# 国立環境研究所における温室効果ガスモニタリングのための標準ガス製造・維持・管理の取り組み


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大気微量成分の観測における

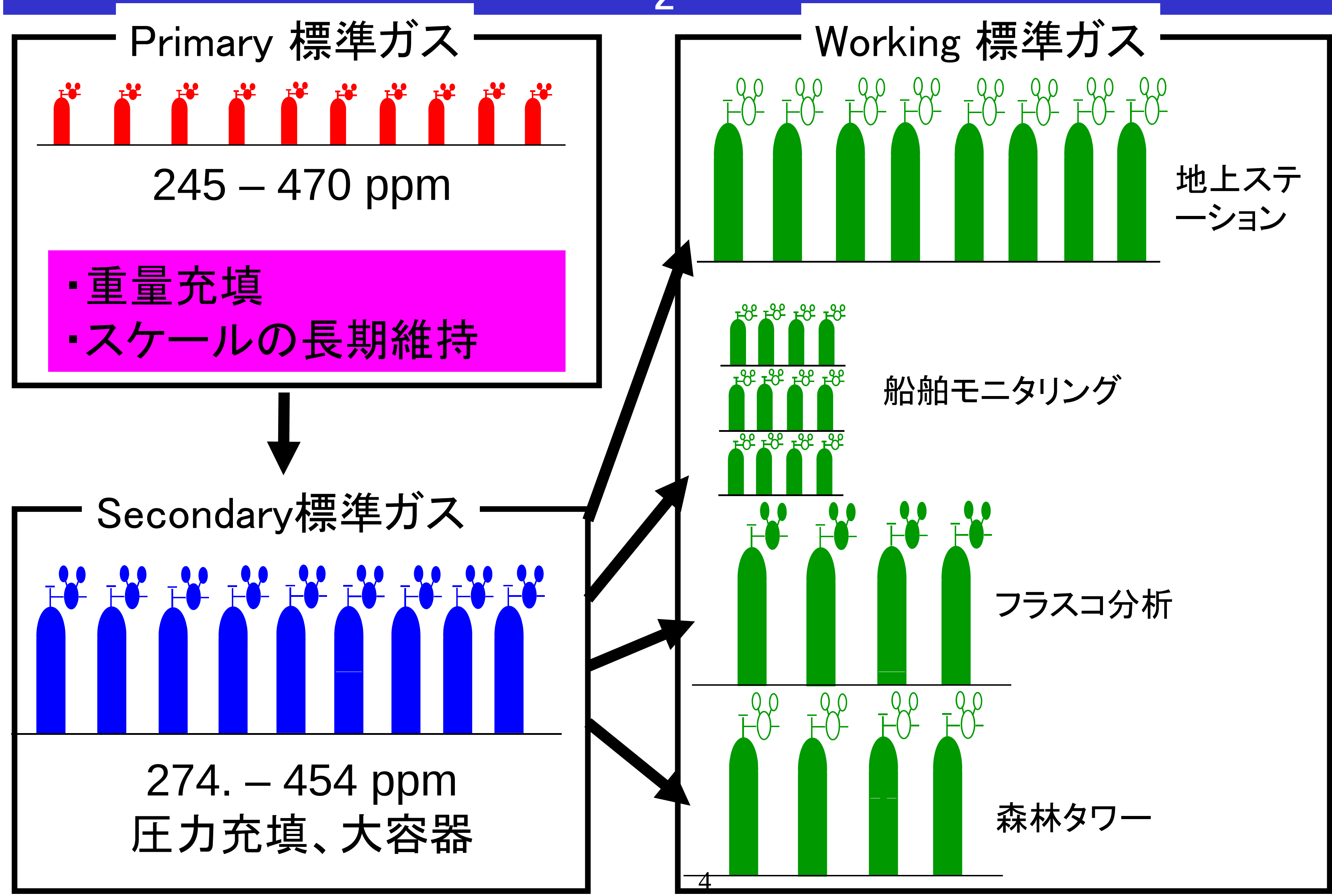
# トレーサビリティの重要性

- 経年変動を保証するもの
(Long-term Trend)
- 空間分布を保証するもの
(Spatial Distribution)
- 各機関の観測値を比較可能にするもの
(Inter-laboratory Comparison)

# NIES 標準ガス系列

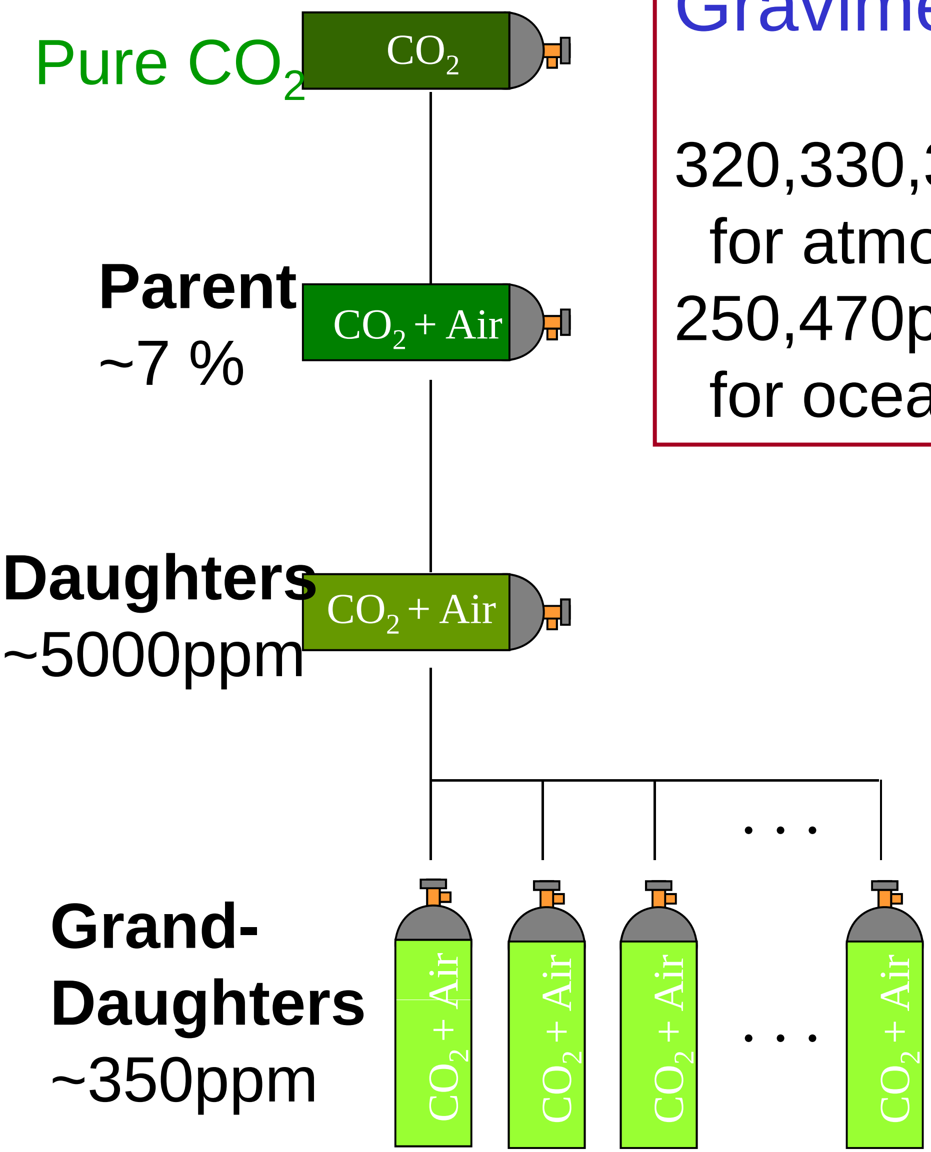
| Gas | Scale | range |
|---|---|---|
| $CO_2$ | NIES-09 | 340 – 450ppm |
| $CH_4$ | NIES-94 | 1.2 – 2.5ppm |
| $N_2O$ | NIES-96 | 250 – 400ppb |
| CO | NIES-09 | 0 – 5000ppb |
| $H_2$ | NIES-02 | 400 – 700ppb |
| $SF_6$ | NIES-01 | 3-16ppb |
| Halocarbon | testing | Sub ppb |
| Isotopes | NARCIS-Ⅰ, NARCIS-Ⅱ | -8.5 per mil, 1.95 per mil |
| $O_3$ | NIES-GPT/SRP35 | 0 – 180ppb |
| Oxygen | trying | |
| NO | NIES-04 | 100ppm/200ppb |

