Gaseous reference materials to underpin measurements of amount fraction and isotopic composition of greenhouse gases

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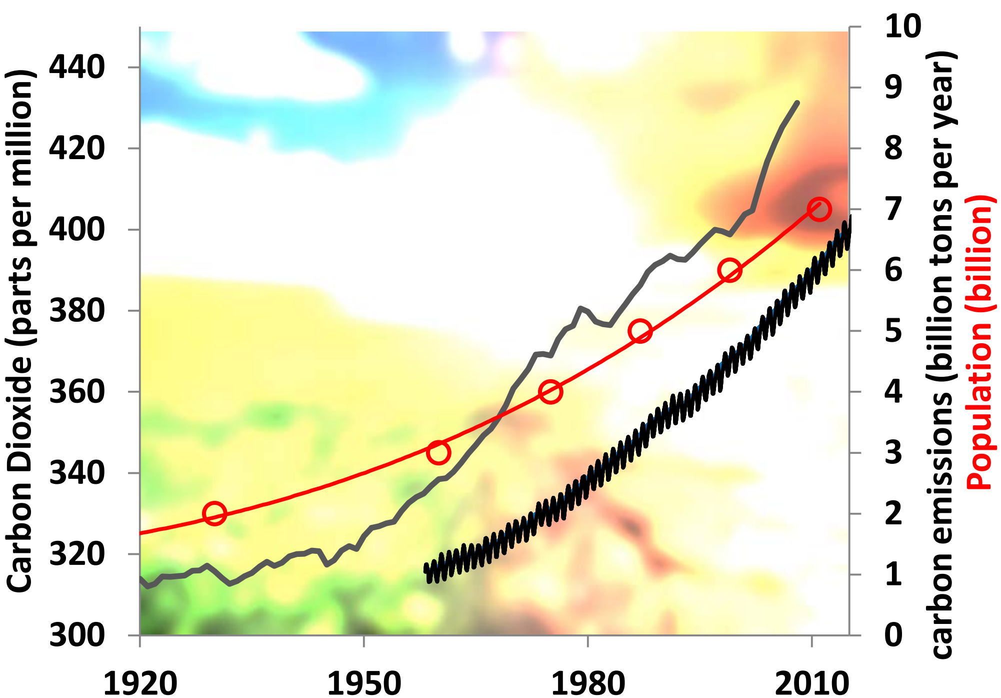
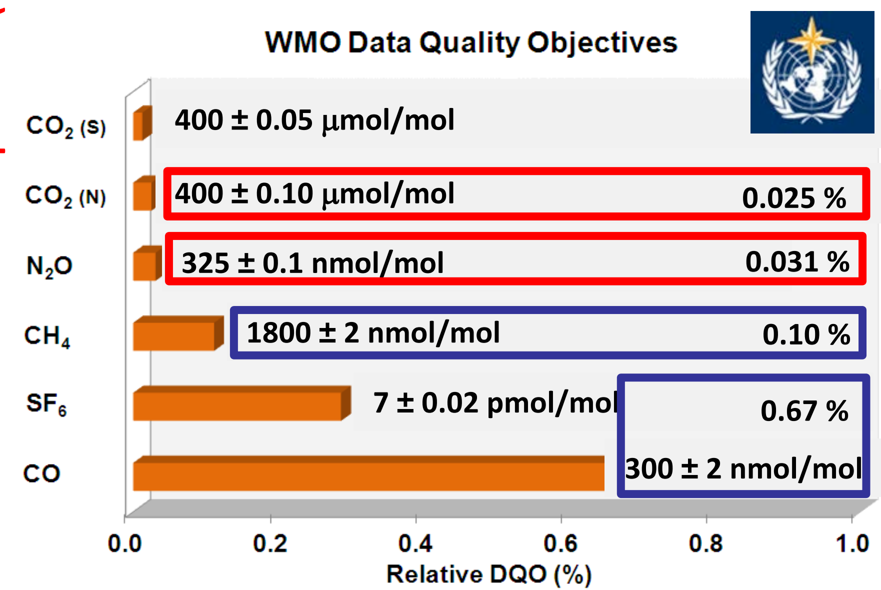
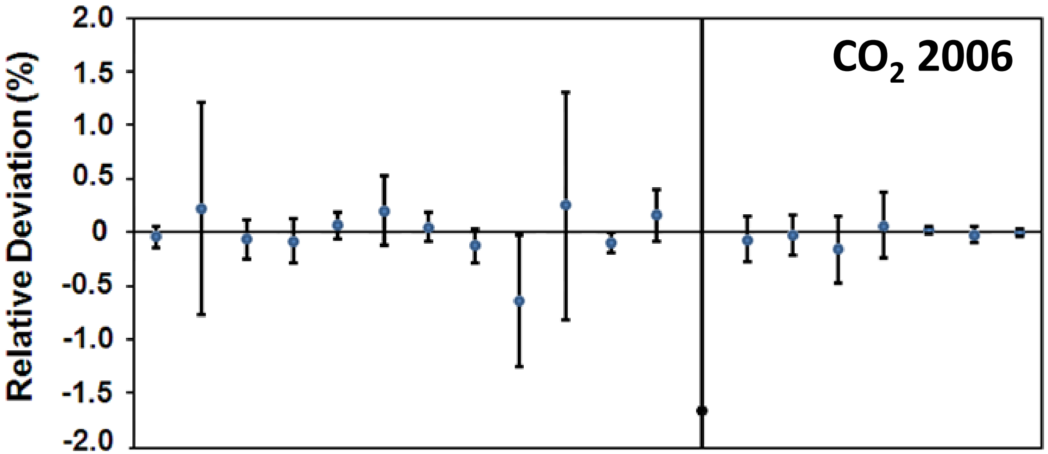
Rationale

