Stellar Stakeholder meeting, 26-2-2021

C1 WP1: Next generation carbon dioxide isotope ratio gas reference materials

(**RUG**, NPL, MPI-BGC, AL, UEF, TUBITAK, INRIM, JSI, PTB, LGC, EMPA)

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Work Package Leader

The aim of work package 1 is to **considerably improve** gas reference materials of carbon dioxide that were developed as part of the EMPIR funded SIRS project (16ENV06). …

…reduce the uncertainties of available atmospheric carbon dioxide standards

First: get pure CO_2 with accurate isotope values, expressed with respect to the internationally accepted scales: VPDB and VSMOW

Then: "dissolve" this CO_2 into CO_2-free air to create CO_2 in air of which the isotope values are known as well

In parallel: try to realise that isotope ratio values for CO_2 gas will be directly traceable to SI, with sufficient acuracy

First: get pure CO_2 with accurate isotope values, expressed with respect to the internationally accepted scales: VPDB and VSMOW

MPI-BGC, RUG, JSI and UEF will **develop technical capabilities** to perform the carbonate (using IAEA-603) and **phosphoric acid reaction** The reproducibility of the syntheses will be at least 0.01 ‰ and 0.05 ‰ for $\delta^{13}C$- and $\delta^{18}O$-CO_2 respectively. The inter-laboratory compatibility will be tested.

Max Planck Institute for Biogeochemistry

- Synthesis of pure CO_2 from calcium carbonate standards MAR-J1 and IAEA-603 using ARAMIS (**A**cid **R**eaction and **A**ir **M**ixing **S**ystem)
- Testing different methods to minimize target uncertainties
  - Degassing of H_3PO_4 over different time periods
  - Using different materials for equipment (gold container, glass stirrer etc.)

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Preliminary Data MPI-BGC

- Only "good" tries included
- Goal: target uncertainties of 0.05 ‰ for $\delta^{13}C$-CO_2 and 0.1 ‰ for $\delta^{18}O$-CO_2

Name	d 13C [‰]	d 18O [‰]	Offset d13C	Offset d18O	Comments
MAR-J1 20202177 - Batch 697	1.976	-1.993	0.019	0.108	2nd try
MAR-J1 20202200 - Batch 698	1.983	-1.984	0.026	0.117	Problems with pressure (forgot to grease O-ring), gold container not fully cleaned/wet? Some MAR-J1 powder at edge looked wet
MAR-J1 20202245 - Batch 699	1.951	-2.011	0.006	0.090	
MAR-J1 20202245 - Batch 699	1.952	-2.016	0.005	0.085	
MAR-J1 20202256 - Batch 700	1.964	-1.977	0.007	0.124	
MAR-J1 20202256 - Batch 700	1.961	-1.963	0.004	0.138	
MAR-J1 20202259 - Batch 701	1.984	-2.007	0.027	0.094	different H3PO4
MAR-J1 20202259 - Batch 701	1.989	-2.026	0.032	0.075	
MAR-J1 20210128 - Batch 703	1.949	-2.127	0.008	0.026	new glass stirrer which was stuck for a few hours and thus didn't stirr, usual H3PO4, degassed H3PO4 for a day
MAR-J1 20210128 - Batch 703	1.950	-2.132	0.007	0.031	rep ok

- Already in target range, newest Batches not measured yet
- Next steps: Continue to synthesize 6 MAR-J1 and 4 IAEA-603 samples

Jožef Stefan Institute

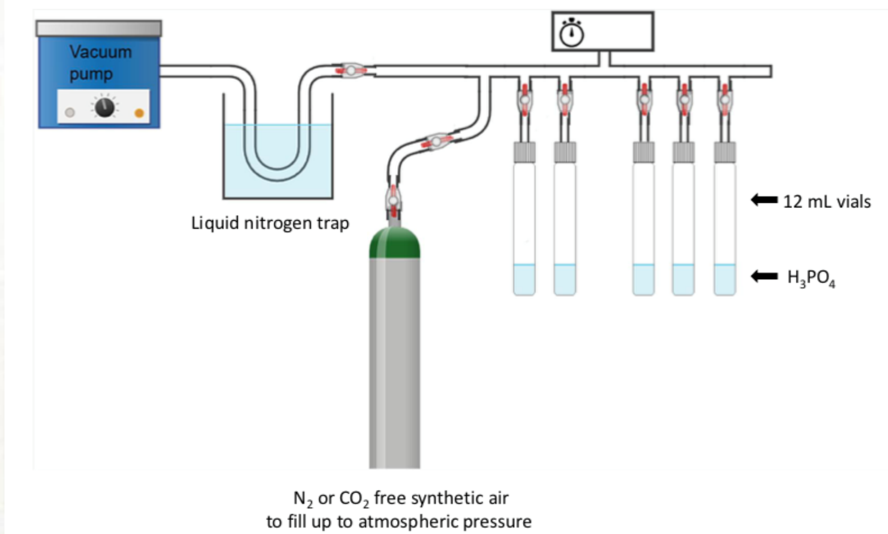
Mar-J1 measurements on Europa Scientific 20-20 IRMS with ANCA TG with modification of $CaCO_3$ - H_3PO_4 gas evolving techniques with objective to use lesser amounts of RMs