# NIES $CO_2$ 標準ガス



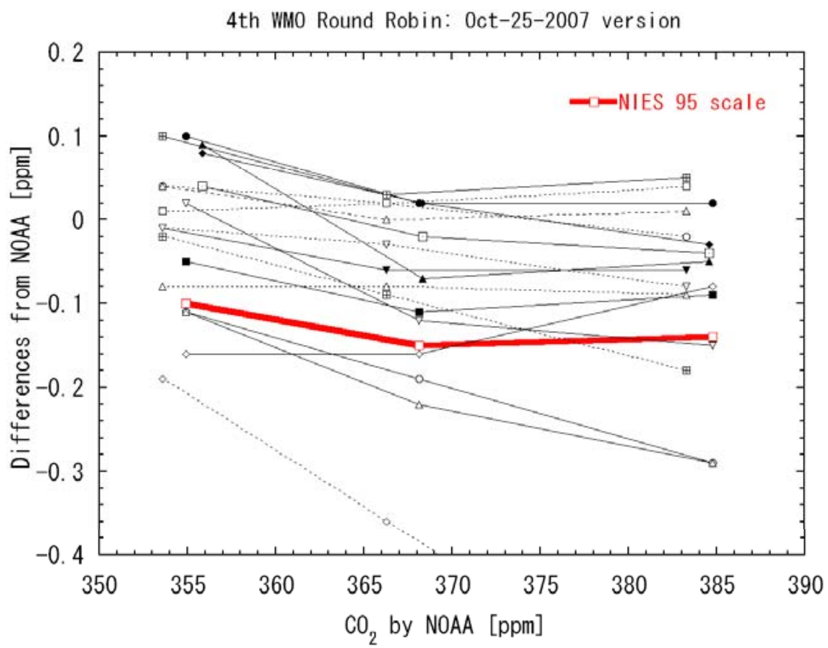
# NIES 標準ガス較正システム

# NIES 95 $CO_2$ Scale




**Gravimetric 3-step dilution**

320,330,340,350,360,370,380,390ppm
for atmospheric $CO_2$
250,470ppm
for oceanic $pCO_2$ (Machida et al.[2009],WMO report 186.)

