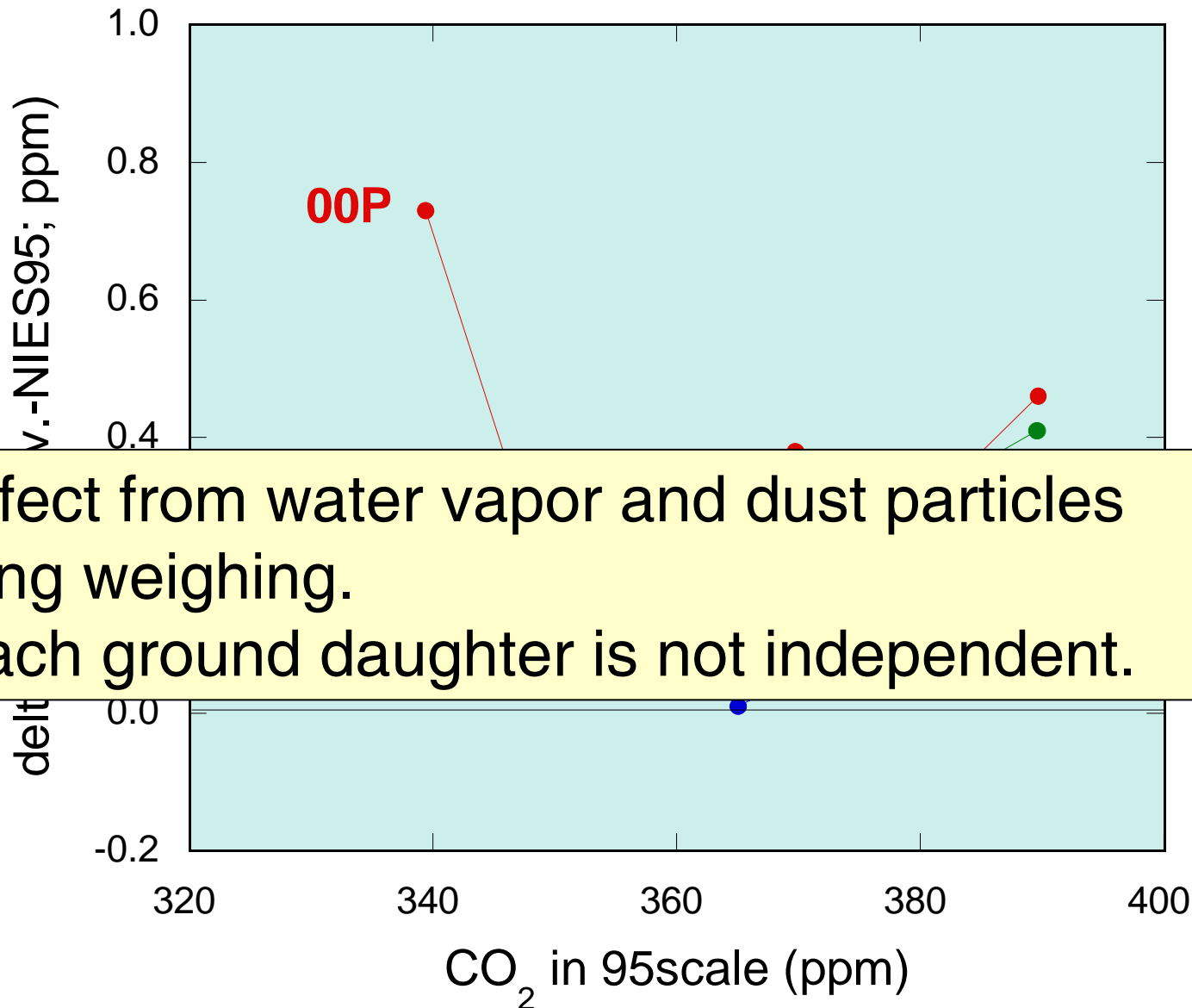


Grand-  
Daughters  
~350 ppm



Courtesy of Lingxi ZHOU

# Reproducibility of Gravimetric 3-step Dilution



# One-step Dilution Method

## Flow Chart

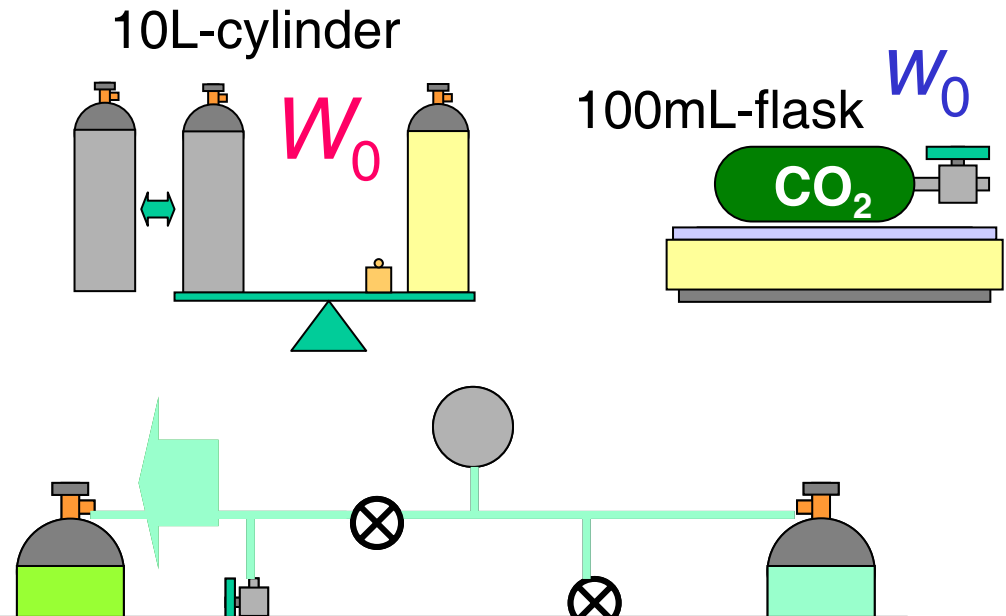
Weigh 10L-cylinder ( $W_0$ )



Weigh CO<sub>2</sub> flask ( $w_0$ )