Expected values (Brandt t al., 2009)

Determination	$\delta^{13}C$ ‰ (VPDB)	SD (replicates)	$\delta^{18}O$ ‰ (VPDB	SD
Mar-J1	1.957	0.11	−2.101	0.013

Our preliminary results (carbon)

Determination	$\delta^{13}C$ ‰ (VPDB)	SD
Mar-J1	2.02	0.02 (n=10)



university of groningen

experienced with carbonates-phosphoric acid,
but corona-related delays.
Intercomparisons with MPI-BGC performed in the recent past

UNIVERSITY OF EASTERN FINLAND

wants to develop a system similar to JSI,
but corona-related delays

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Next: “dissolve” the known CO_2 into CO_2-free air to create CO_2 in air of which the isotope values are known as well

Produce mixtures at an ambient amount fraction (410 µmol mol^{-1}).
CO_2-free air matrix such that the remaining CO_2 has negligible influence.
carbon dioxide will be added by using the gravimetric method and also by dynamic dilution
Resulting CO_2 in air calibrated on the JRAS-06 scale

Air Liquide

Empty cylinders with internal treatment

- 26 B10 l cyl prepared and waiting for sending to NPL in the Spanish custom (NPLvalve)

- 20 B05 l and 2 B10 l cyl with DIN-1 or UNI 11144-5 valves for VSL, TUBITAK and INRIM in preparation for Aculife III Megalong treatment

Pure gases N2, O2 & Ar 50 L 200 bar

Brexit delays!

- 12 cyl N2 + 3 cyl O2 + 1 Cyl Ar sent to NPL Nov 2020
- 14 cyl N2 waiting for sending to NPL in the Spanish custom

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NPL National Physical Laboratory

Pure gases from Air Liquide

10 L cylinders from Air Liquide (Aculife – Megalong passivation)

N_2 78.1 %
O_2 20.93 %
Ar 0.93 %
N_2O 330 ppb

NPL
INRIM
TUBITAK

410 ppm CO_2 mixtures to be made by M12 using SIRS pure CO_2 RMs.

First batch to be sent by end of March 2021

- Cylinders conditioned with 5 bar dry N2 (H2O < 3 ppm), evacuated to < 5 x10^{-7} mBar.
- Preparation by gravimetry: **N2** 78.1 % **O2** 20.93 % **Ar** 0.93 % **N_2O** 330 ppb
  - Validation of composition using existing NPL standards. (GC and CRDS)
- Analysis of residual CO2/CH4/CO/H2O in selected cylinders from each batch
  - Dynamic dilution using existing NPL standards. (CRDS)

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- Dynamic gas mixture generation and measurement system

IRMS facility (Thermo Finnigan MAT 253 with an autosampler gas injection to GC-IRMS)

CRDS (Picarro G2401) $CO/CO_2/CH_4/H_2O$ Analyzer equipped with 16-Port Distribution Manifold

Dynamic dilution system

Already experienced in this technique from the previous project, now for higher accuracy

In parallel: try to realise that isotope ratio values for CO_2 gas will be directly traceable to SI, with sufficient acuracy

select and purchase suitable compounds (including carbon dioxide gases) enriched in ^{13}C and ^{12}C isotopes to be used in preparation of calibration mixtures. Chemical and isotopic purity of these compounds will be assessed.