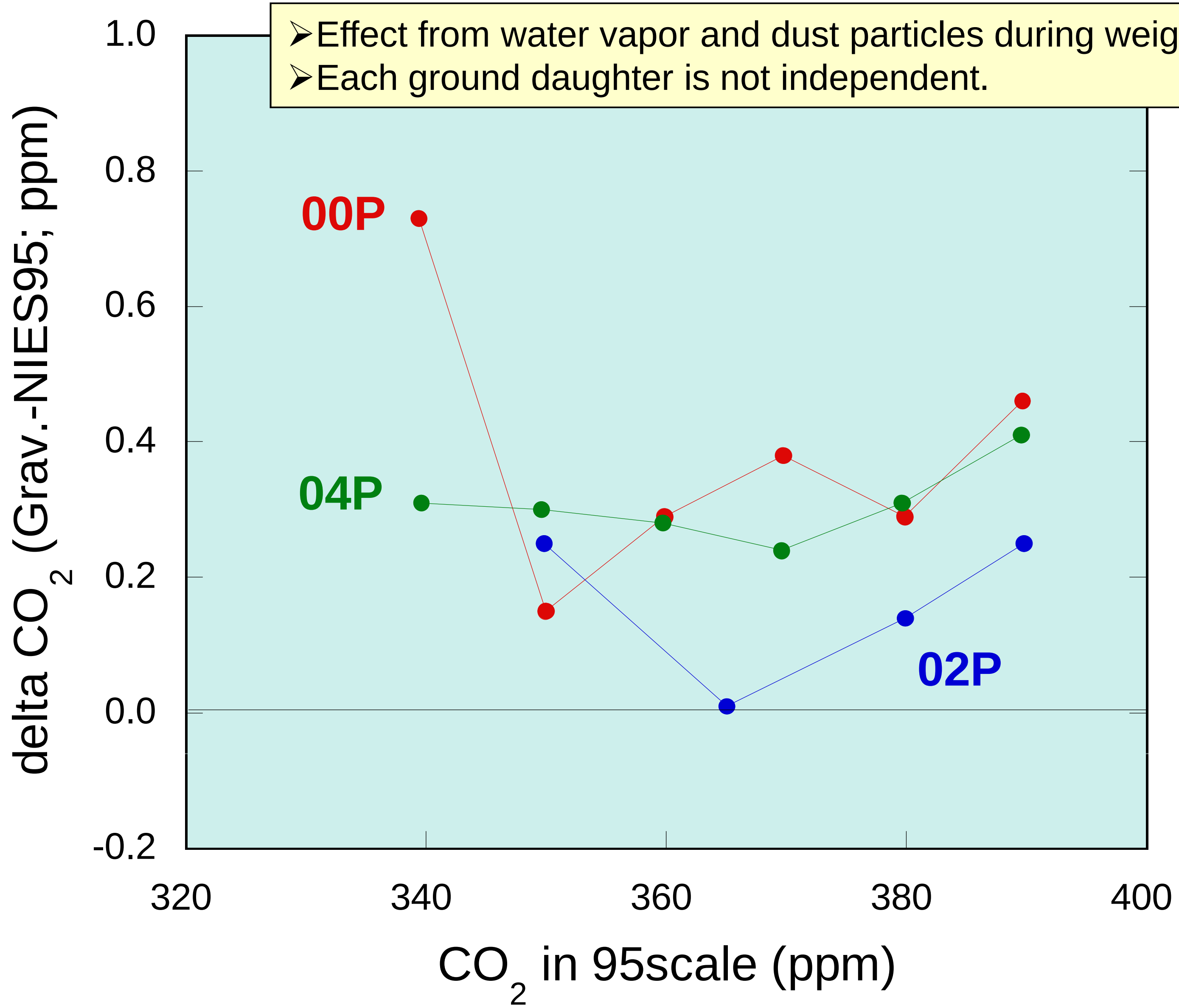




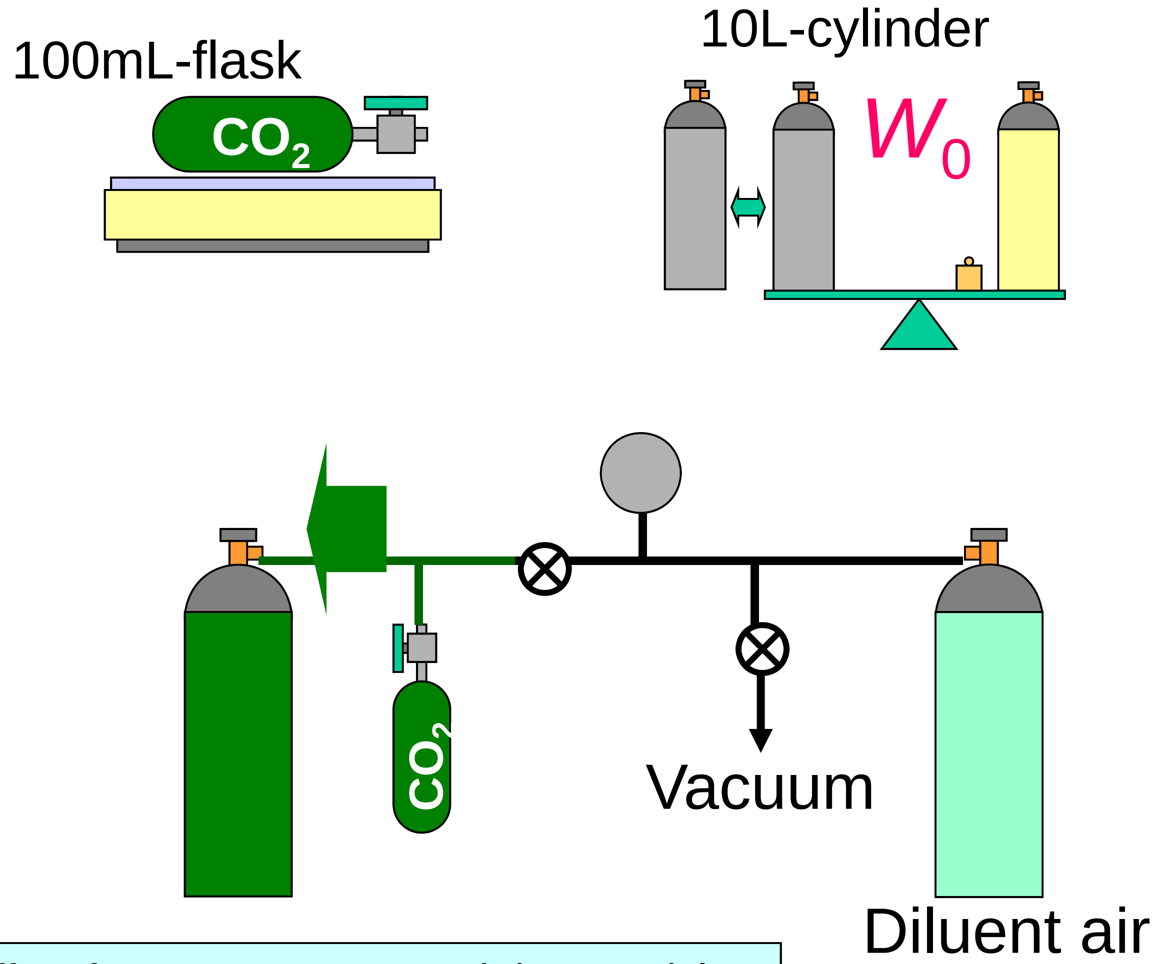

Courtesy of Lingxi ZHOU

# Reproducibility of Gravimetric 3-step Dilution

- Effect from water vapor and dust particles during weighing.
- Each ground daughter is not independent.



# One-step Dilution Method

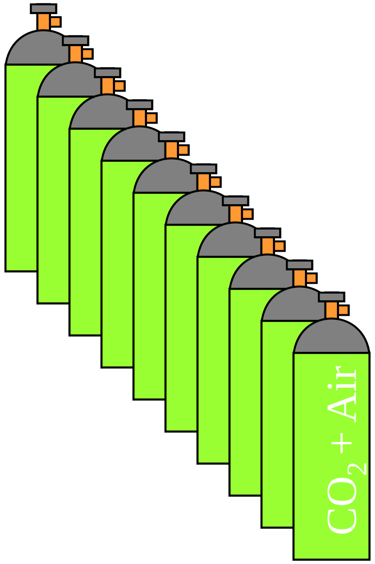



- Reduce the effect from water vapor and dust particles.
- Each ground daughter is independent.