Fill 10L-cylinder with CO<sub>2</sub>



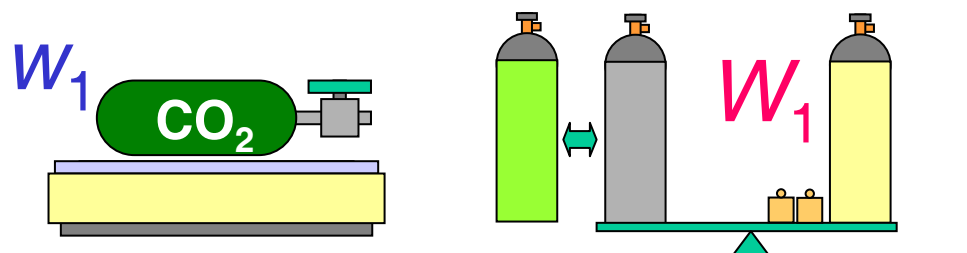
➤ Reduce the effect from water vapor and dust particles.

➤ Each ground daughter is independent.

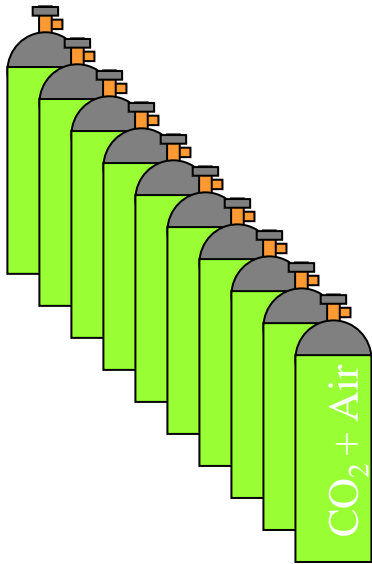
Weigh CO<sub>2</sub> flask ( $w_1$ )



Weigh 10L-cylinder ( $W_1$ )

