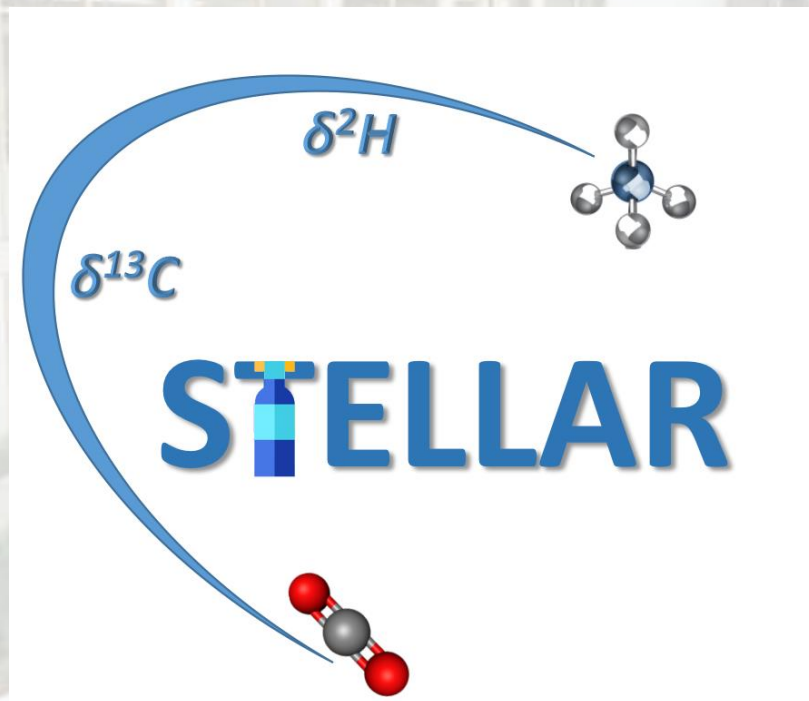


Stellar Stakeholder meeting, 26-2-2021

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

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

Harro A.J. Meijer, Centre for Isotope Research, University of Groningen (RUG)
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 CO₂ with accurate isotope values, expressed with respect to the internationally accepted scales: VPDB and VSMOW

Then: “dissolve” this CO₂ into CO₂-free air to create CO₂ in air of which the isotope values are known as well

In parallel: try to realise that isotope ratio values for CO₂ gas will be directly traceable to SI, with sufficient accuracy

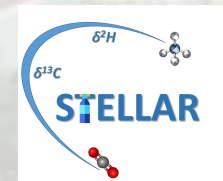
First: get pure CO₂ with accurate isotope values, expressed with respect to the internationally accepted scales: VPDB and VSMOW

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 $\delta^{13}\text{C}$ - and $\delta^{18}\text{O}$ -CO₂ respectively. The inter-laboratory compatibility will be tested.

Max Planck Institute
for Biogeochemistry



- ▶ Synthesis of pure CO₂ from calcium carbonate standards MAR-J1 and IAEA-603 using ARAMIS (Acid Reaction and Air Mixing System)
- ▶ Testing different methods to minimize target uncertainties
 - ▶ Degassing of H₃PO₄ over different time periods
 - ▶ Using different materials for equipment (gold container, glass stirrer etc.)



Preliminary Data MPI-BGC

- ▶ Only “good” tries included
- ▶ Goal: target uncertainties of 0.05 ‰ for $\delta^{13}\text{C-CO}_2$ and 0.1 ‰ for $\delta^{18}\text{O-CO}_2$

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 stir, 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

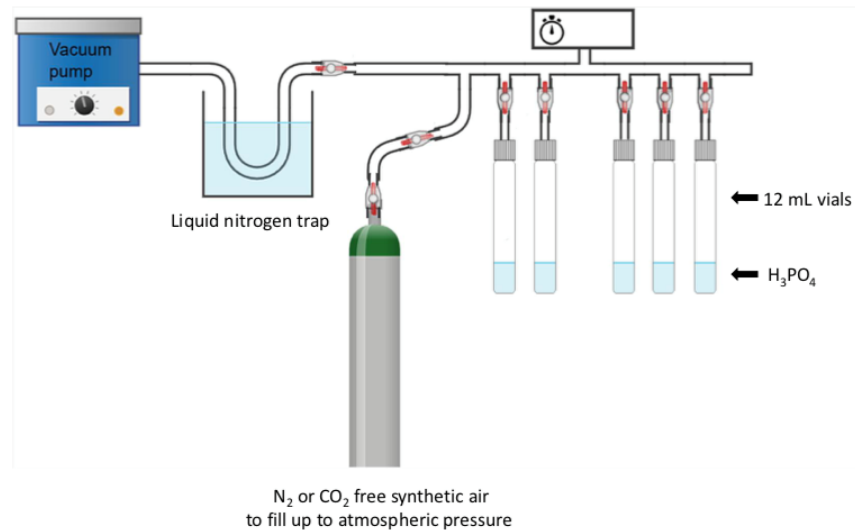
Mar-J1 measurements on Europa Scientific 20-20 IRMS with ANCA TG with modification of $\text{CaCO}_3 - \text{H}_3\text{PO}_4$ gas evolving techniques with objective to use lesser amounts of RMs

Expected values (Brandt et al., 2009)

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

Our preliminary results (carbon)

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



experienced with carbonates-phosphoric acid, but corona-related delays.