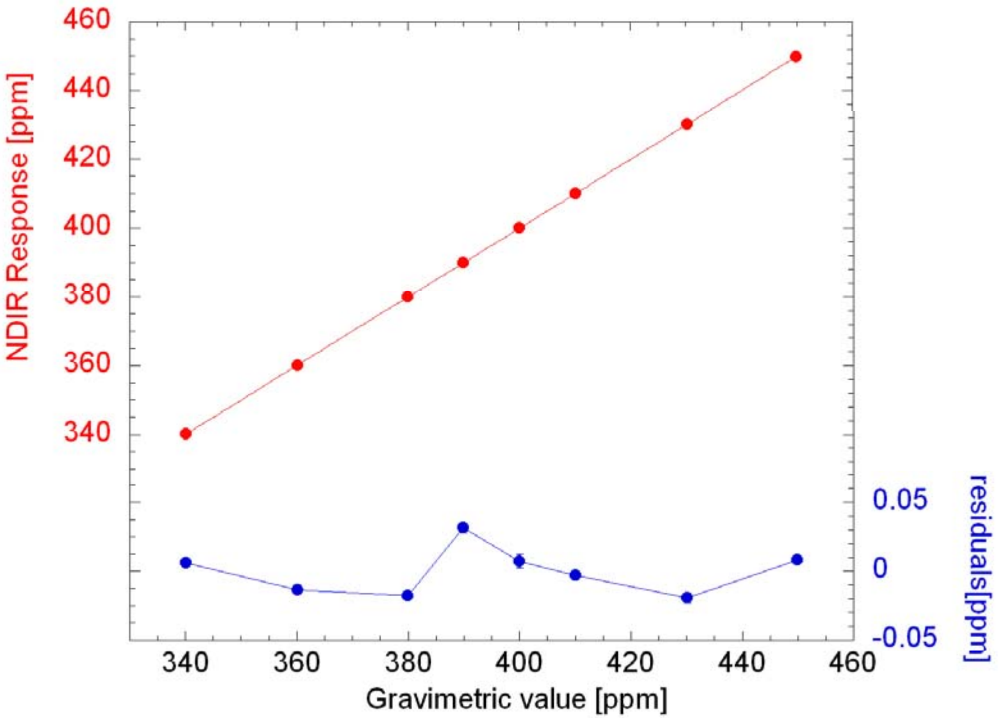
Tohjima et al.[2006],WMO Report 168

# Toward the New $CO_2$ Scale




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

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

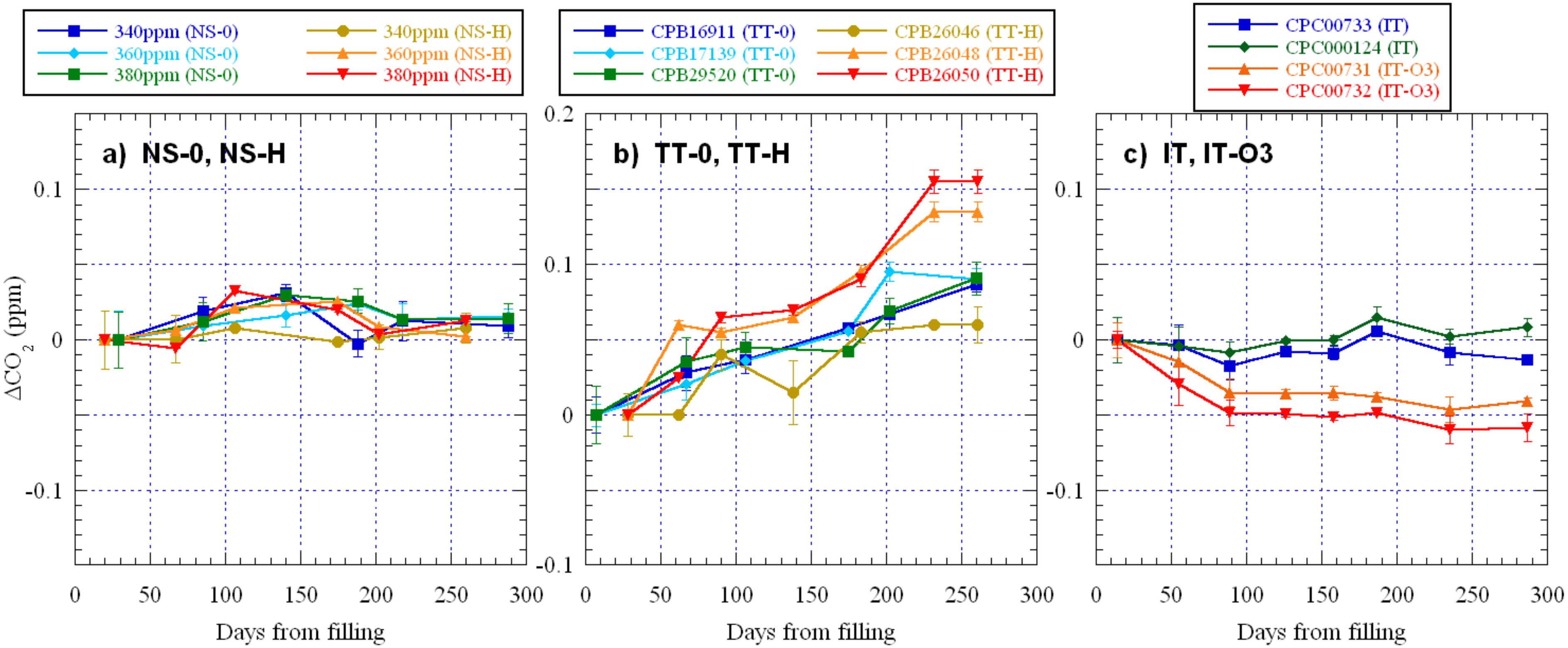



Good correlation in 8 independent cylinders.

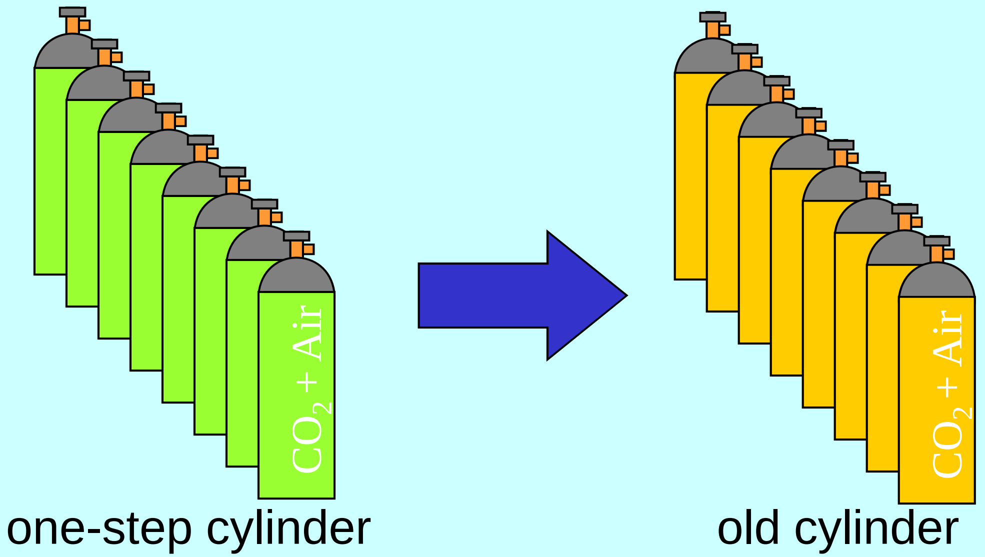
→Confirm reproducibility of gravimetric one-step dilution

→Candidate for New $CO_2$ Scale.