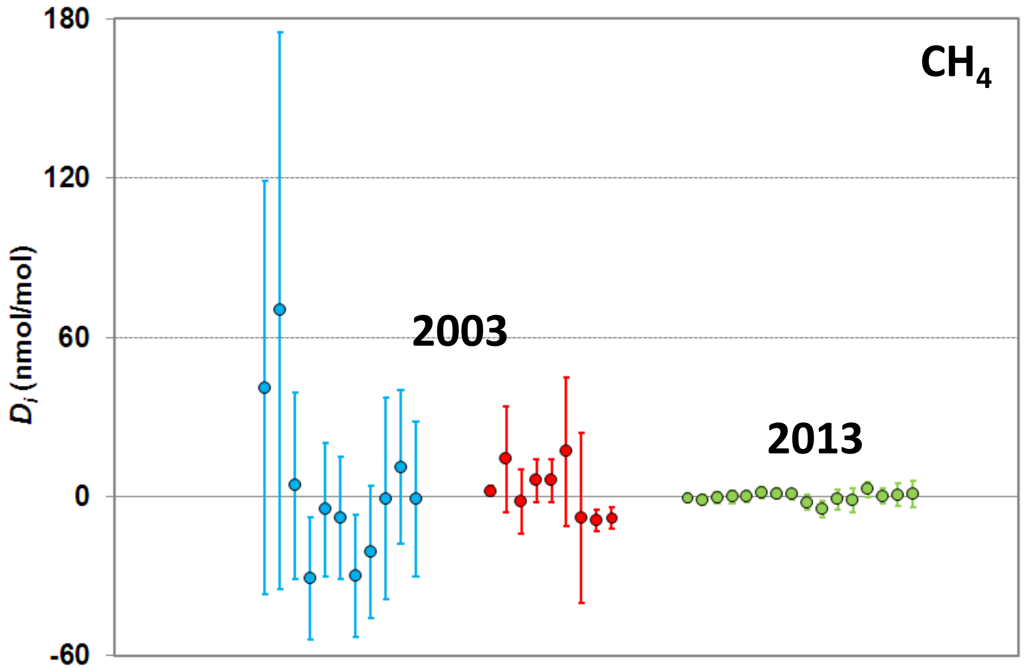
- Requirement for traceability from the primary realisation of the mole
- Legislation aimed at reducing emissions and their measurement
- Long-term observations based on accurate and stable standards

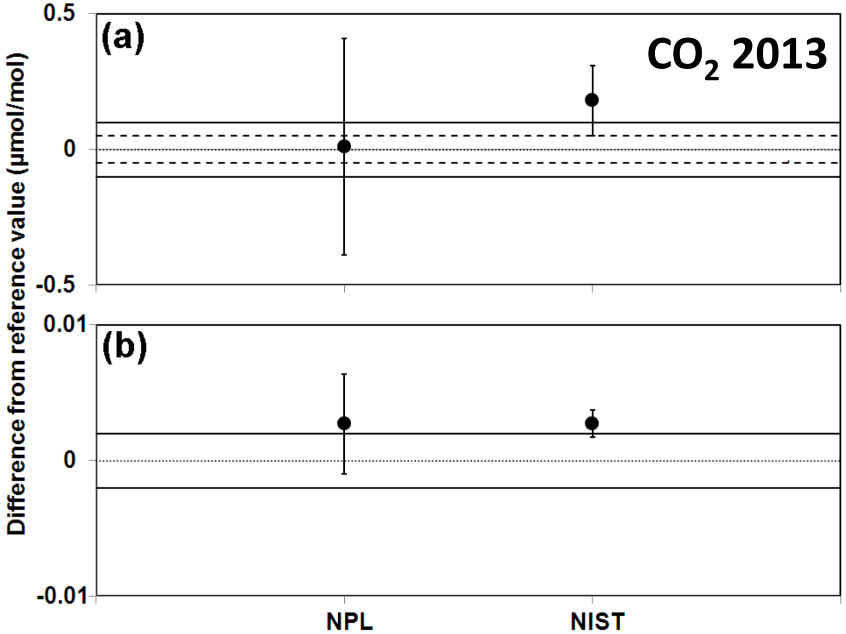




Comparability







- Isotopic composition of $^{12}CO2$ - $^{13}CO2$ matched to natural abundance
- Uncertainty < 0.05 % for CO_2 and < 0.1 % for CH_4 (k=1)

Synthetic Reference Standards

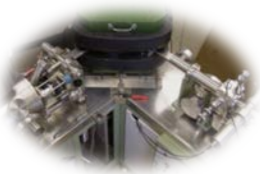
- Gravimetric preparation
- Purity analysis
- Analytical validation