Glucose and alanine are chemical compounds considered for use as calibrants

99% ^{13}C isotope
1% ^{12}C isotope

0.1% ^{13}C isotope
99.9% ^{12}C isotope

Solution of ^{13}C isotope enriched material (A)

Solution of ^{13}C isotope depleted material (B)

Preparation of synthetic isotope mixtures from materials A and B with different $n(^{13}C)/n(^{12}C)$ ratios

Measurements of $^{13}C/^{12}C$ isotope ratios in parent isotopically enriched materials, synthetic isotope mixtures and samples of glucose or alanine with natural isotopic composition

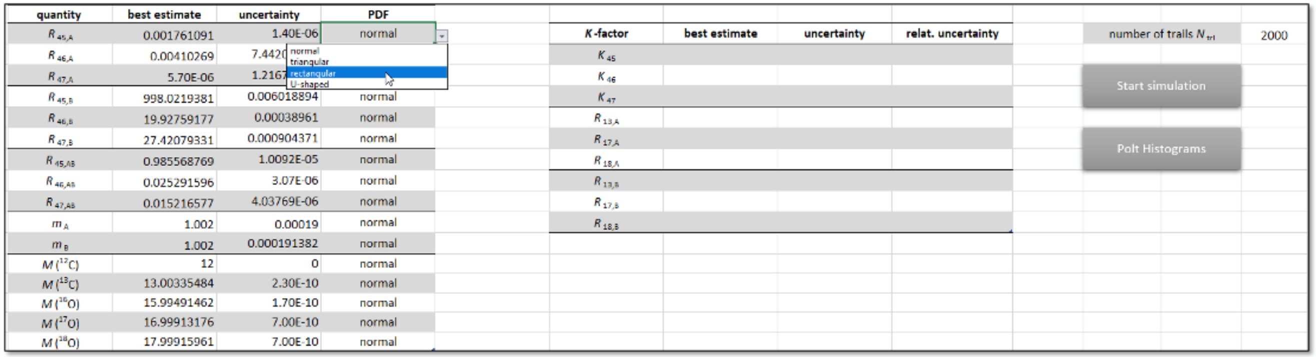
PTB and LGC will set up MS Excel-based spreadsheets for performing all calculations