# ワーキングシリンダの安定性に向けた対策（内面処理の影響）

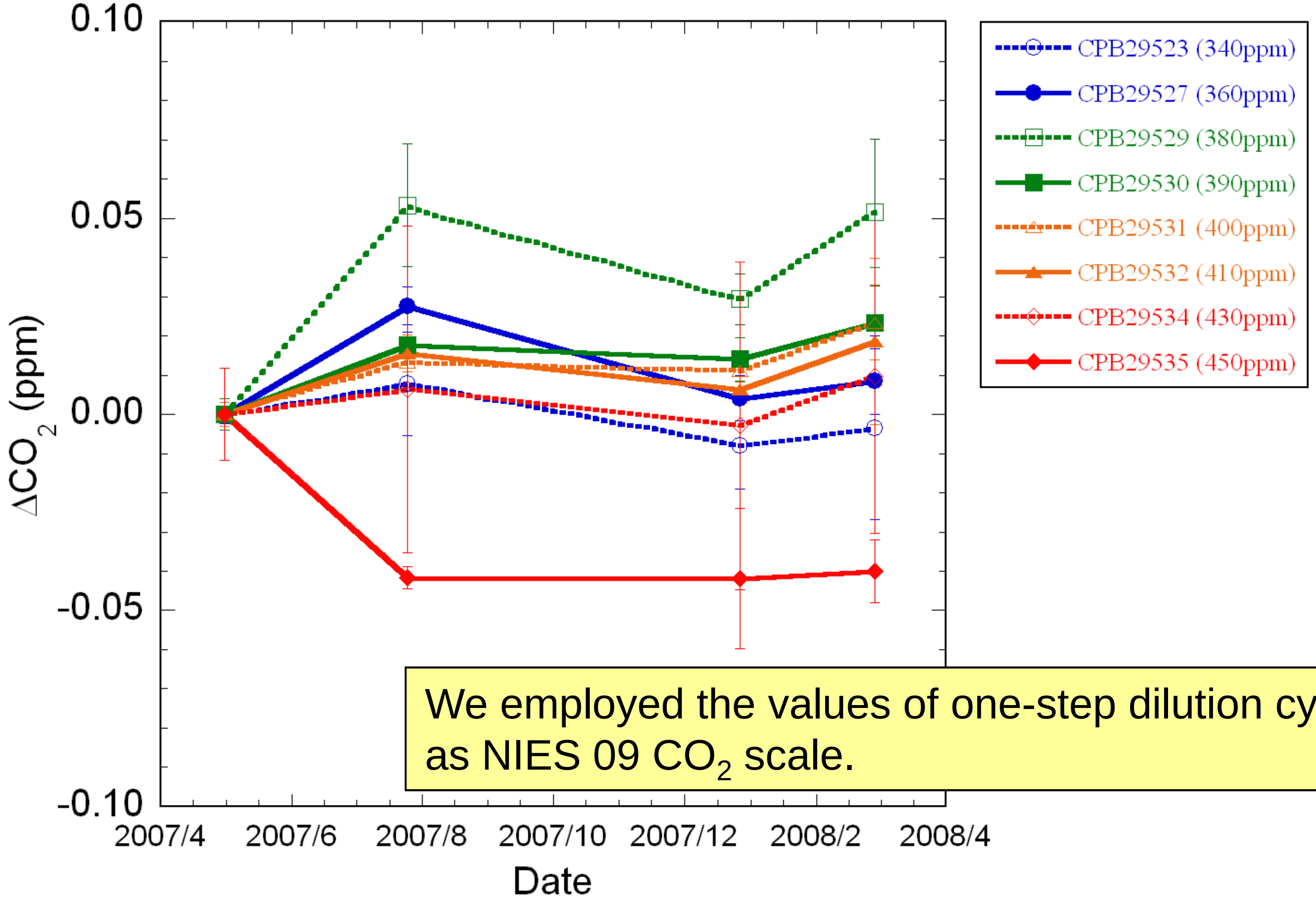


# $CO_2$ Drift in Aluminum Cylinders




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

# Stability of Old Cylinders

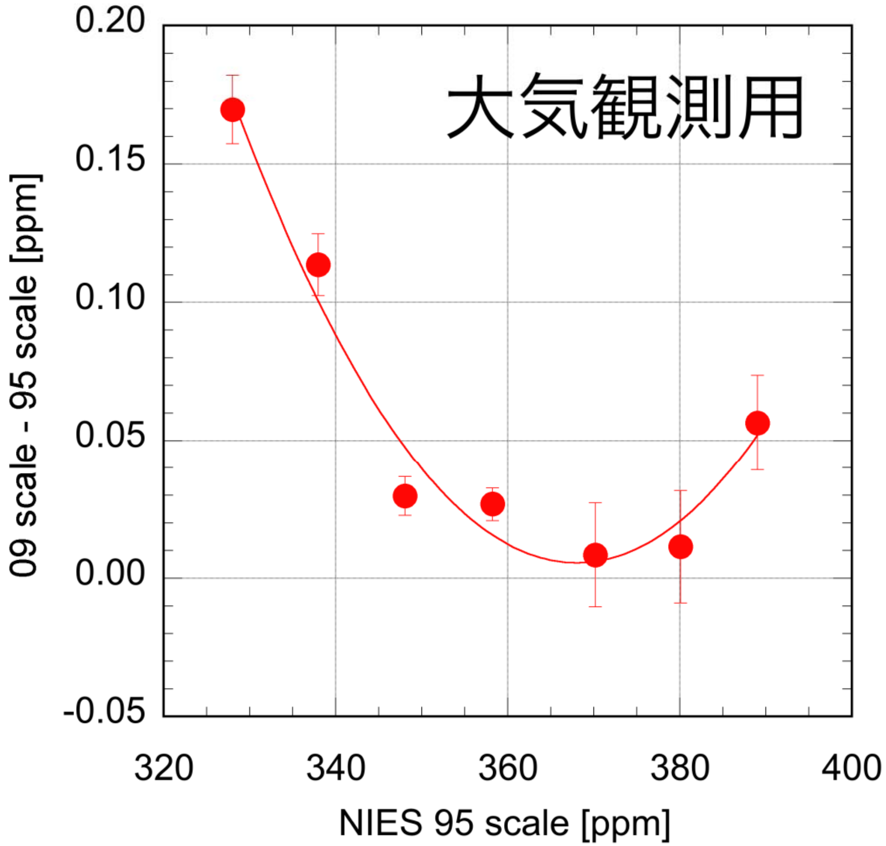



We employed the values of one-step dilution cylinders as NIES 09 $CO_2$ scale.

Rather stable in these 12 months.