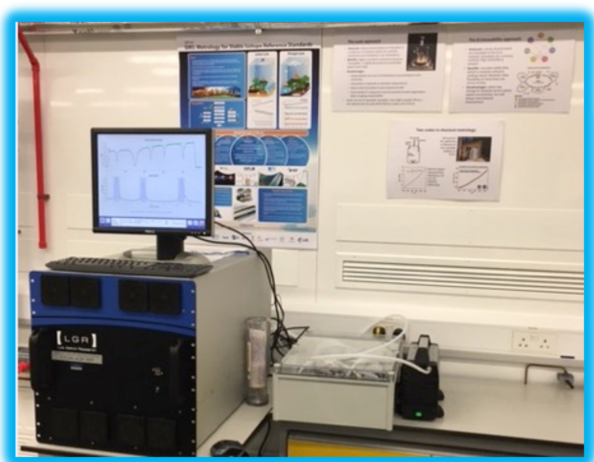
Challenges

Purity and gravimetry

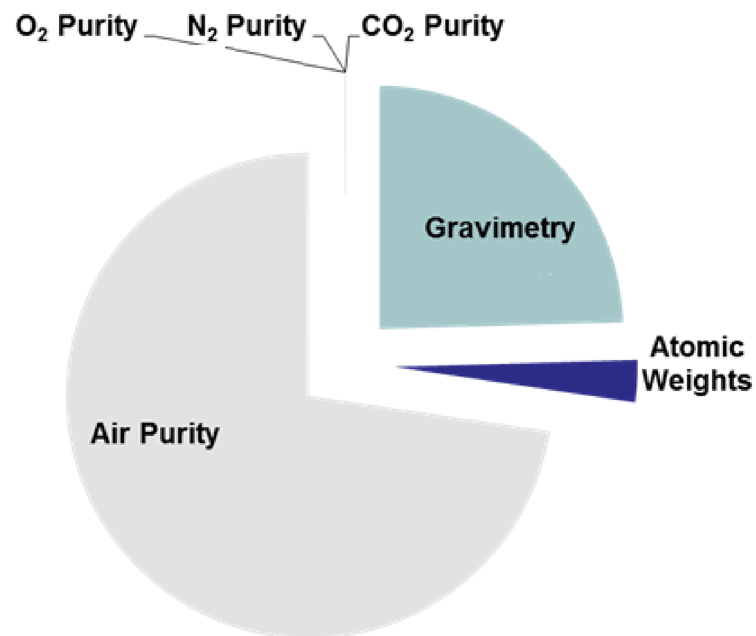
Stability

Commutability

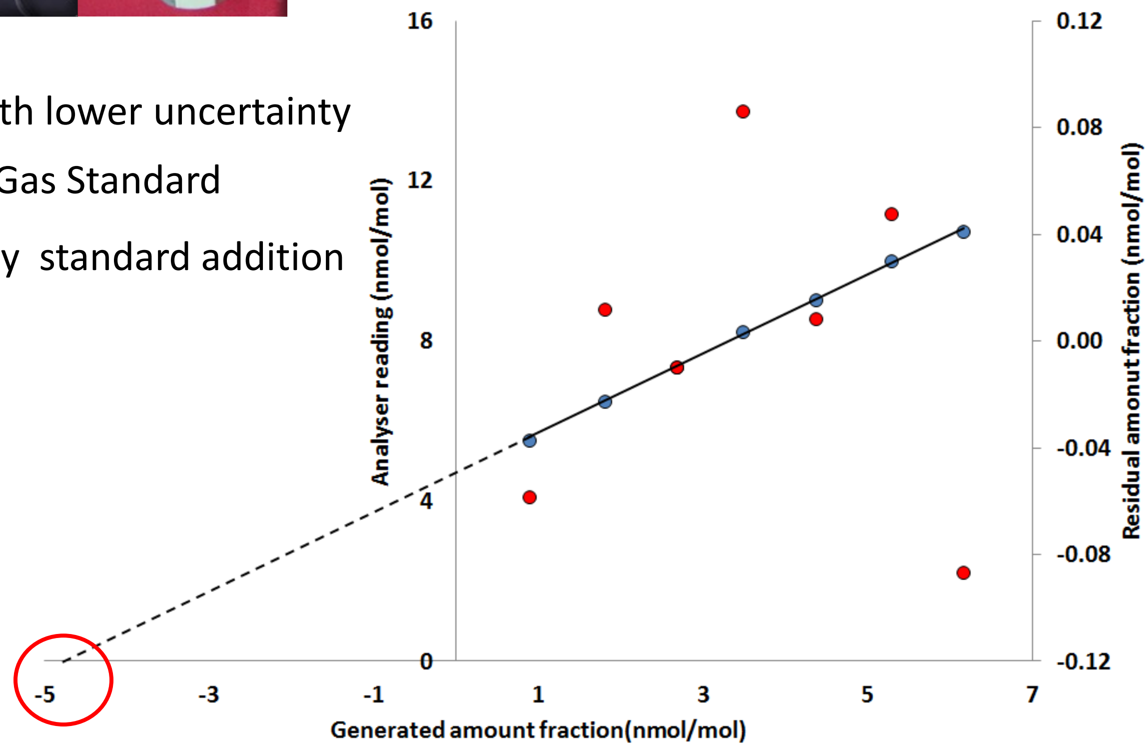