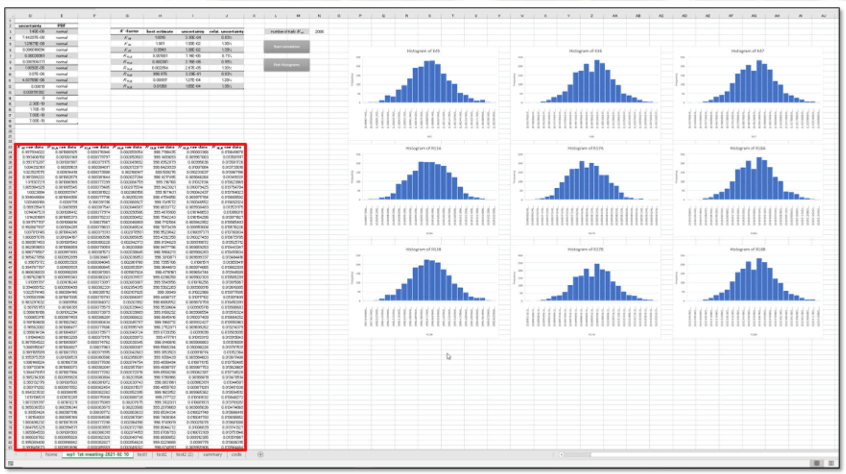
PTB

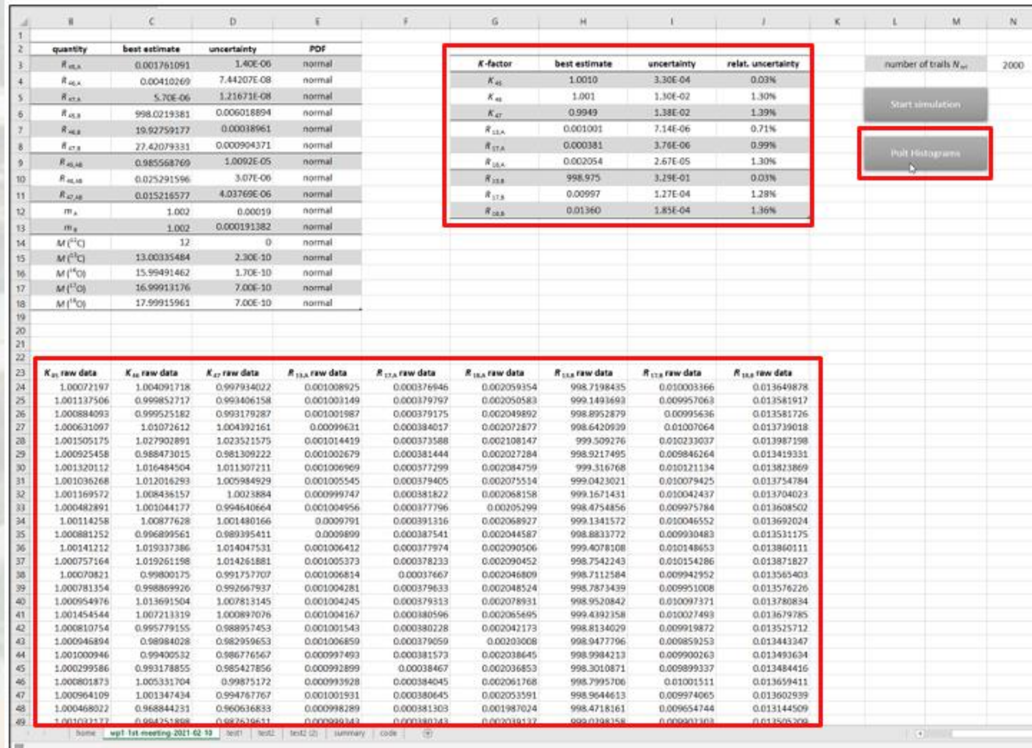
$$0 = K_{45} \times R^{\mathrm{m}}_{45\mathrm{AB}} - \frac{\left[\frac{m_{\mathrm{A}}\times R_{13,\mathrm{A}}}{(R_{13,\mathrm{A}}+1)\left(\frac{M(^{12}\mathrm{C})}{R_{13,\mathrm{A}}+1}+\frac{M(^{13}\mathrm{C})\times R_{13,\mathrm{A}}}{R_{13,\mathrm{A}}+1}+2\left(\frac{M(^{16}\mathrm{O})}{R_{17,\mathrm{A}}+R_{18,\mathrm{A}}+1}+\frac{M(^{17}\mathrm{O})\times R_{17,\mathrm{A}}}{R_{17,\mathrm{A}}+R_{18,\mathrm{A}}+1}+\frac{M(^{18}\mathrm{O})\times R_{18,\mathrm{A}}}{R_{17,\mathrm{A}}+R_{18,\mathrm{A}}+1}\right)\right)}+\frac{m_{\mathrm{B}}\times R_{13,\mathrm{B}}}{(R_{13,\mathrm{B}}+1)\left(\frac{M(^{12}\mathrm{C})}{R_{13,\mathrm{B}}+1}+\frac{M(^{13}\mathrm{C})\times R_{13,\mathrm{B}}}{R_{13,\mathrm{B}}+1}+2\left(\frac{M(^{16}\mathrm{O})}{R_{17,\mathrm{B}}+R_{18,\mathrm{B}}+1}+\frac{M(^{17}\mathrm{O})\times R_{17,\mathrm{B}}}{R_{17,\mathrm{B}}+R_{1(,\mathrm{B}}+1}+\frac{M(^{18}\mathrm{O})\times R_{18,\mathrm{B}}}{R_{17,\mathrm{B}}+R_{18,\mathrm{B}}+1}\right)\right)}\right]}{\left[\frac{m_{\mathrm{A}}}{(R_{13,\mathrm{A}}+1)\left(\frac{M(^{12}\mathrm{C})}{R_{13,\mathrm{A}}+1}+\frac{M(^{13}\mathrm{C})\times R_{13,\mathrm{A}}}{R_{13,\mathrm{A}}+1}+2\left(\frac{M(^{16}\mathrm{O})}{R_{17,\mathrm{A}}+R_{18,\mathrm{A}}+1}+\frac{M(^{17}\mathrm{O})\times R_{17,\mathrm{A}}}{R_{17,\mathrm{A}}+R_{18,\mathrm{A}}+1}+\frac{M(^{18}\mathrm{O})\times R_{18,\mathrm{A}}}{R_{17,\mathrm{A}}+R_{18,\mathrm{A}}+1}\right)\right)}+\frac{m_{\mathrm{B}}}{(R_{13,\mathrm{B}}+1)\left(\frac{M(^{12}\mathrm{C})}{R_{13,\mathrm{B}}+1}+\frac{M(^{13}\mathrm{C})\times R_{13,\mathrm{B}}}{R_{13,\mathrm{B}}+1}+2\left(\frac{M(^{16}\mathrm{O})}{R_{17,\mathrm{B}}+R_{18,\mathrm{B}}+1}+\frac{M(^{17}\mathrm{O})\times R_{17,\mathrm{B}}}{R_{17,\mathrm{B}}+R_{18,\mathrm{B}}+1}+\frac{M(^{18}\mathrm{O})\times R_{18,\mathrm{B}}}{R_{17,\mathrm{B}}+R_{18,\mathrm{B}}+1}\right)\right)}\right]} + \frac{\left[2\times\left(\frac{m_{\mathrm{A}}\times R_{17,\mathrm{A}}}{(R_{17,\mathrm{A}}+R_{18,\mathrm{A}}+1)\left(\frac{M(^{12}\mathrm{C})}{R_{13,\mathrm{A}}+1}+\frac{M(^{13}\mathrm{C})\times R_{13,\mathrm{A}}}{R_{13,\mathrm{A}}+1}+2\left(\frac{M(^{16}\mathrm{O})}{R_{17,\mathrm{A}}+R_{18,\mathrm{A}}+1}+\frac{M(^{17}\mathrm{O})\times