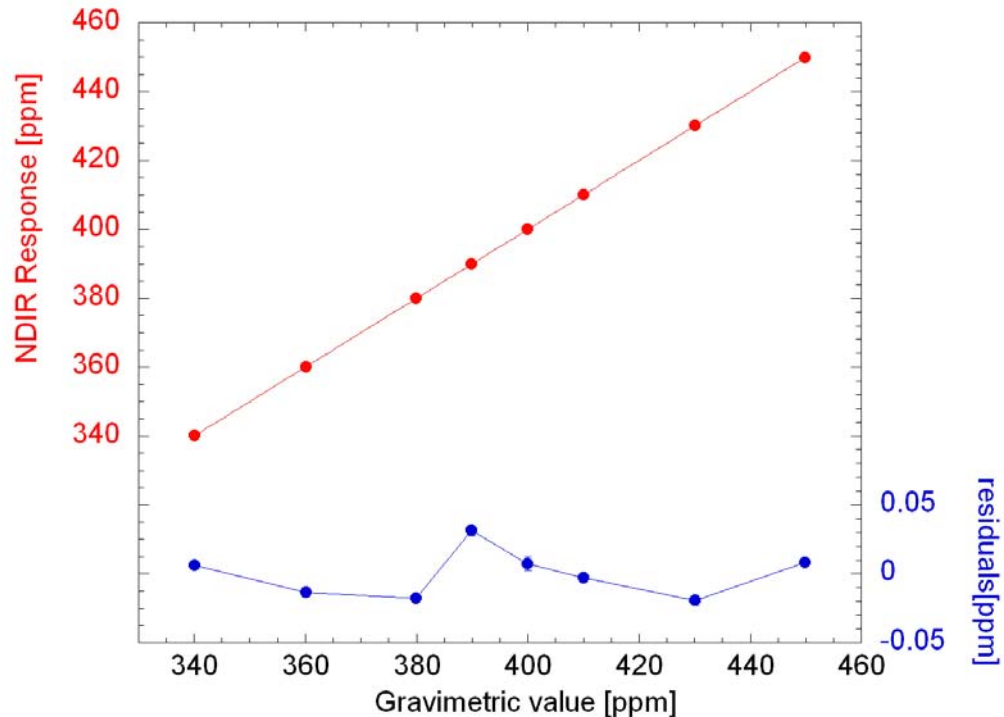


# Toward the New CO<sub>2</sub> Scale



10 of gravimetric one-step dilution cylinders  
(in 2007)

250,340,360,380,390,400,410,430,450,530ppm

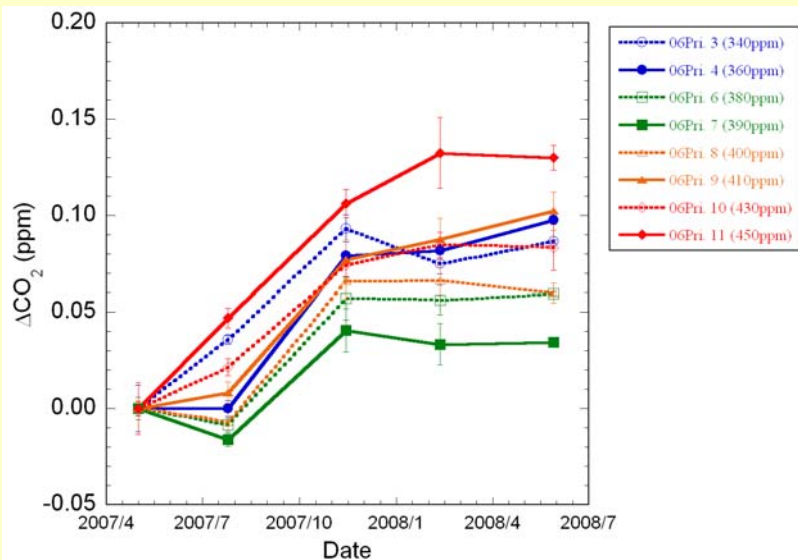


Good correlation in 8 independent cylinders.

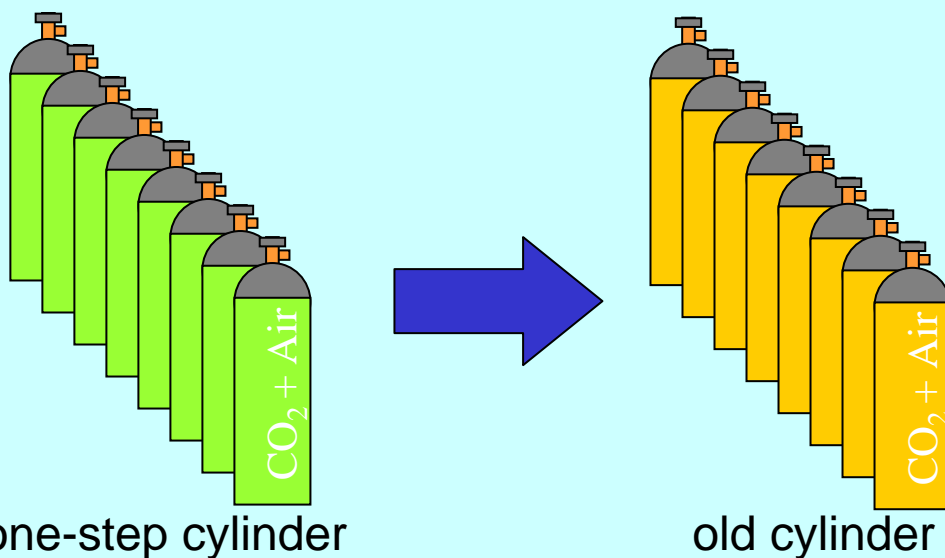
→ Confirm reproducibility of gravimetric one-step dilution

→ Candidate for New CO<sub>2</sub> Scale.

