Meeting the demand for isotopic carbon dioxide and methane gas reference materials for underpinning global observations

1. Background

- To support governments verifying emissions and demonstrating national reduction targets, it is necessary to discriminate between the natural and various man-made sources of greenhouse gases.
- Separating manmade emissions from measured carbon dioxide and methane amount fractions is challenging and requires information on the isotopic composition.

Currently there is no infrastructure to meet the demand for carbon dioxide and methane isotopic gas reference materials with the required uncertainties to underpin global observations, compromising the comparability of measurement data.

Additionally, metrology is also required to ensure advances in optical spectroscopy result in field deployable techniques that meet uncertainty requirements.

STELLAR

The STELLAR project aims to address the existing traceability gap in the measurement of isotopes of CO_2 and CH_4 by developing gas reference materials, calibration methods and dissemination mechanisms, which are traceable to existing scales (e.g. VPDB - Vienna Pee Dee Belemnite - and VSMOW/SLAP - Vienna Standard Mean Ocean Water/ Standard Light Antarctic Precipitation) and the SI.

2. Challenges

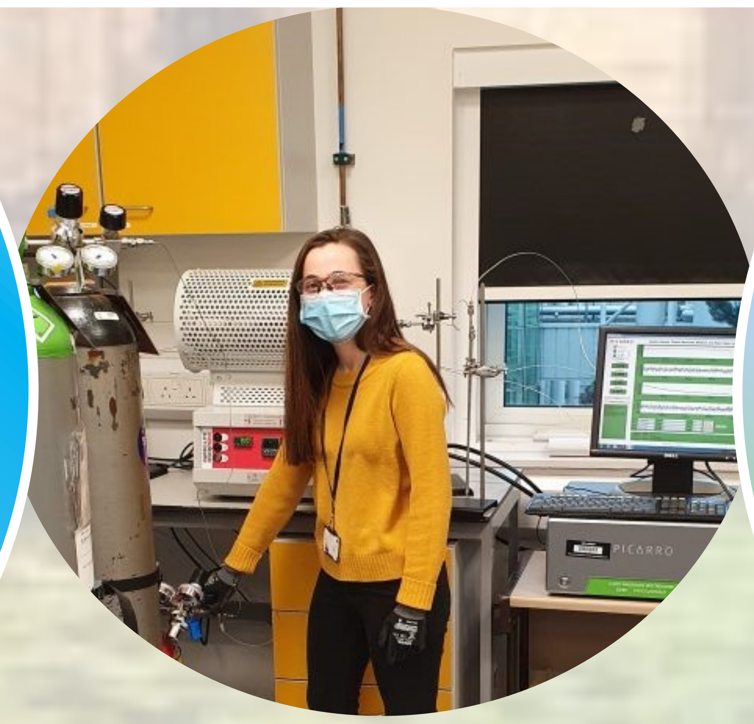
CO_2 from carbonates for underpinning isotope ratio is currently limited and prohibitively expensive.

Independent capabilities for the whole traceability chain and an improved understanding of the influence of gravimetric preparation parameters on isotopic fractionation is essential.

No absolute isotope ratio measurements, traceable to the SI, have been achieved with the desired uncertainty.

Isotope ratio remains a traceability exception under the CIPM-MRA.

SI traceable methods are required for absolute isotope ratio measurements of CO_2.



Low uncertainty and high volume CO_2 and CH_4 gas reference materials traceable to VPDB and VSMOW/SLAP scales for $\delta^{13}C$, $\delta^{18}O$ & $\delta^{2}H$ are needed to underpin global measurements.

There is currently no CCL at the WMO-GAW level for CH_4 to ensure compatibility of global observations.

Validation routines, recommendations and traceability chains for field-deployable spectroscopic techniques that meet the precision specifications of IRMS are required.

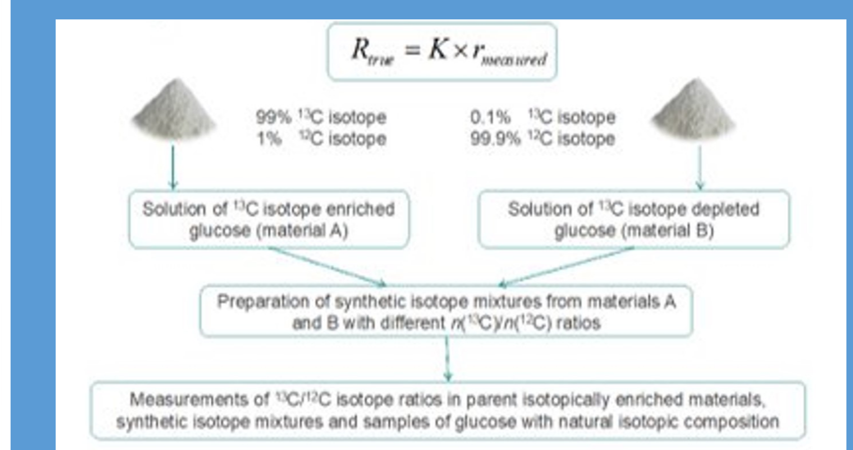
3. Achievements

Carbonate-phosphoric acid reaction: interlaboratory comparability.