Intercomparisons with MPI-BGC performed in the recent past



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

Next: “dissolve” the known CO₂ into CO₂-free air to create CO₂ in air of which the isotope values are known as well

Produce mixtures at an ambient amount fraction (410 μmol mol⁻¹).
CO₂-free air matrix such that the remaining CO₂ has negligible influence.
carbon dioxide will be added by using the gravimetric method and also by dynamic dilution
Resulting CO₂ in air calibrated on the JRAS-06 scale



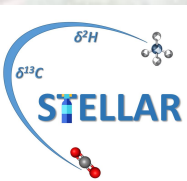
Empty cylinders with internal treatment

- 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

- 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

Brexit delays!



Pure gases from Air Liquide

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

N₂ 78.1 %
O₂ 20.93 %
Ar 0.93 %
N₂O 330 ppb

**NPL
INRIM
TUBITAK**

410 ppm CO₂
mixtures to be made
by M12 using SIRS
pure CO₂ RMs.

First batch to be sent
by end of March 2021

- Cylinders conditioned with 5 bar dry N₂ (H₂O < 3 ppm), evacuated to < 5 x 10⁻⁷ mBar.
- Preparation by gravimetry: **N₂** 78.1 % **O₂** 20.93 % **Ar** 0.93 % **N₂O** 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)

- 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/CO₂/CH₄/H₂O 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 CO₂ gas will be directly traceable to SI, with sufficient accuracy

select and purchase **suitable compounds** (including carbon dioxide gases) enriched in ¹³C and ¹²C 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% ¹³C isotope
1% ¹²C isotope

0.1% ¹³C isotope
99.9% ¹²C isotope

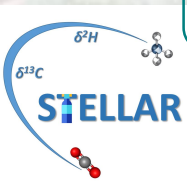


Solution of ¹³C isotope enriched material (A)

Solution of ¹³C isotope depleted material (B)

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

Measurements of ¹³C/¹²C 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



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

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



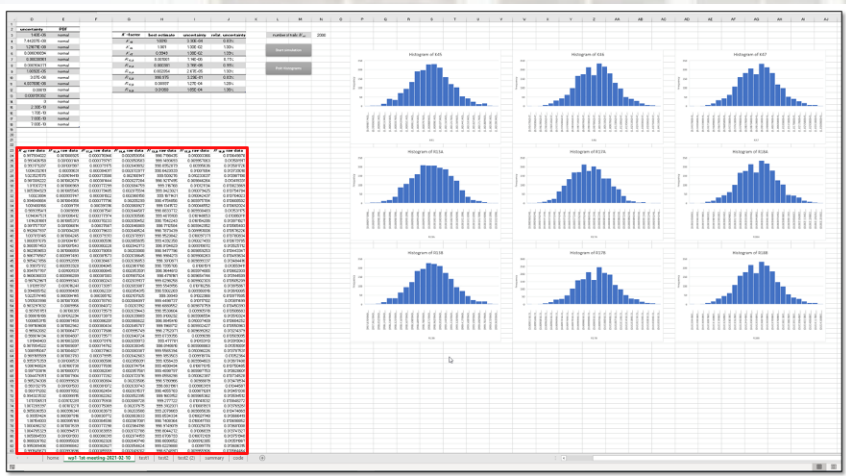


quantity	best estimate	uncertainty	PDF
$R_{45,A}$	0.001761091	1.40E-06	normal
$R_{46,A}$	0.00410269	7.442E-06	normal
$R_{47,A}$	5.70E-06	1.216E-06	rectangular U-shaped
$R_{45,B}$	998.0219381	0.006018894	normal
$R_{46,B}$	19.92759177	0.00038961	normal
$R_{47,B}$	27.42079331	0.000904371	normal
$R_{45,AB}$	0.985568769	1.0092E-05	normal
$R_{46,AB}$	0.025291596	3.07E-06	normal
$R_{47,AB}$	0.015216577	4.03769E-06	normal
m_A	1.002	0.00019	normal
m_B	1.002	0.000191382	normal
$M(^{12}C)$	12	0	normal
$M(^{13}C)$	13.00335484	2.30E-10	normal
$M(^{16}O)$	15.99491462	1.70E-10	normal
$M(^{17}O)$	16.99913176	7.00E-10	normal
$M(^{18}O)$	17.99915961	7.00E-10	normal

number of trials N_{tr} 2000

Start simulation

Plot Histograms



quantity	best estimate	uncertainty	PDF
$R_{45,A}$	0.001761091	1.40E-06	normal
$R_{46,A}$	0.00410269	7.44207E-06	normal
$R_{47,A}$	5.70E-06	1.21671E-06	normal
$R_{45,B}$	998.0219381	0.006018894	normal
$R_{46,B}$	19.92759177	0.00018961	normal
$R_{47,B}$	27.42079331	0.000904371	normal
$R_{45,AB}$	0.985568769	1.0092E-05	normal
$R_{46,AB}$	0.025291596	3.07E-06	normal
$R_{47,AB}$	0.015216577	4.03769E-06	normal
m_A	1.002	0.00019	normal
m_B	1.002	0.000191382	normal
$M(^{12}C)$	12	0	normal
$M(^{13}C)$	13.00335484	2.30E-10	normal
$M(^{16}O)$	15.99491462	1.70E-10	normal
$M(^{17}O)$	16.99913176	7.00E-10	normal
$M(^{18}O)$	17.99915961	7.00E-10	normal