# CO<sub>2</sub> Drift in Aluminum Cylinders

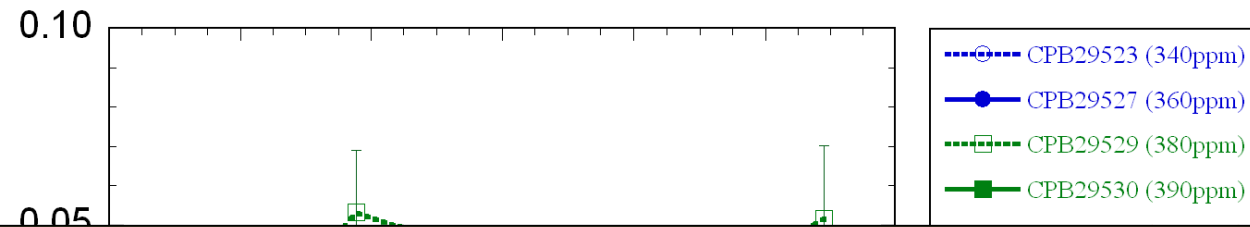


Recent manufactured aluminum cylinders show substantial CO<sub>2</sub> drift.

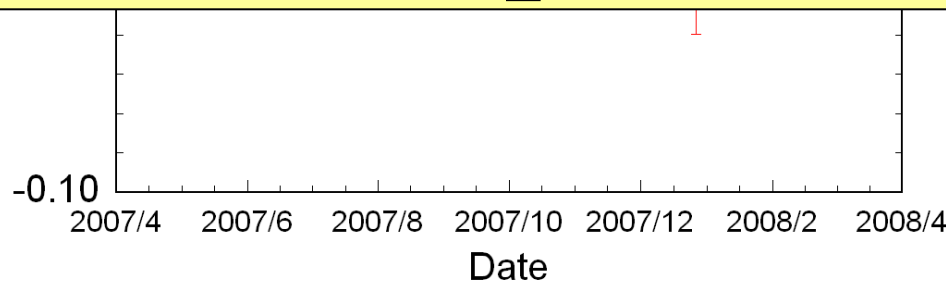


One-step gravimetric values were transferred to old stable cylinders just after manufactured.

