J-RAS: A high precision reference for the isotopic composition of CO_2 in air

W. A. Brand, M. Patecki, P. Ghosh, M. Rothe, J. Richter, Max-Planck-Institute for Biogeochemistry, Jena

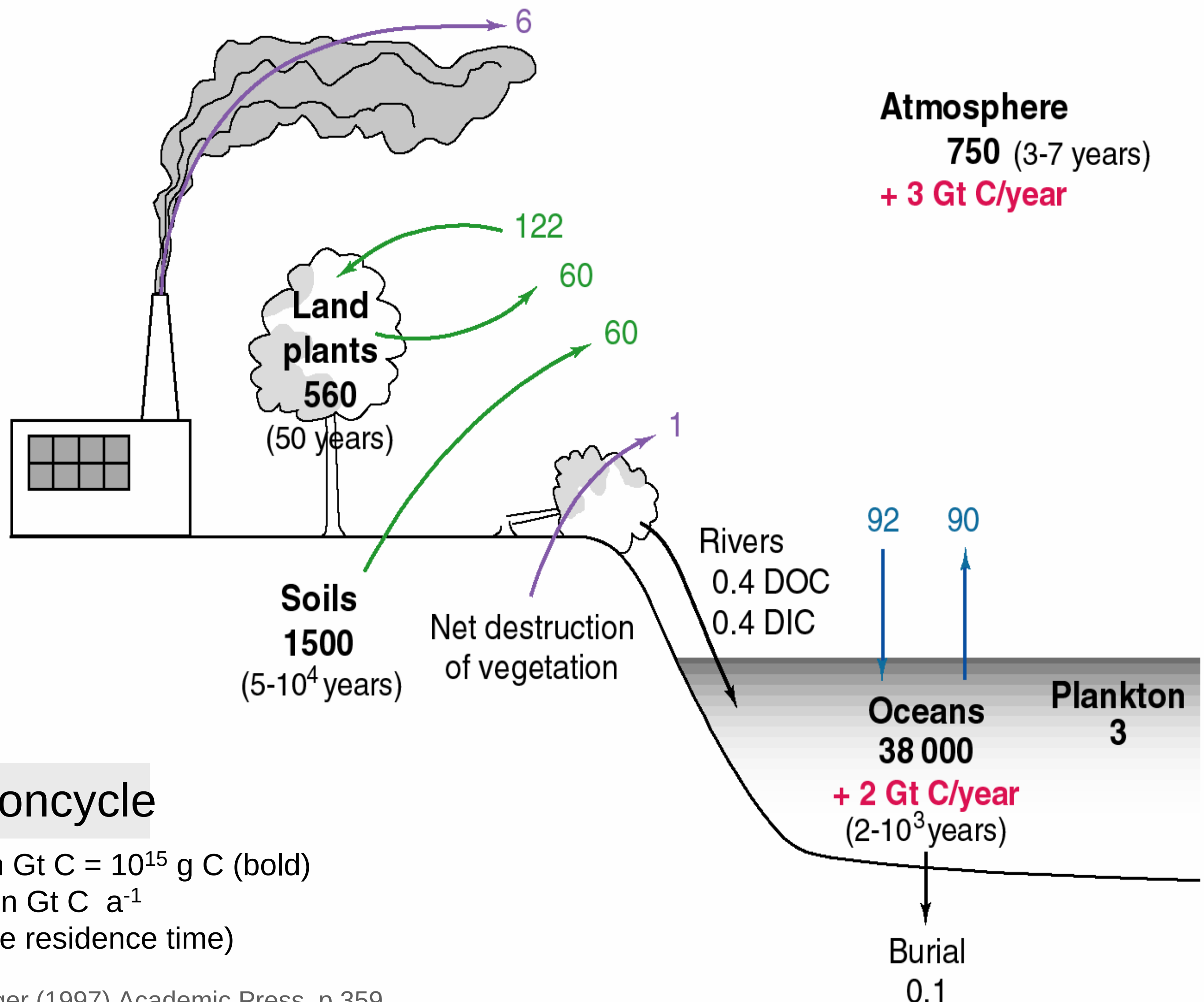
Outline:

- The global carbon cycle and the stable isotopes of CO_2 in air
- The referencing concept and the ARAMIS line
  - Materials
  - Results for carbonates from different sources and plain CO_2 reference materials
- η-Effect and a new scaling rule for the VPDB scale
- The J-RAS package
  - Glass flasks and alterations during storage
  - First J-RAS intercomparison results and outlook

*J-RAS = 'Jena-Reference Air Set'

GASIR annual meeting, Jena, Oct. 2005

wbrand@bgc-jena.mpg.de



Carboncycle

Pools in Gt C = 10^{15} g C (bold)
Fluxes in Gt C a^{-1}
(average residence time)

Schlesinger (1997) Academic Press, p.359

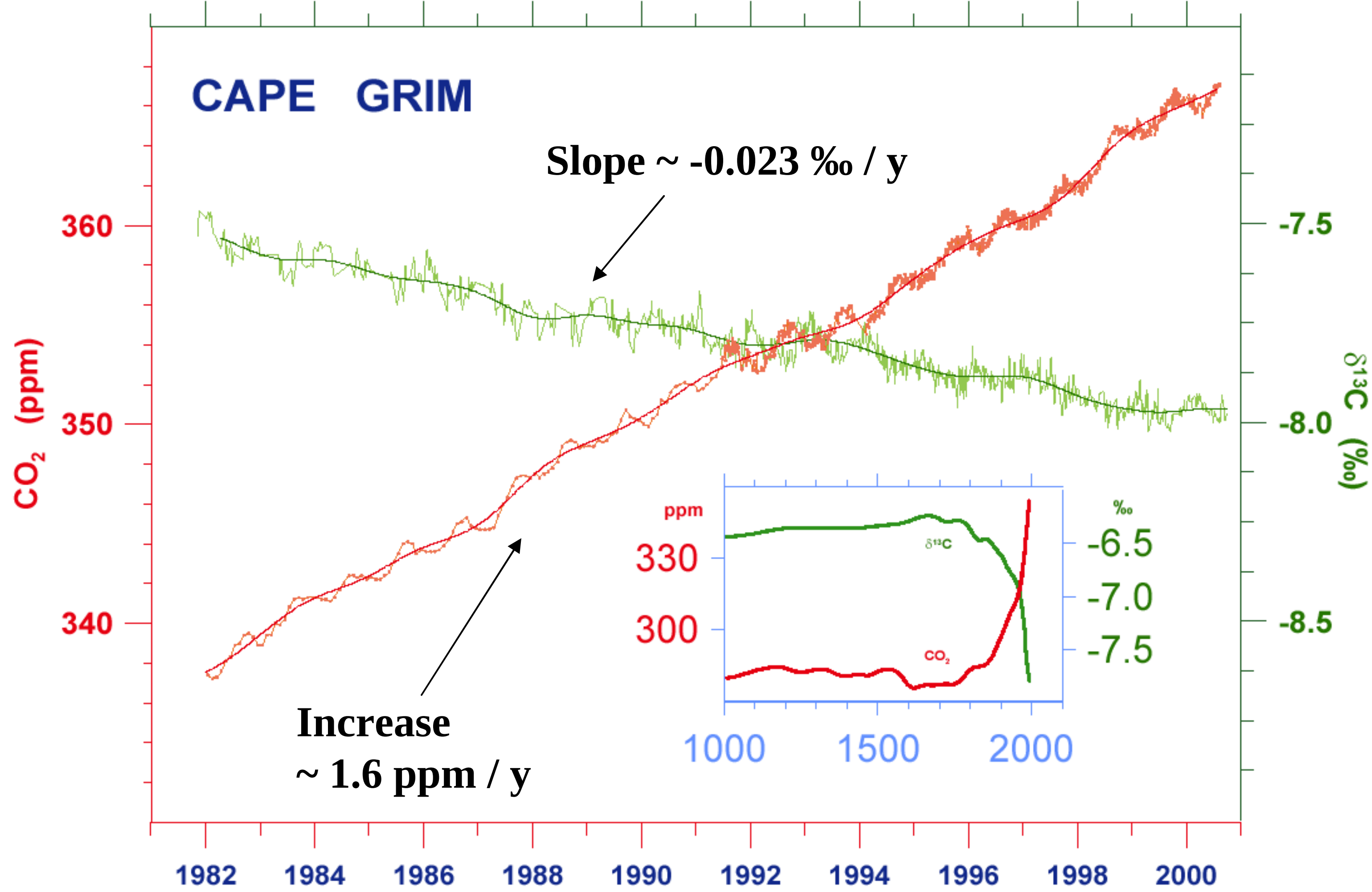