# スケール改訂　NIES 09 $CO_2$ scale

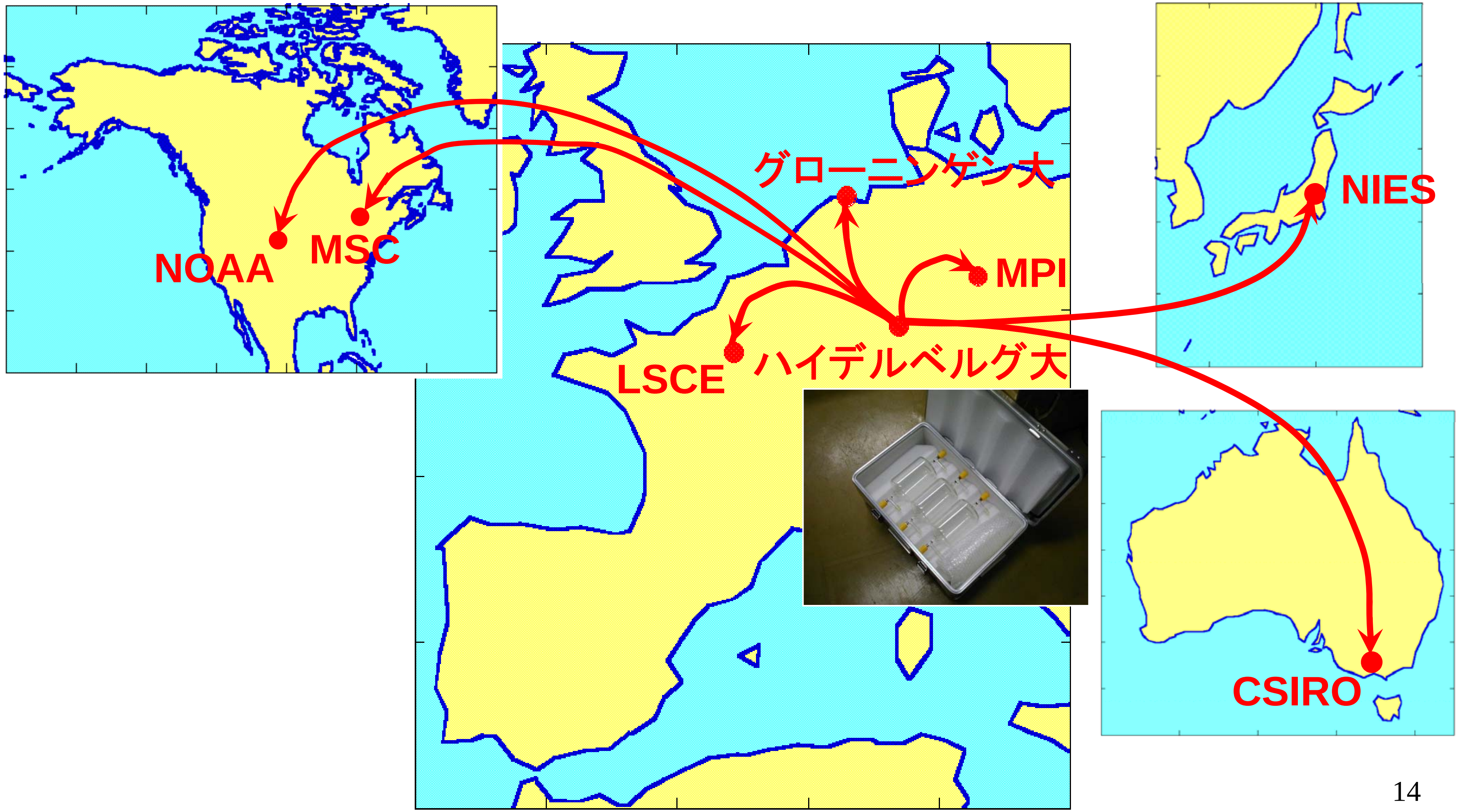
- NIES95スケールからNIES09スケールへの変換

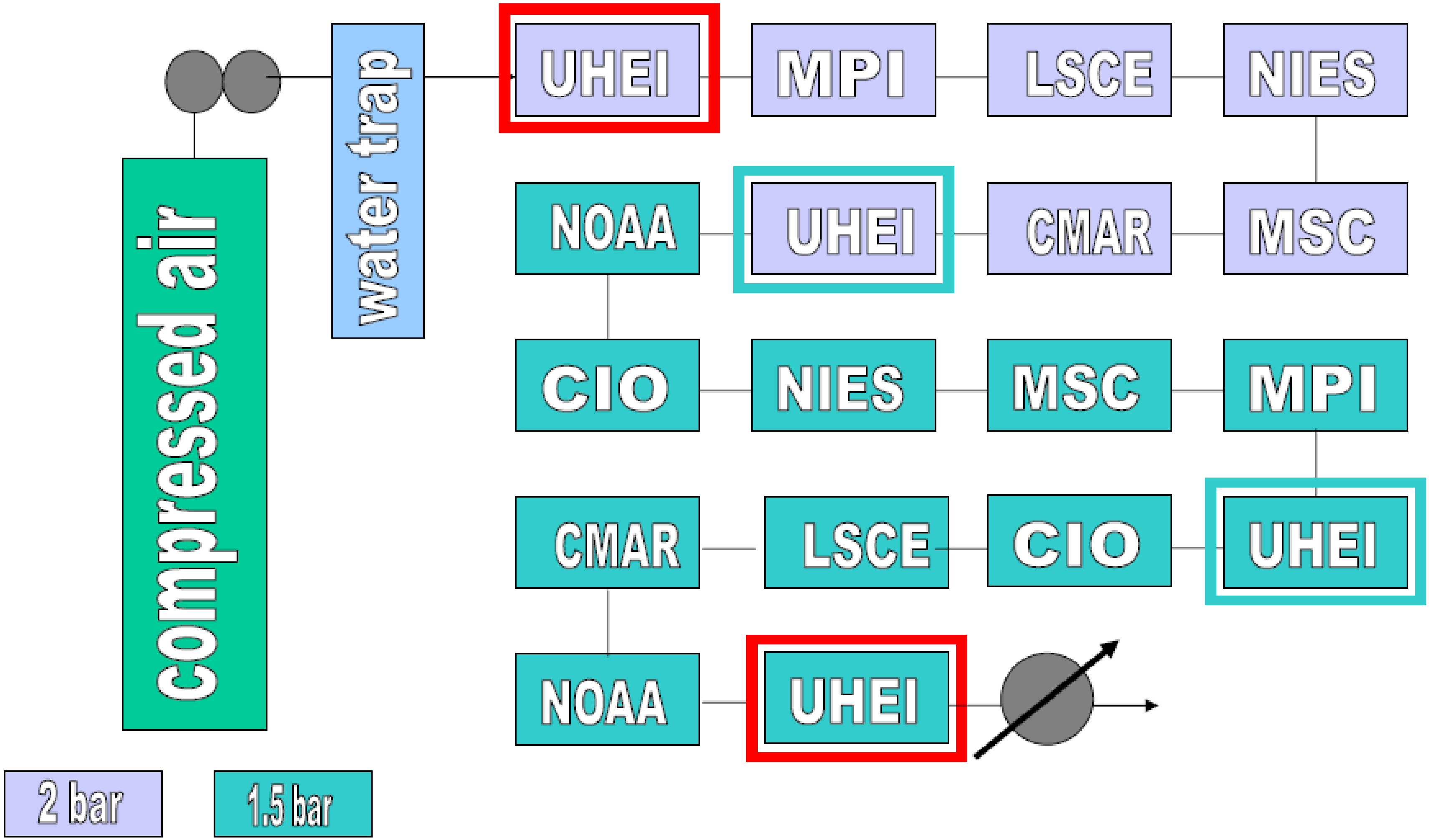



$$C_{09}=8.9015 \times 10^{-5} C_{95}^{2}+0.935031 C_{95}+11.891$$

# Sausageプロジェクト

・圧縮空気をフラスコに充填し、各機関で分析
・High、Middle、Lowの3濃度を2本ずつ（計6本）




compressed air
water trap
UHEI
MPI
LSCE
NIES
NOAA
UHEI
CMAR
MSC
CIO
NIES
MSC
MPI
CMAR
LSCE
CIO
UHEI
NOAA
UHEI
2 bar
1.5 bar

# 各研究機関へ配布

・圧縮空気をフラスコに充填し、各機関で分析
・High、Middle、Lowの３濃度を２本ずつ（計６本）
・2ヶ月に１回
・分析後は速やかに報告
・参加機関はWebにて比較結果を取得できる