# Stability of Old Cylinders

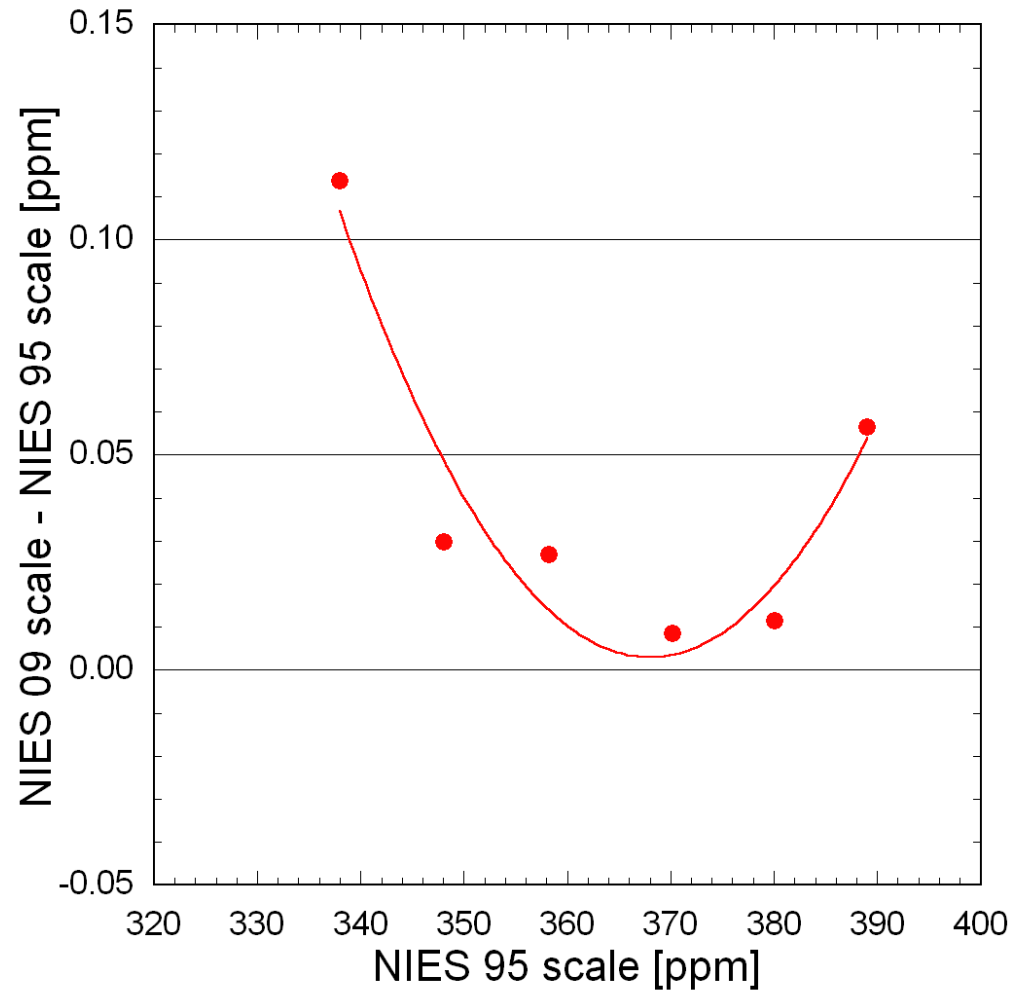


We employed the values of one-step dilution cylinders as NIES 09 CO<sub>2</sub> scale.



Rather stable in these 12 months.