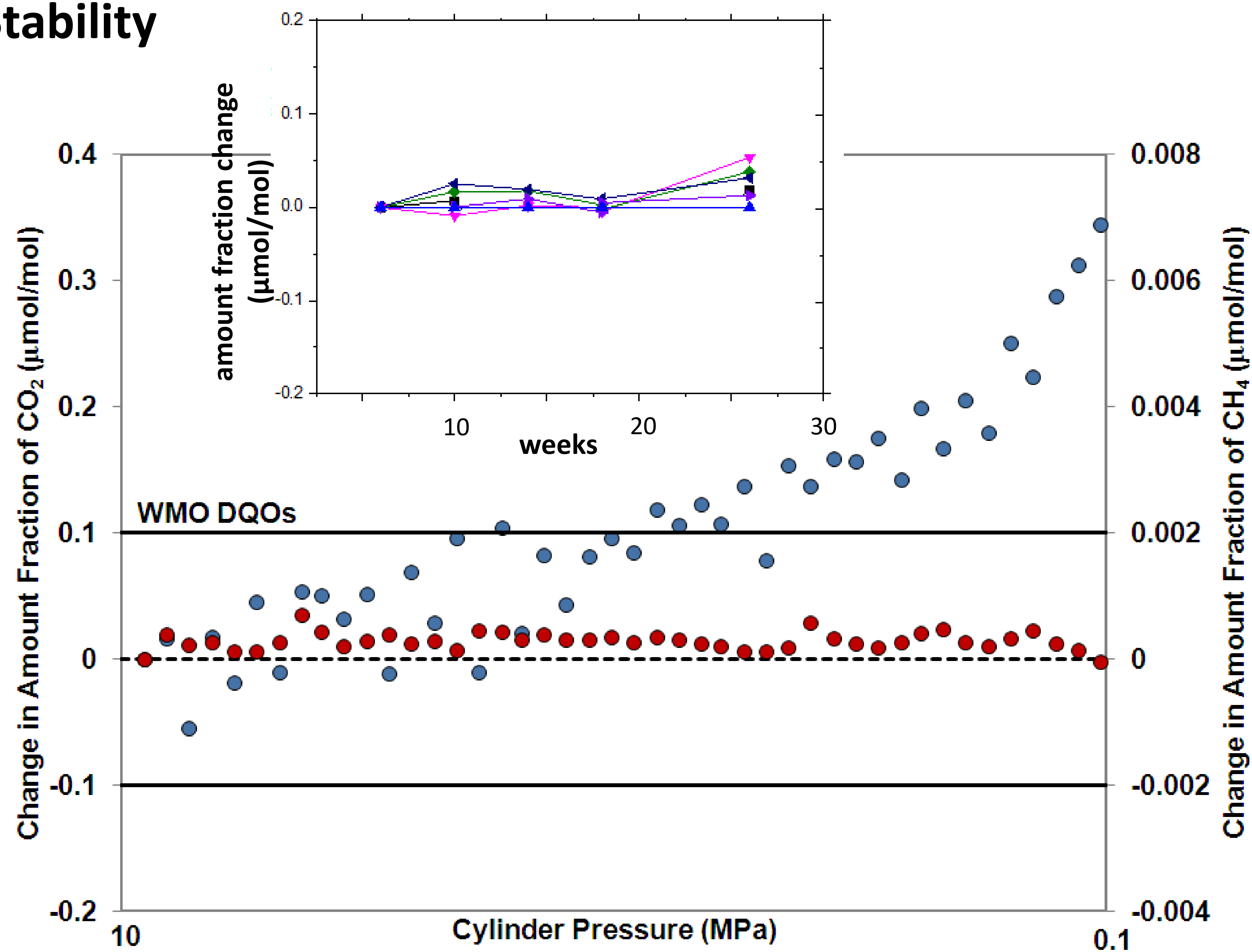
Purity and gravimetry



- New method with lower uncertainty
- NPL Adjustable Gas Standard
- Quantification by standard addition