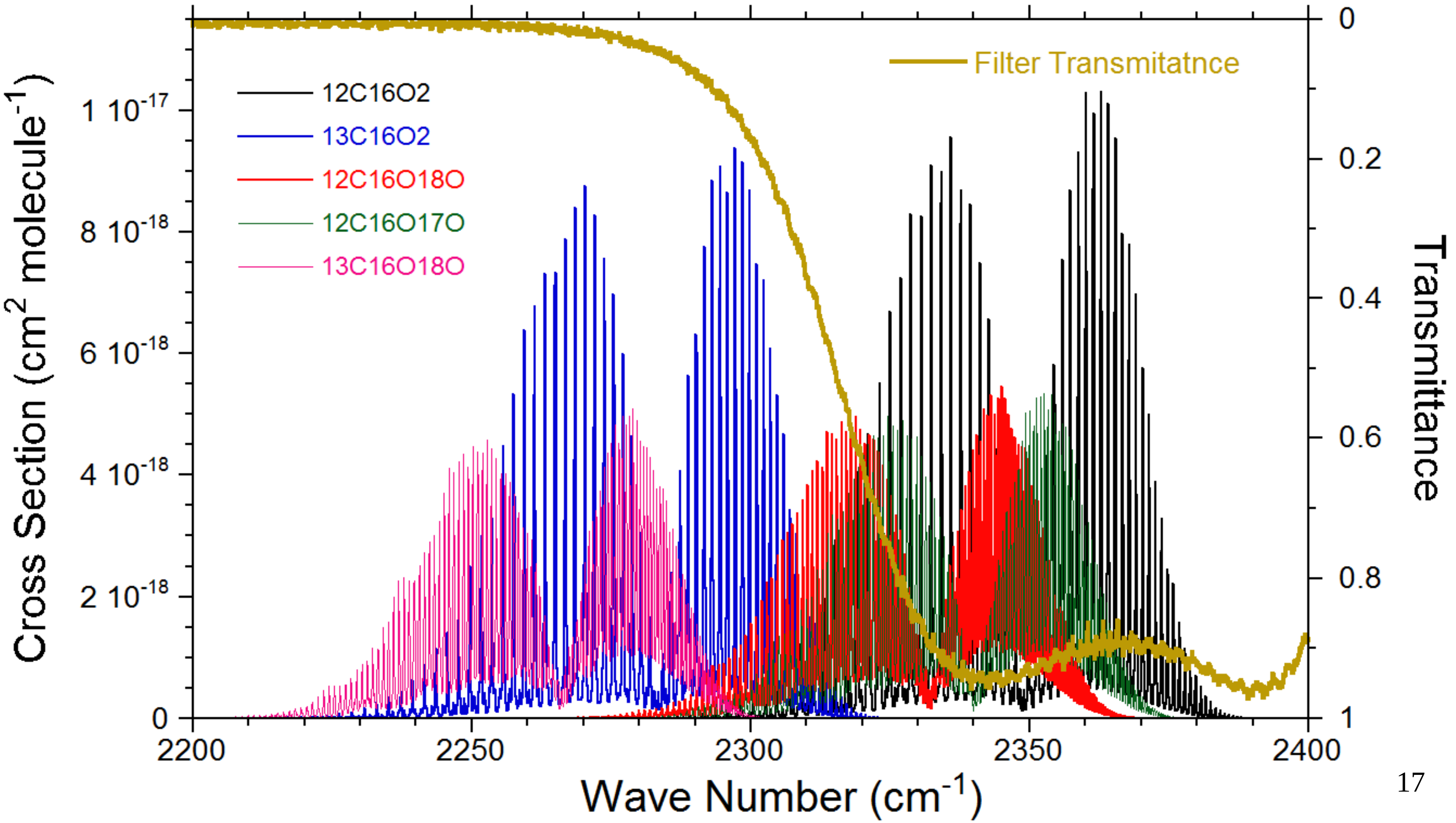

・輸送が簡易
・速報性
・実際のサンプル分析誤差に近い評価ができる
（フラスコの保存性、試料導入方法・・・）

when comparison with other scale,

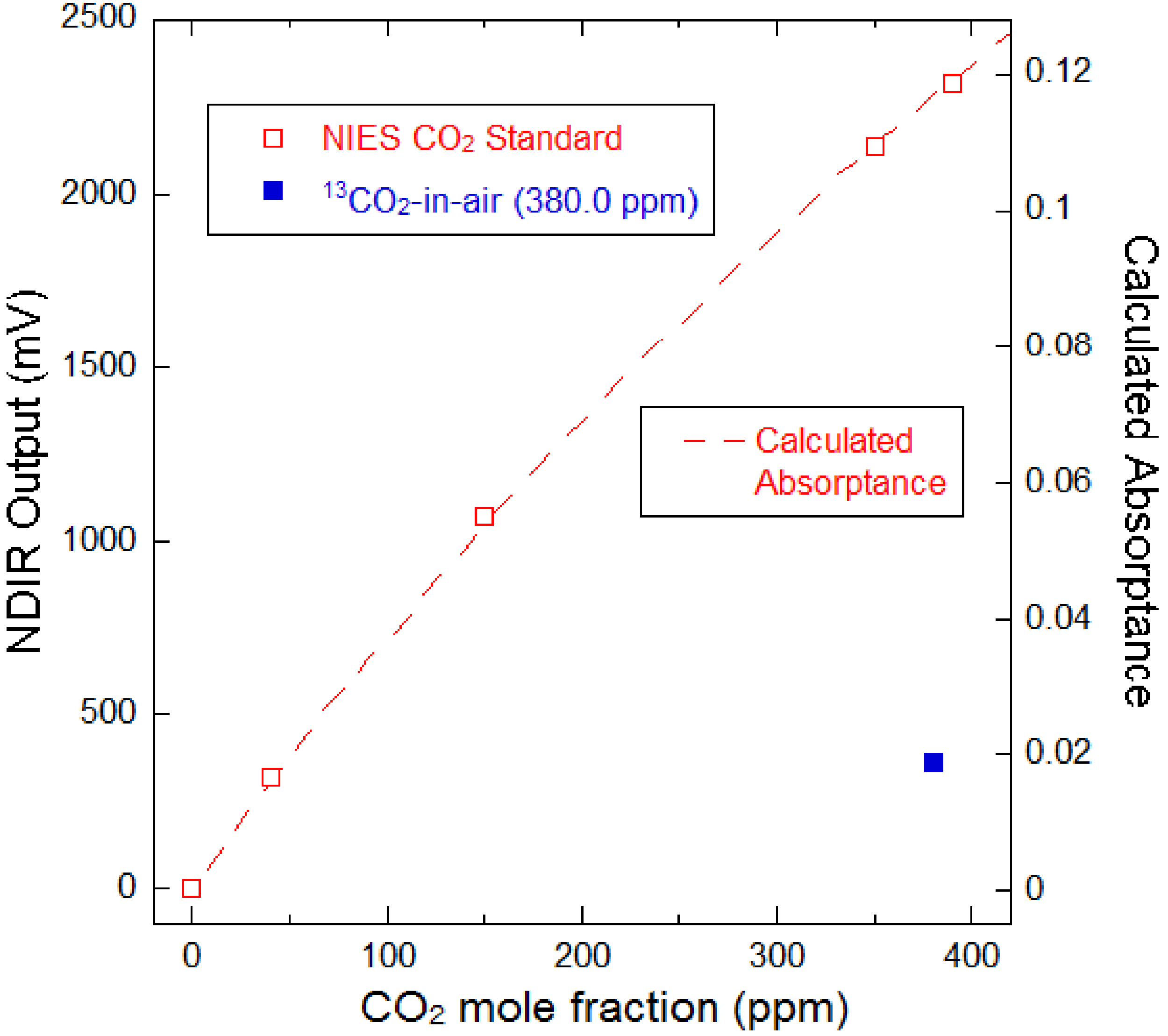
# Isotope Effect on NDIR should be considered.

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

One example of LI-COR filter.