Fig.1 Atmospheric CO_2 concentration and $\delta^{13}C$ at Cape Grim, Tasmania, over the last20 yrs. The two records over the last 1000 years (from Antarctic ice cores) are shown as an inset.

Useful numbers and common state of the art measurement precision

Average CO_2 content of the atmosphere:	~ 380 ppm » 750 Pg C
Contemporary CO_2 growth rate:	~ 1.6 ppm / y » 3 Pg C / y
Best (installed) measurement precision:	~ 0.1 ppm
Fossil Fuel emissions:	~ 6 Pg C / y
^{13}C of atmospheric CO_2	~ -7.8 ‰
^{13}C rate of change	~ -0.023 ‰ / y
Best (reported) measurement precision	~ ±0.01 ‰

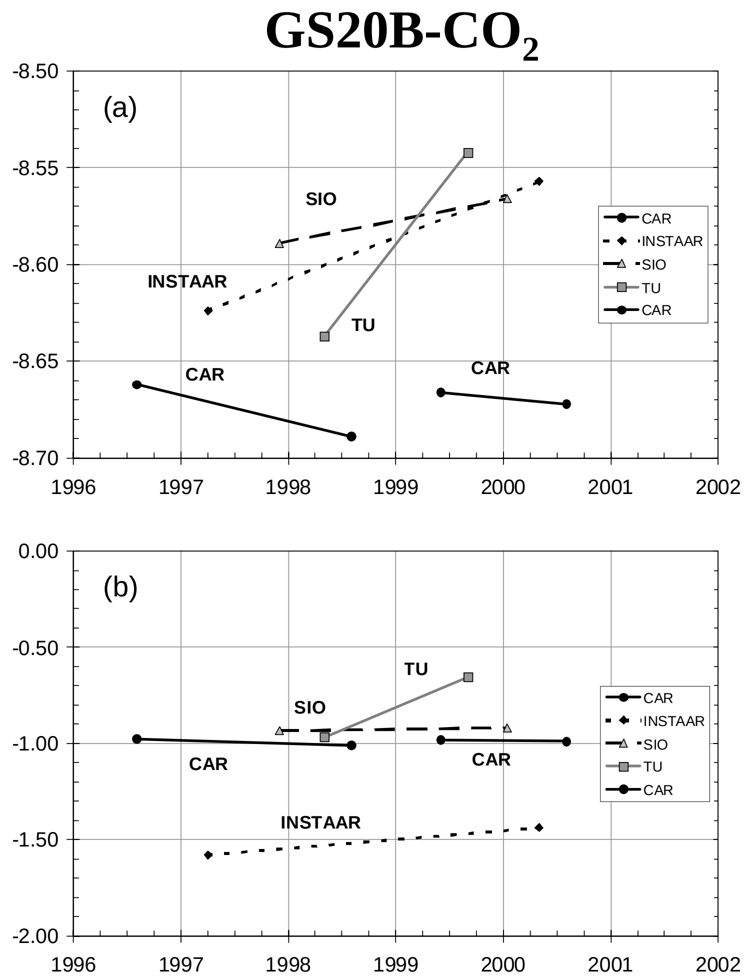
Comparison:

Precision / Mixing ratio change : 0.1/1.6 = 0.063 or 6.3 % rel.
Precision / ^{13}C Isotope ratio change: 0.01/0.023 = 0.43 or 43 % rel.