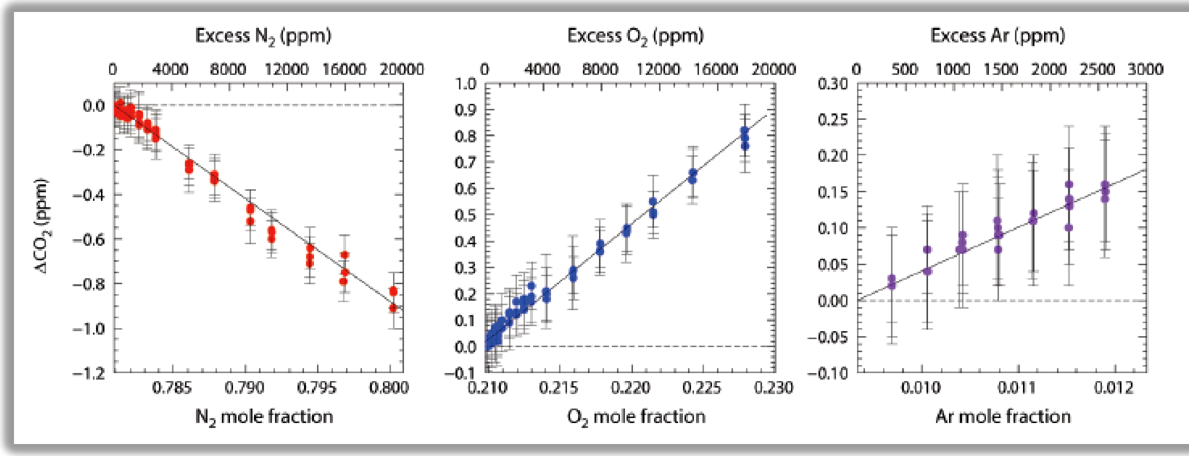
Stability



Change in Amount Fraction of CO_2 (µmol/mol)
Change in Amount Fraction of CH_4 (µmol/mol)
Cylinder Pressure (MPa)
10
0.1
0.4
0.3
0.2
0.1
0
-0.1
-0.2
0.008
0.006
0.004
0.002
0
-0.002
-0.004
WMO DQOs
amount fraction change (µmol/mol)
weeks
0.2
0.1
0.0
-0.1
-0.2
10
20
30

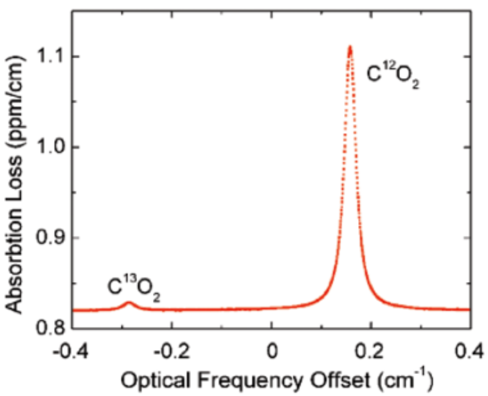
Commutability

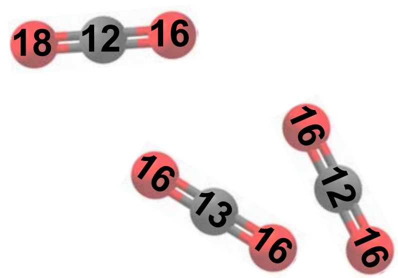
- Influence of matrix composition on spectroscopy (requirement for 0.1 cmol mol^{-1})
- More pronounced for CO_2

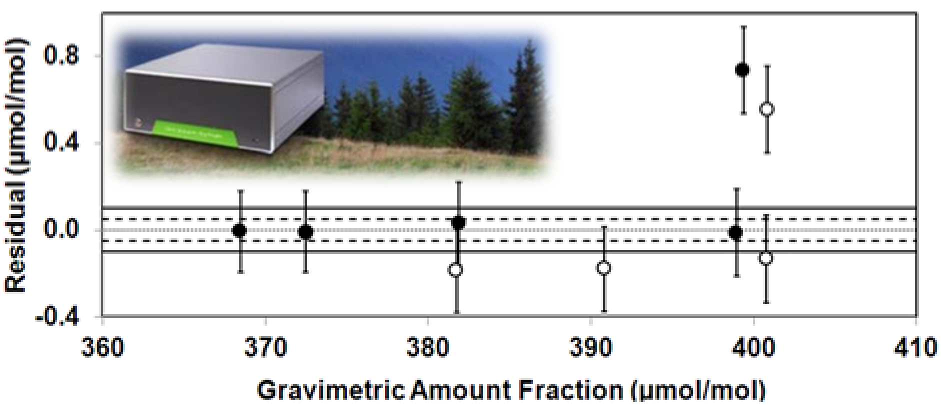


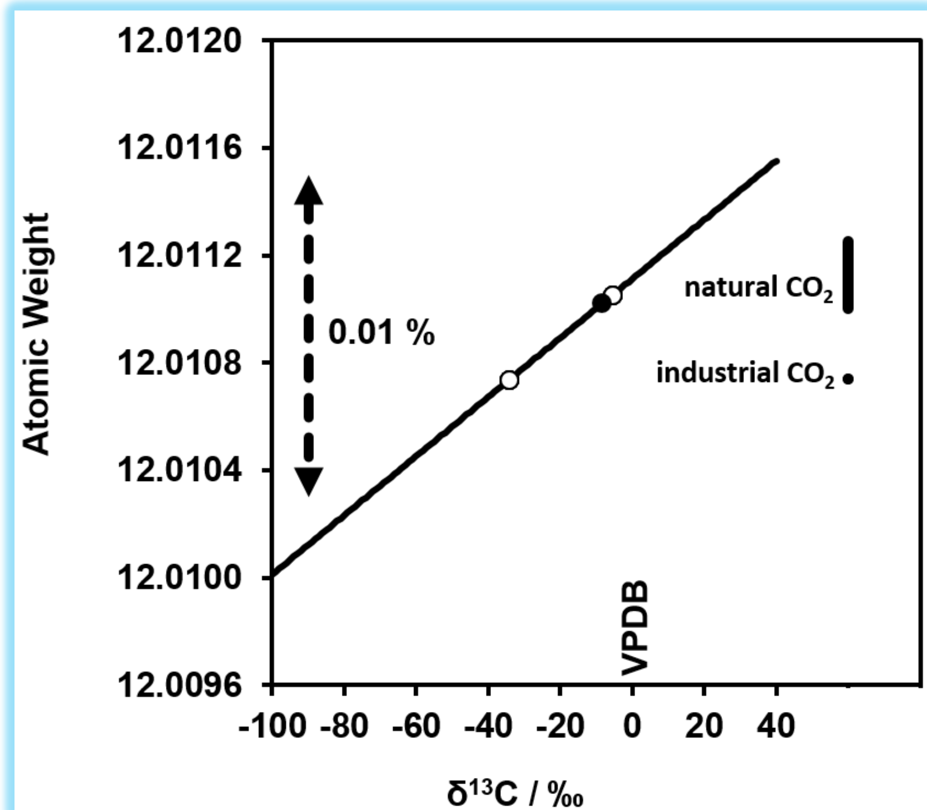
H. Nara, H. Tanimoto, Y. Tohjima, H. Mukai, Y. Nojiri, K. Katsumata and C. W. Rella, *Atmos. Meas. Tech.*, **5**, 2689–2701, (2012).