K-factor	best estimate	uncertainty	relat. uncertainty
K_{45}	1.0010	3.30E-04	0.03%
K_{46}	1.001	1.30E-02	1.30%
K_{47}	0.9949	5.38E-02	1.30%
$R_{13,A}$	0.001001	7.14E-06	0.71%
$R_{17,A}$	0.000381	3.79E-06	0.99%
$R_{18,A}$	0.002054	2.67E-05	1.30%
$R_{13,B}$	998.975	3.19E-01	0.03%
$R_{17,B}$	0.00997	1.27E-04	1.28%
$R_{18,B}$	0.01360	1.83E-04	1.36%

number of trials N_{tr} 2000

Start simulation

Plot Histograms

K_{45} raw data	K_{46} raw data	K_{47} raw data	$R_{13,A}$ raw data	$R_{17,A}$ raw data	$R_{18,A}$ raw data	$R_{13,B}$ raw data	$R_{17,B}$ raw data	$R_{18,B}$ raw data
1.00072197	1.004091718	0.997934022	0.001038925	0.000376846	0.002059354	998.7198445	0.010003166	0.013649878
1.001139506	0.998852172	0.994046158	0.001001149	0.000379797	0.002050583	999.1491693	0.009957063	0.01381917
1.000884093	0.999525787	0.993179287	0.001001987	0.000379175	0.002049892	998.8952879	0.00995636	0.013581726
1.000631097	1.01072612	1.004392161	0.00099631	0.000384017	0.002072877	998.6420939	0.01007064	0.013739018
1.001505175	1.027902891	1.023513175	0.001014419	0.000373588	0.002108147	999.5992276	0.010233037	0.013987198
1.000925458	0.988473015	0.981309222	0.001002079	0.000381444	0.002027284	998.9217495	0.009846164	0.013492331
1.001320112	1.016484904	1.011307211	0.001006699	0.000372999	0.002084759	999.116768	0.010121134	0.013823869
1.001036268	1.012016293	1.009984929	0.001005545	0.000379405	0.002075514	999.0423021	0.010079425	0.013754784
1.001169572	1.008436157	1.0023884	0.000999747	0.000381822	0.002068158	999.1571431	0.010044337	0.013740423
1.000482891	1.001044177	0.994840664	0.001004956	0.000377796	0.002052999	998.4754856	0.009957184	0.013608502
1.00114258	1.00877628	1.001480166	0.0009791	0.000391316	0.002068927	999.1341572	0.010046552	0.013692024
1.000981252	0.99899561	0.990395411	0.0009899	0.000375441	0.002044587	998.8833772	0.009939483	0.01351175
1.00141212	1.019317386	1.014047531	0.001006412	0.000377974	0.002090506	999.4078108	0.010148653	0.013860111
1.000757164	1.019261158	1.014261881	0.001005373	0.000378233	0.002090452	998.7542243	0.010154286	0.013871827
1.00070821	0.99800175	0.991737707	0.001006614	0.000376697	0.002046809	998.7112584	0.009941952	0.013565403
1.000781354	0.998869920	0.992667937	0.001004281	0.000379633	0.002048524	998.7873439	0.009951008	0.013576226
1.000954976	1.013691504	1.007813145	0.001004245	0.000378913	0.002078931	998.9520842	0.010091737	0.013780884
1.001454544	1.007213319	1.000897076	0.001004167	0.000380596	0.002065495	999.4382358	0.010027493	0.013679785
1.000810754	0.995772915	0.988991743	0.001001543	0.000380228	0.002042173	998.8134029	0.009919872	0.013525712
1.000946894	0.98984028	0.982959653	0.001006850	0.000379059	0.002030008	998.9477796	0.009895153	0.013443347
1.001000946	0.99409532	0.986776567	0.000997493	0.000381573	0.002038645	998.9984213	0.009900263	0.013493634
1.000299586	0.993178855	0.985427856	0.000992899	0.000384667	0.002036853	998.3010871	0.009899337	0.013484416
1.000801873	1.005331704	0.99875172	0.000993928	0.000384045	0.002061708	998.7995706	0.01001511	0.013659411
1.000994109	1.00134744	0.994787767	0.001001511	0.000380645	0.002051591	998.5644613	0.009974065	0.013603039
1.000469012	0.948844231	0.960656853	0.000998289	0.000381503	0.002098720	998.4718161	0.009654744	0.013144509
1.001021117	0.944251898	0.952651961	0.000998143	0.000380343	0.002018137	989.0188158	0.009603163	0.013205209



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