A change in the CO_2 mixing ratio can be determined with 7 times better precision than a change in ^{13}C!

The CLASSIC experiment

(Allison et al, WMO-GAW 148)



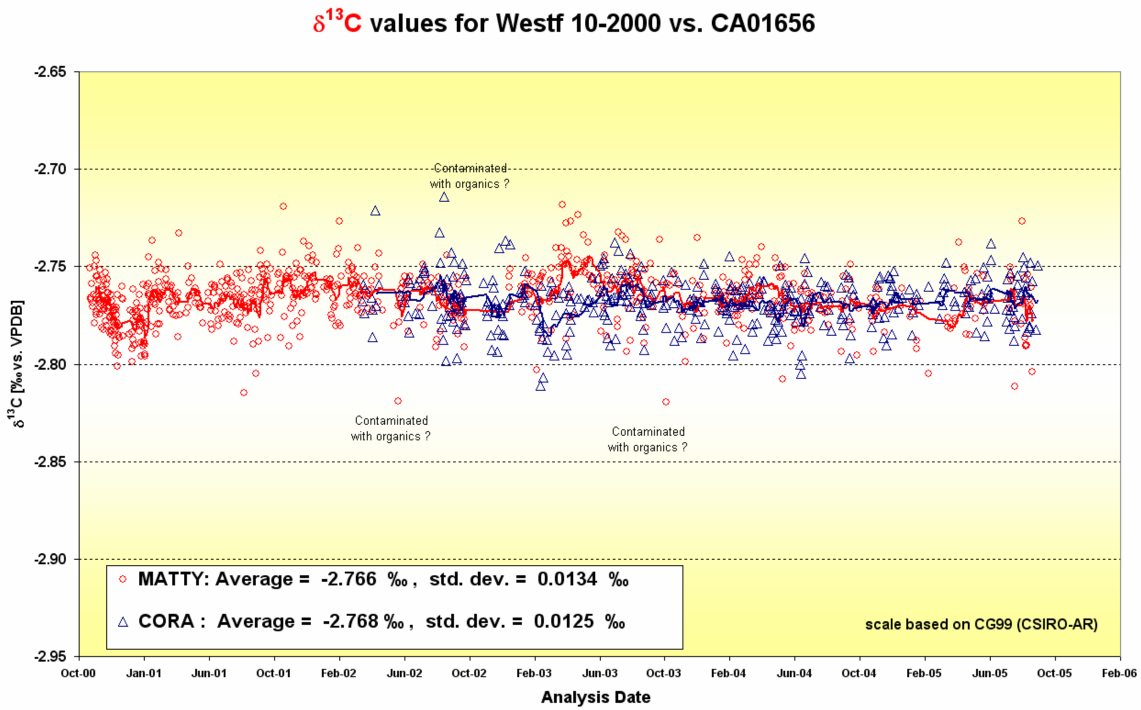