1 ‰ corresponds to ~ 4 nmol/mol

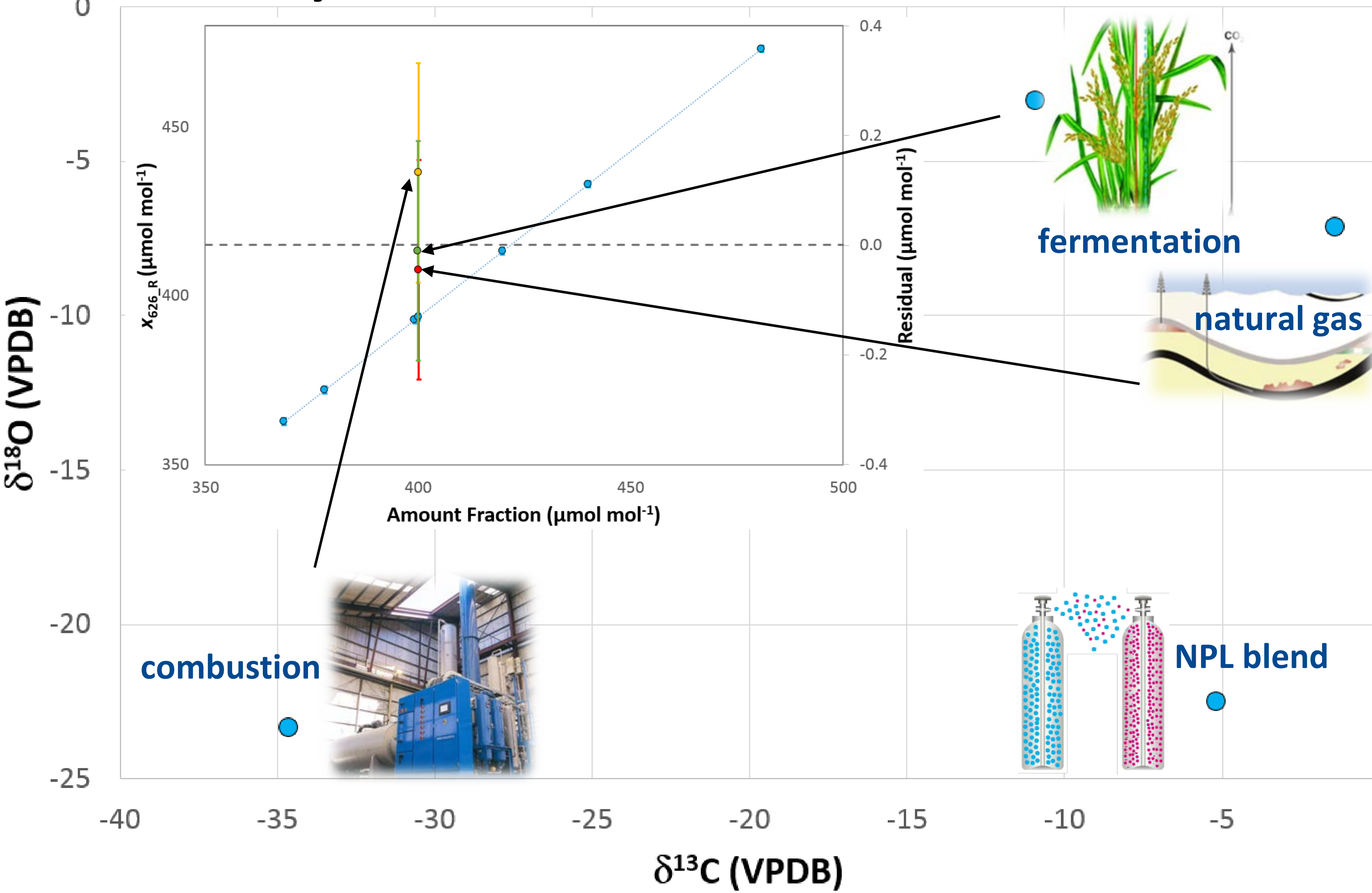




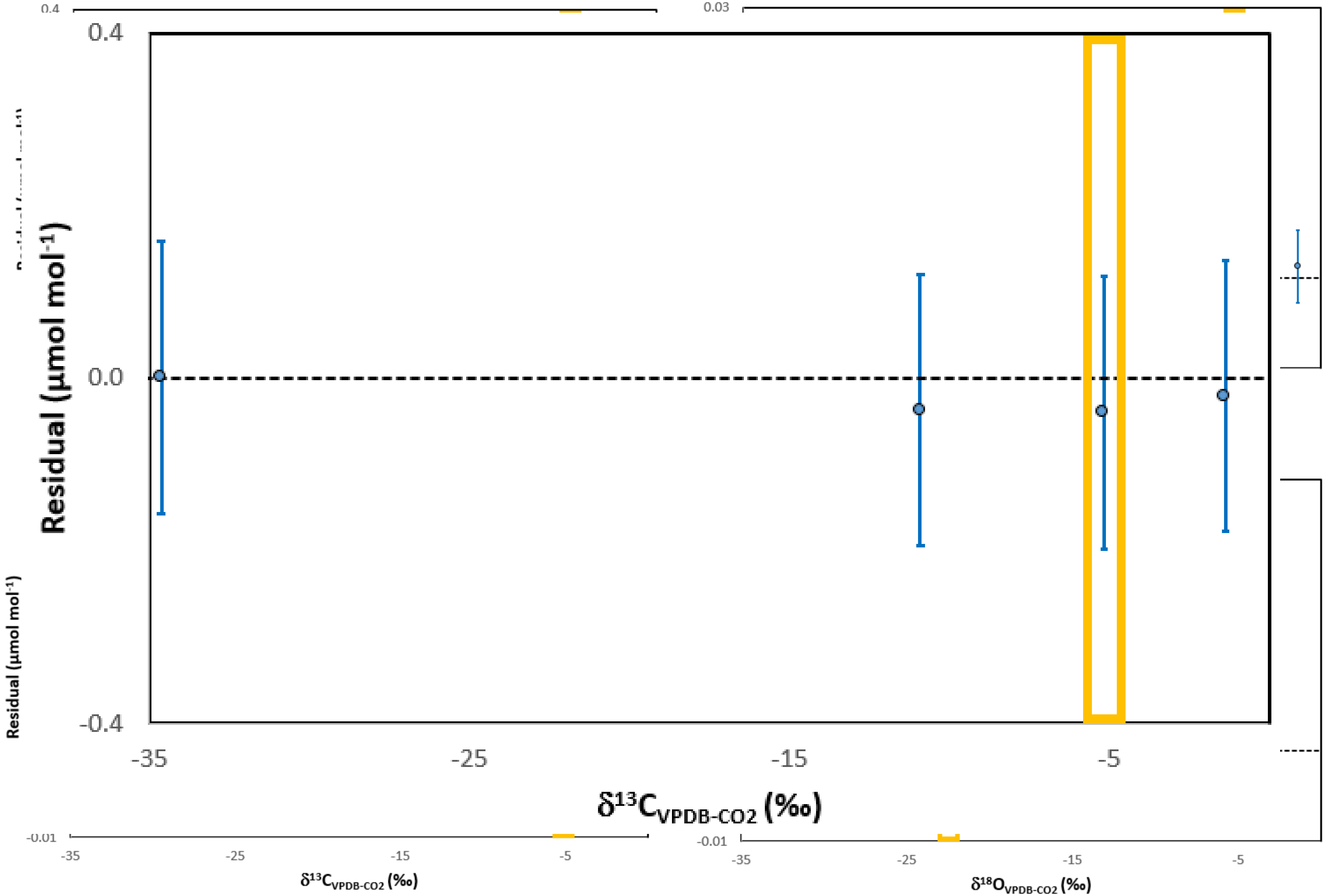




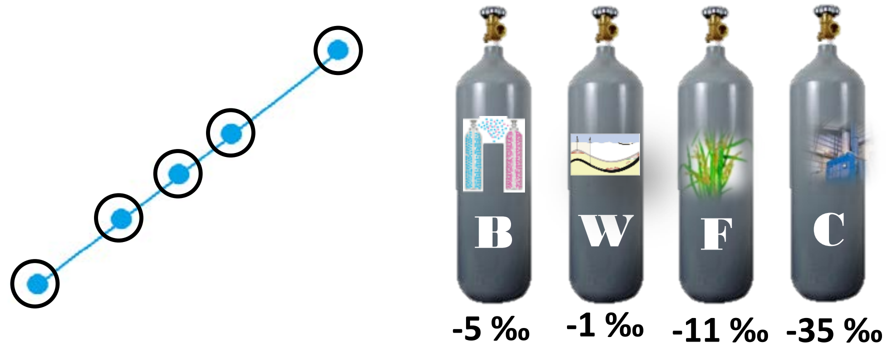
Commutability

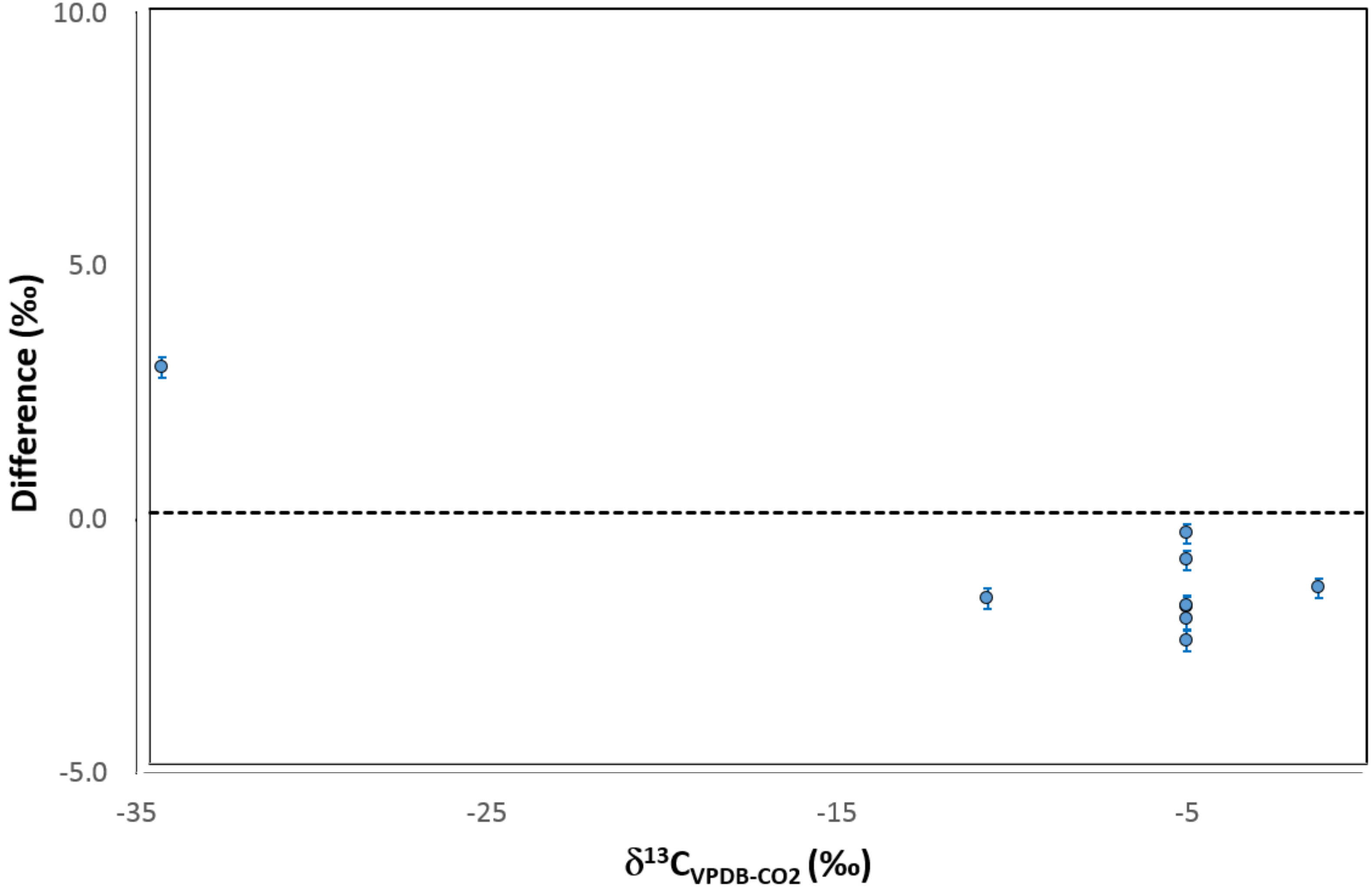


Calibration



Influence of the calibration





Metrology for Stable Isotope Reference Standards (SIRS)

EURAMET

The project will address:

- Limitations in infrastructure to deliver international gaseous CO_2 reference materials
- Absence of international gaseous N_2O reference materials with stated uncertainties
- Advances in optical spectroscopy for traceable field deployable techniques

New reference materials, calibration methods and instrumentation