R_{17,\mathrm{A}}}{R_{17,\mathrm{A}}+R_{18,\mathrm{A}}+1}+\frac{M(^{18}\mathrm{O})\times R_{18,\mathrm{A}}}{R_{17,\mathrm{A}}+R_{18,\mathrm{A}}+1}\right)\right)}+\frac{m_{\mathrm{B}}\times R_{17,\mathrm{B}}}{(R_{17,\mathrm{B}}+R_{18,\mathrm{B}}+1)\left(\frac{M(^{12}\mathrm{C})}{R_{13,\mathrm{B}}+1}+\frac{M(^{13}\mathrm{C})\times R_{13,\mathrm{B}}}{R_{13,\mathrm{B}}+1}+2\left(\frac{M(^{16}\mathrm{O})}{R_{17,\mathrm{B}}+R_{18,\mathrm{B}}+1}+\frac{M(^{17}\mathrm{O})\times R_{17,\mathrm{B}}}{R_{17,\mathrm{B}}+R_{18,\mathrm{B}}+1}+\frac{M(^{18}\mathrm{O})\times R_{18,\mathrm{B}}}{R_{17,\mathrm{B}}+R_{18,\mathrm{B}}+1}\right)\right)}\right)\right]}{\left[\frac{m_{\mathrm{A}}}{(R_{17,\mathrm{A}}+R_{18,\mathrm{A}}+1)\left(\frac{M(^{12}\mathrm{C})}{R_{13,\mathrm{A}}+1}+\frac{M(^{13}\mathrm{C})\times R_{13,\mathrm{A}}}{R_{13,\mathrm{A}}+1}+2\left(\frac{M(^{16}\mathrm{O})}{R_{17,\mathrm{A}}+R_{18,\mathrm{A}}+1}+\frac{M(^{17}\mathrm{O})\times R_{17,\mathrm{A}}}{R_{17,\mathrm{A}}+R_{18,\mathrm{A}}+1}+\frac{M(^{18}\mathrm{O})\times R_{18,\mathrm{A}}}{R_{17,\mathrm{A}}+R_{18,\mathrm{A}}+1}\right)\right)}+\frac{m_{\mathrm{B}}}{(R_{17,\mathrm{B}}+R_{18,\mathrm{B}}+1)\left(\frac{M(^{12}\mathrm{C})}{R_{13,\mathrm{B}}+1}+\frac{M(^{13}\mathrm{C})\times R_{13,\mathrm{B}}}{R_{13,\mathrm{B}}+1}+2\left(\frac{M(^{16}\mathrm{O})}{R_{17,\mathrm{B}}+R_{18,\mathrm{B}}+1}+\frac{M(^{17}\mathrm{O})\times R_{17,\mathrm{B}}}{R_{17,\mathrm{B}}+R_{18,\mathrm{B}}+1}+\frac{M(^{18}\mathrm{O})\times R_{18,\mathrm{B}}}{R_{17,\mathrm{B}}+R_{18,\mathrm{B}}+1}\right)\right)}\right]}$$

δ^2H $\delta^{13}C$ STELLAR

develop an EXCEL tool for solving this system of nine equations…







Tool is ready, and thoroughly tested by comparing with previously developed Mathematica code.

Fully transparant (code included)

Stellar, WP1, Summary of the initial phase:

Project has started, first developments visible and delivered.

Delays all over the place due to corona, and some also due to the Brexit.

And the pandemic is not over yet, so more delays might happen…

Collaboration between partners runs smoothly, since
most partners have collaborated in the previous project.
Being accustomed to on-line meetings and workshops is an advantage.

Still, 9 months report is expected to be full of missed deadlines
(typical delay is 3-6 months for most activities)

Thank you for your attention