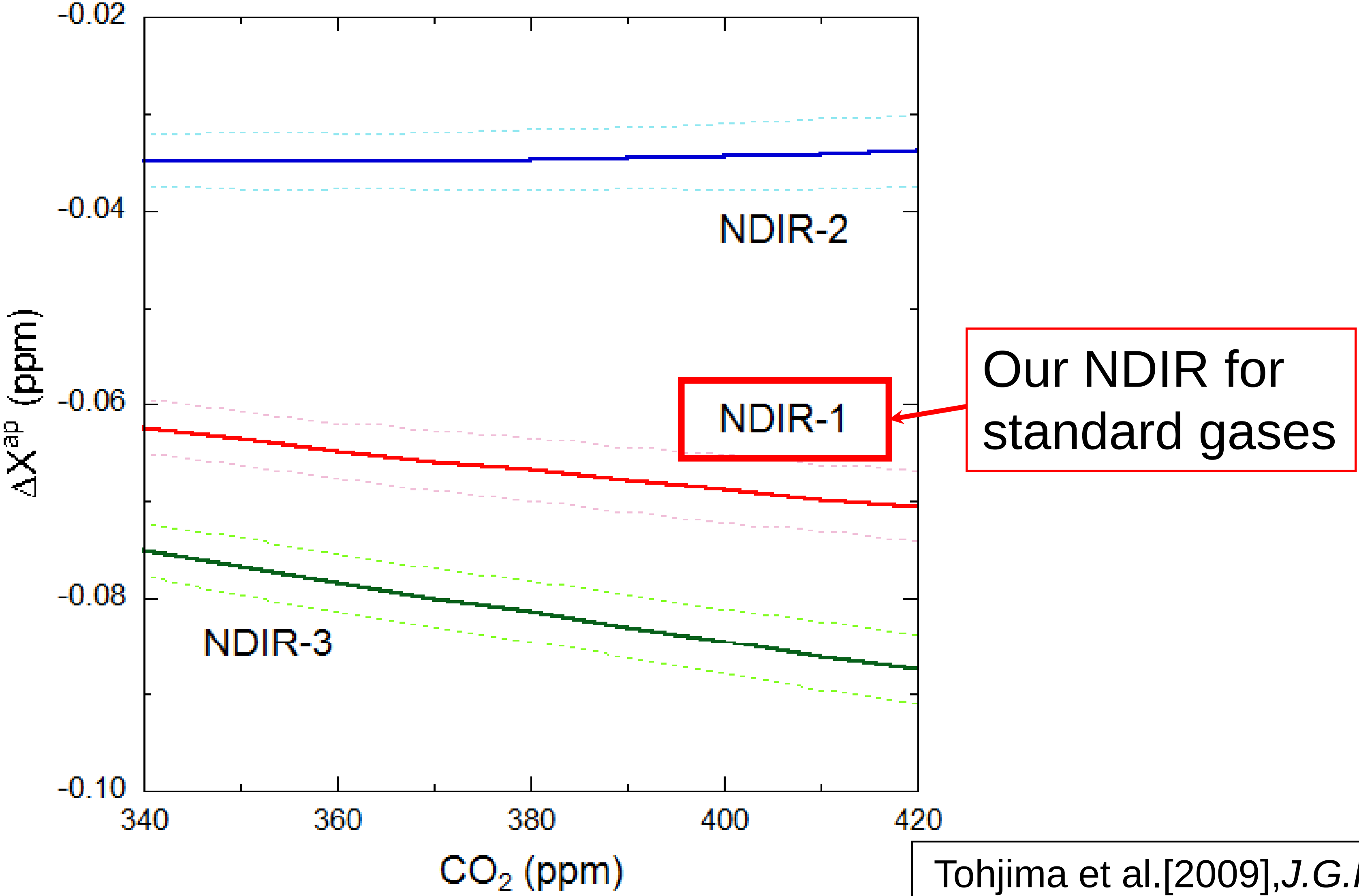
# NDIR response of $^{13}CO_2$




Very small output for $^{13}CO_2$-in-air gas

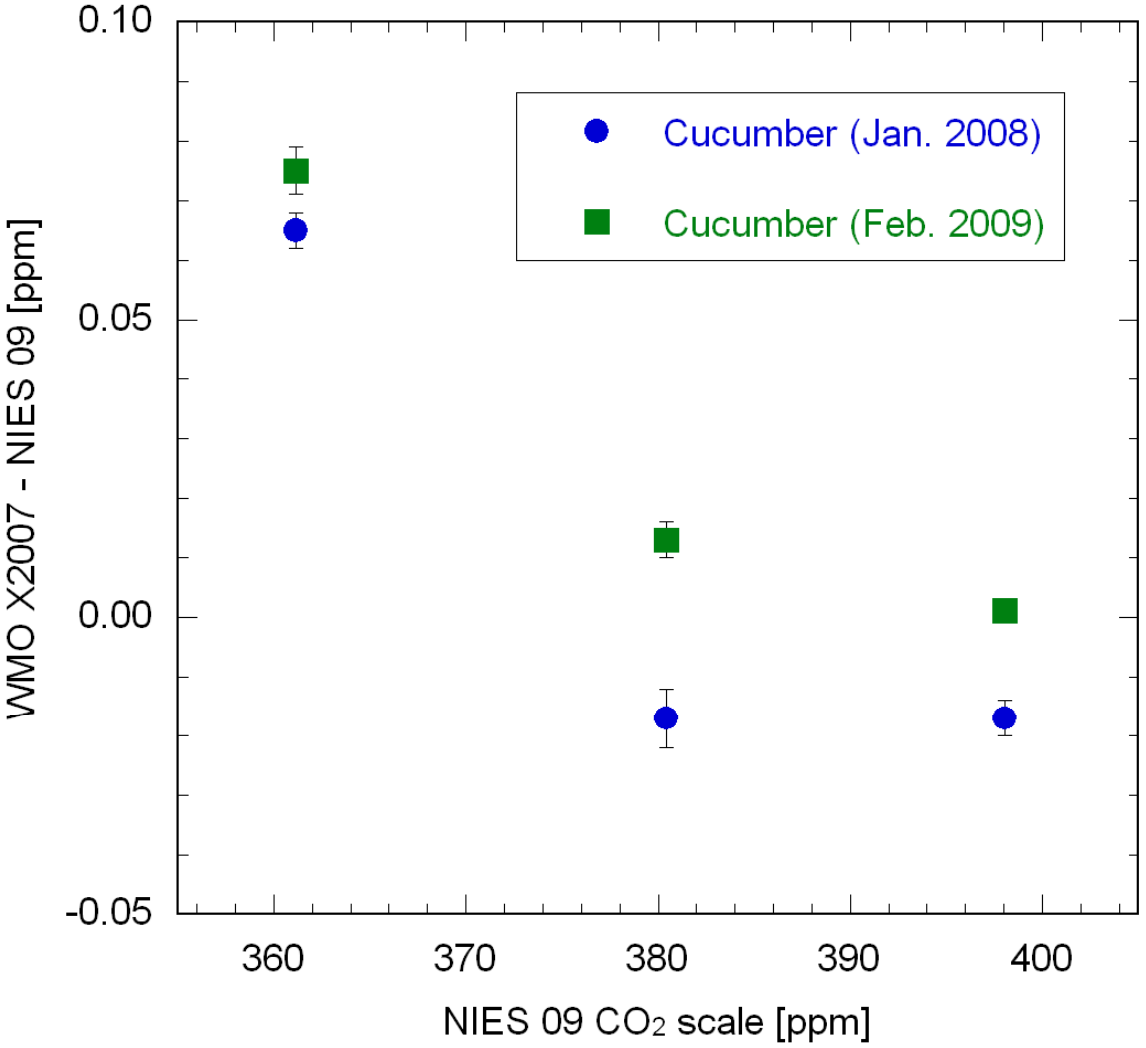
# Apparent signal difference in different $\delta^{13}C$

Apparent $CO_2$ difference between $\delta^{13}C$=-32‰ and -8‰




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

# Difference between NIES 09 and NOAA-X2007




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

Courtesy of Andrew Manning and Armin Jordan

# Conclusion

Gravimetric $CO_2$, $CH_4$, $N_2O$, $SF_6$, CO and $H_2$

Primary – Secondary – Working

Interaction from inner surface of the cylinder

One-step dilution method
→NIES 09 $CO_2$ scale

Substantial Difference from other Scales

Isotope Effect on NDIR
→also on Cavity Ring-Down Spectroscopy