# Relation between 95 and 09 scales



<0.03ppm in 360-380ppm

+0.11ppm at 340ppm and +0.06ppm at 390ppm

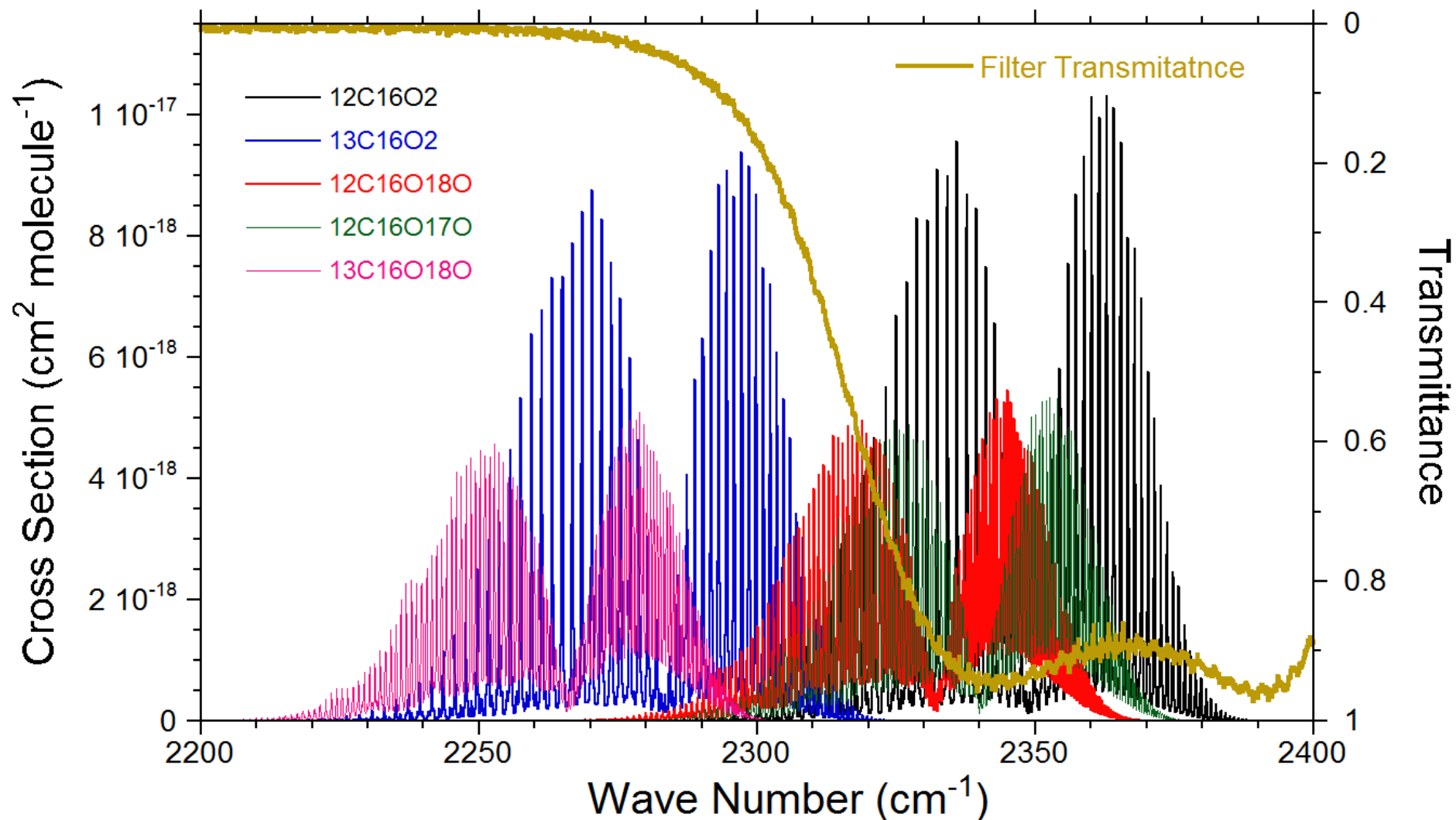


when comparison with other scale,

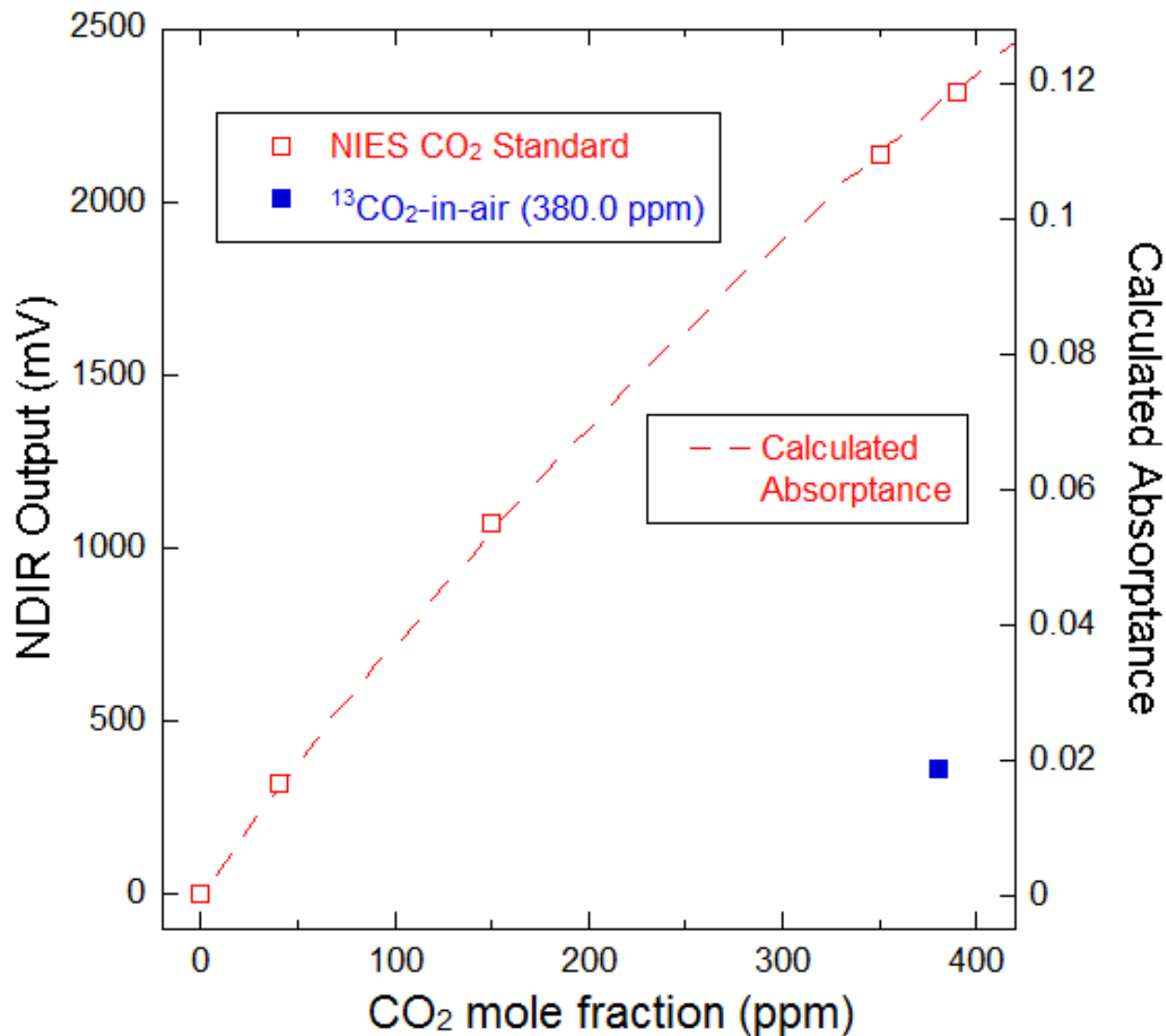
# Isotope Effect on NDIR should be considered.