- Partners produced CO_2 from IAEA-603 which was analysed at the (BGC-IsoLab).
- The interlaboratory comparability meets the required reproducibility of ***0.01‰ and 0.05‰ for $\delta^{13}C$ and $\delta^{18}O$*** respectively.

SI traceability

- Absolute carbon dioxide isotope ratio



- Results compared to CO_2 prepared from enriched and depleted carbonates.

Zero air

Zero air is used to zero analysers and as a matrix gas for reference materials.

Synthetic zero air has been produced with tight composition tolerances to avoid pressure broadening on spectroscopic analysis.

The trace amounts fractions of CO_2 and CH_4 are measured.

Trace gases including Ar, Kr and N_2O are added to match the analysis technique used. Kr and N_2O can be preconcentrated with CH_4 and may affect IRMS measurements if GC separation is not used.

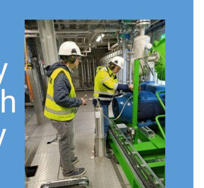
Isotopic CO_2 and CH_4 pure and ambient reference materials

Produced at a range of isotope ratios through blending pure sources of different origin and, when necessary, spiking with enriched gases or treatment with enriched water.

The reference materials have target uncertainties of 0.1‰ for $\delta^{13}C$-CO_2 and 0.5 ‰ for $\delta^{18}O$-CO_2 and 0.2‰ for $\delta^{13}C$-CH_4 and 5‰ for $\delta^{2}H$-CH_4.

δ values are assigned at the BGC—IsoLab by IRMS.

Fossil origin CH_4 (supplied by project partner Air Liquide) is mixed with biogenic CH_4 which supplied by Nordsol from a bio-LNG installation in partnership with Shell and Renewi. Biogenic CH_4 was also supplied by Gasum, Finland.



Field-deployable spectroscopy for isotope ratio

Develop, characterise and improve field-deployable spectroscopic methods and calibration approaches for measurements of;

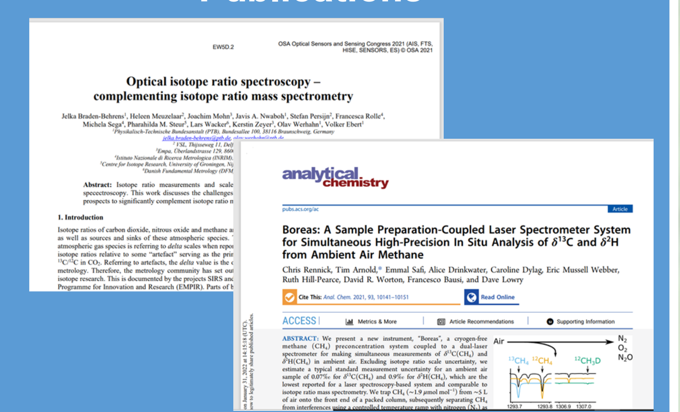
$\delta^{13}C$-CO_2 and $\delta^{18}O$-CO_2—target precision: 0.05 ‰

$\delta^{13}C$-CH_4 and $\delta^{2}H$-CH_4 —target precision: 0.02 ‰

Key factors have been identified which limit precision and accuracy for isotope ratio by OIRS.

- Characterise methods and evaluate calibration approaches.
- Quantify and control sources of uncertainty.
- Link OIRS results (isotopologue amount fractions) & δ scales.

Publications



Acknowledgements

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4. Opportunities for collaboration

For further information, updates, news and events please see our project website http://empir.npl.co.uk/stellarproject/

If you are interested in becoming a collaborator or have a question or if you would like to receive a free sample of isotopic CO_2 gas reference material please e-mail ruth.pearce@npl.co.uk

5. Authors: P.J. Brewer, R. Hill-Pearce, C. Rennick, T. Arnold, F. Camin, T. Jacksier, H.A.J. Meijer, P.M. Steur, S. Persijn, M. Fatima, J. Mohn, C. Biasi, D. Malinovskiy, P. J. H. Dunn, T. Tarhan, F. Rolle, S. Pavarelli, V. Ebert, L. Flierl, D. Balslev-Harder, J. C. Petersen, N. Ogrinc, B. Krajnc.

Collaborators

WMO • FAAM • KRISS • BOC • CEN • ISO • Aerodyne • ABB • NU Instruments • SIAD • LI-COR • NIPPON • Masaryk University • NIWA • Krawkow University of Science and Technology • CNR-Institute for Atmospheric Pollution (Italy) • IUPAC-CIAAW

Partners

NPL National Physical Laboratory • Empa Materials Science and Technology • PTB • VTT • INRiM • DFM • TÜBİTAK UME • university of groningen • Air Liquide • Max-Planck-Gesellschaft • University of Eastern Finland • IJS • VSL National Metrology Institute • LGC