- CO_2 (pure and 400 µmol/mol in air, uncertainties: δ^{13}C-CO_2 0.1 ‰, δ^{18}O-CO_2 0.5 ‰)
- Re-measure absolute CO_2 isotope ratios to provide data for SI traceability
- N_2O (pure and 300 – 1000 nmol/mol in air) reference materials (uncertainties 1.0 ‰ ($\delta^{15}N^{\alpha}$ and $\delta^{15}N^{\beta}$) and 0.5 ‰ (δ^{15}N, δ^{18}O))
- Spectroscopic methods for isotope ratio measurements

Partners

NPL National Physical Laboratory · EMPA · PTB · VTT · INRiM · DFM · university of groningen · AIR LIQUIDE · UNIVERSITY OF EASTERN FINLAND · IJS

Collaborators

WMO · Tiger Optics · BIOS · BOC · CEN · ISO · IUPAC CIAAW · ICOS · KRISS · LGR · Picarro · Royal Holloway Uni · Tokyo Institute of Technology · Elementar · Aerodyne · Karlsruher Institut für Technologie · NILU

Conclusions

- Substantial progress made towards developing an infrastructure to provide SI traceability for measurements of CO_2, CH_4, N_2O and CO
- Research required to deliver gaseous reference materials for isotope ratio of CO_2 and N_2O

Acknowledgements

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ROYAL HOLLOWAY UNIVERSITY OF LONDON

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BIPM

UEA University of East Anglia

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