$\delta^{13}C$

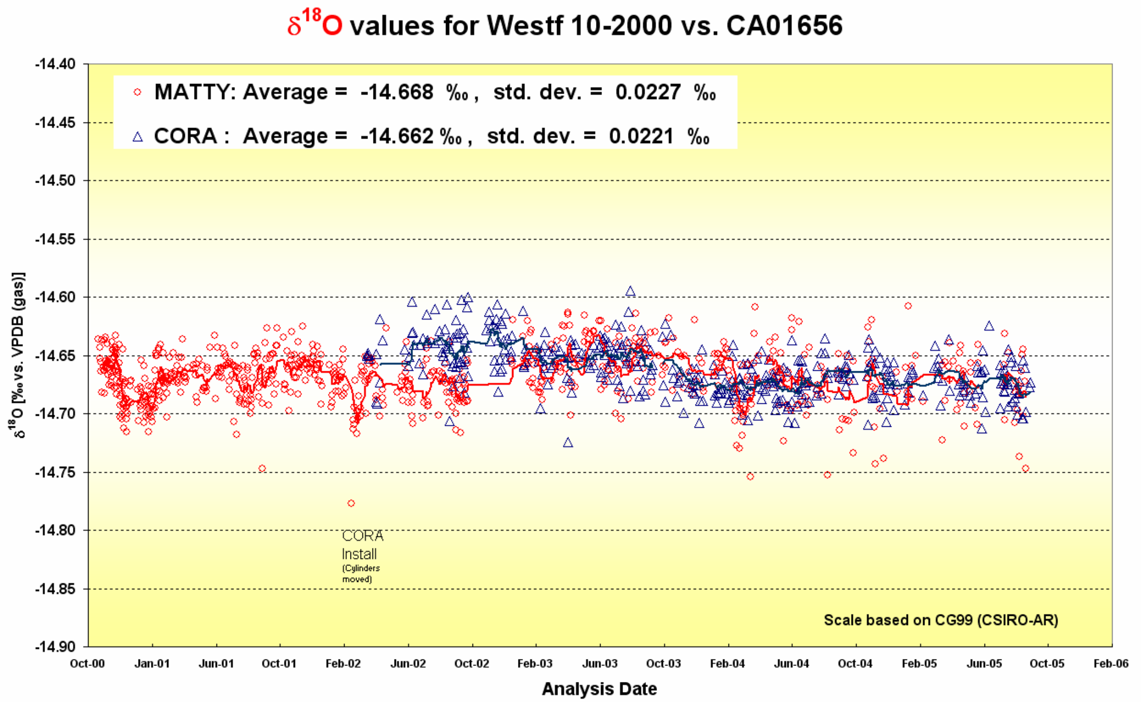
$\delta^{18}O$

Reported isotopic composition of the pure CO_2 gas in canister GS20B: (a) $\delta^{13}C_{VPDB\text{-}CO2}$, (b) $\delta^{18}O_{VPDB\text{-}CO2}$.