Tohjima et al.[2009],*J.G.R.*

One example of LI-COR filter.



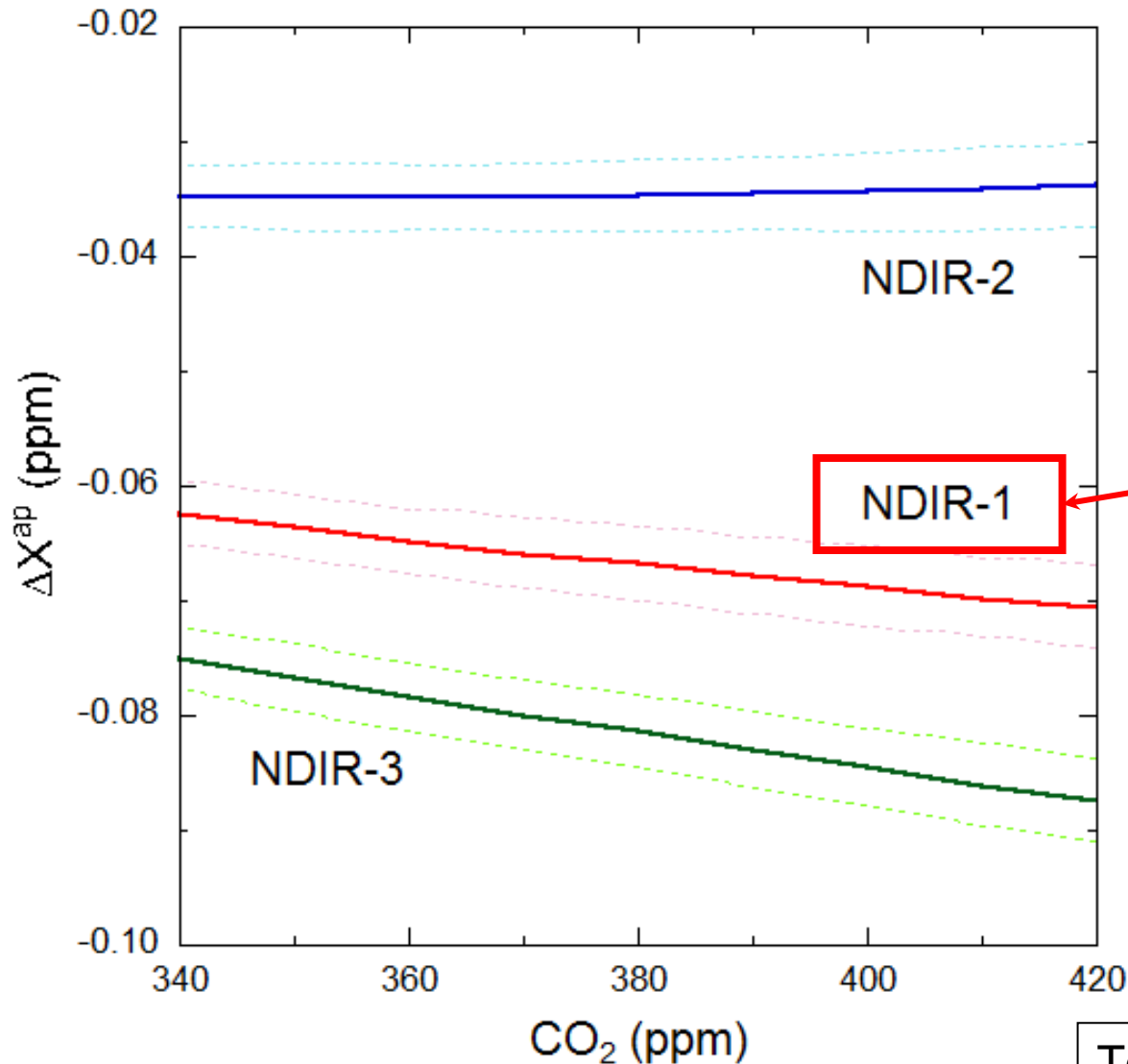
# NDIR response of $^{13}\text{CO}_2$



Very small output for  $^{13}\text{CO}_2$ -in-air gas

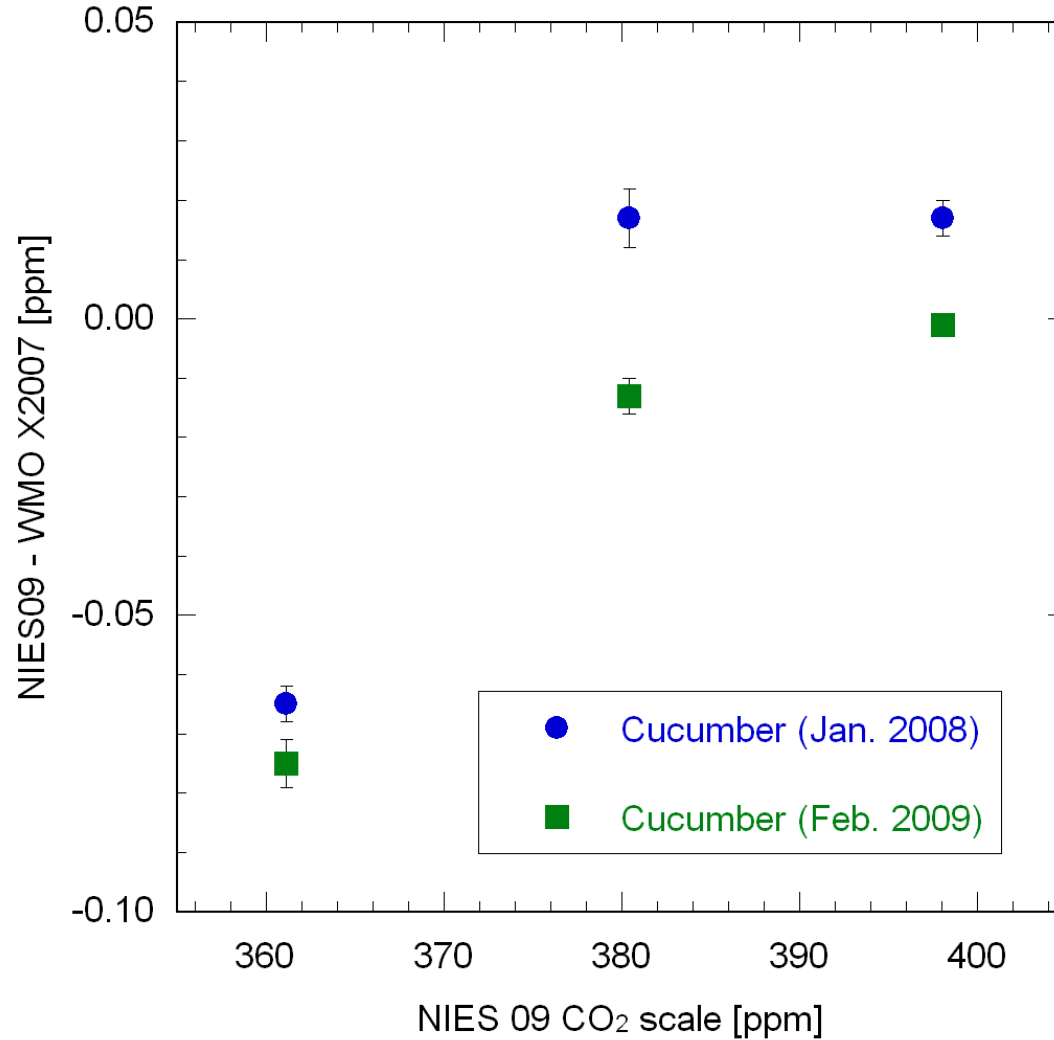
# Apparent signal difference in different $\delta^{13}\text{C}$

Apparent  $\text{CO}_2$  difference between  $\delta^{13}\text{C}=-32\text{‰}$  and  $-8\text{‰}$



Our NDIR for standard gases

# Difference between NIES 09 and NOAA-X2007



-0.07ppm around 360ppm  
Compatible in 380-400ppm

# Conclusion

- Reliable set of standard gases prepared gravimetric one-step dilution set to NIES 09 CO<sub>2</sub> scale.
- Succeeded old cylinders look stable.
- NIES 09 scale is compared with NOAA-X2007 by considering isotope effect on our NDIR.
- NIES 09 is lower by 0.07ppm around 360ppm and similar around 380-400ppm with NOAA-X2007 CO<sub>2</sub> scale.