MPI-BGC Jena

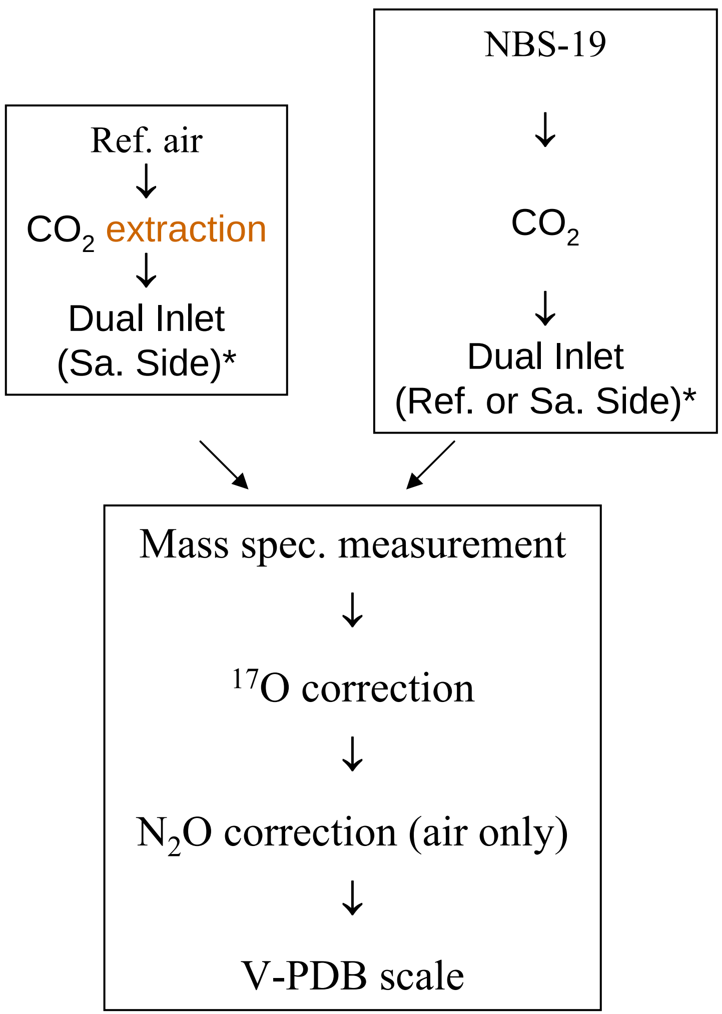
CO_2 in two reference air cylinders





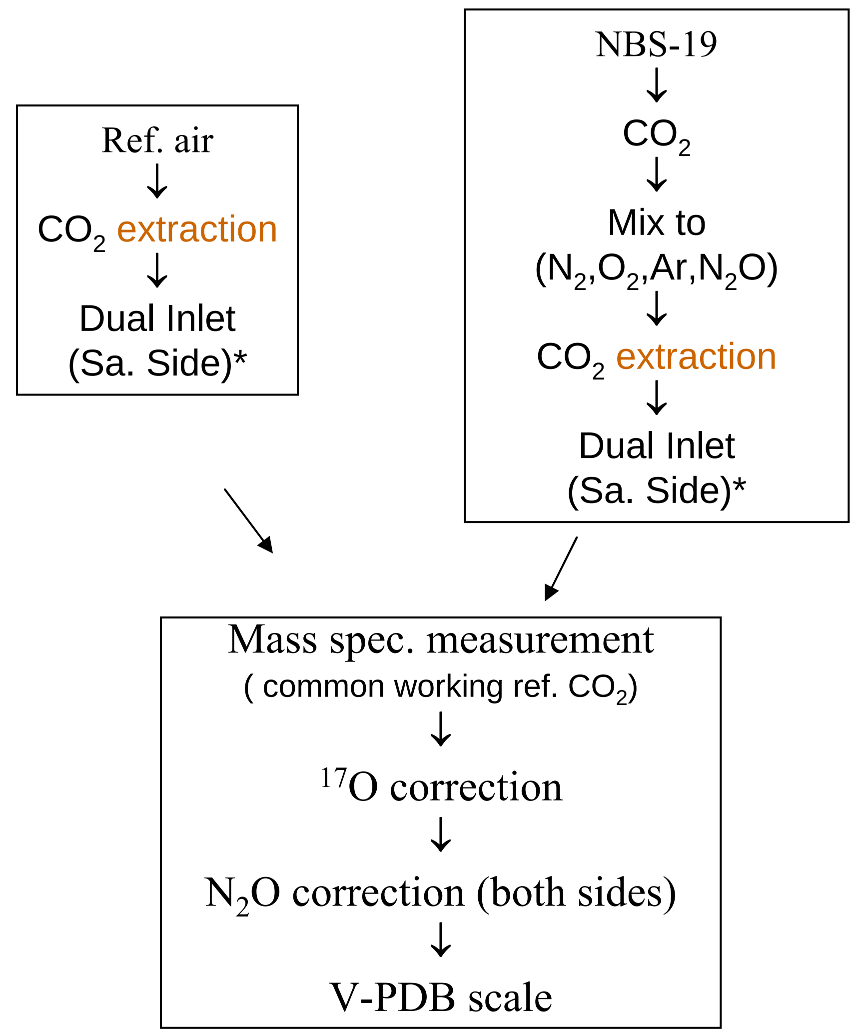
Two Strategies for relating CO_2-in-air to the VPDB scale:

Classical

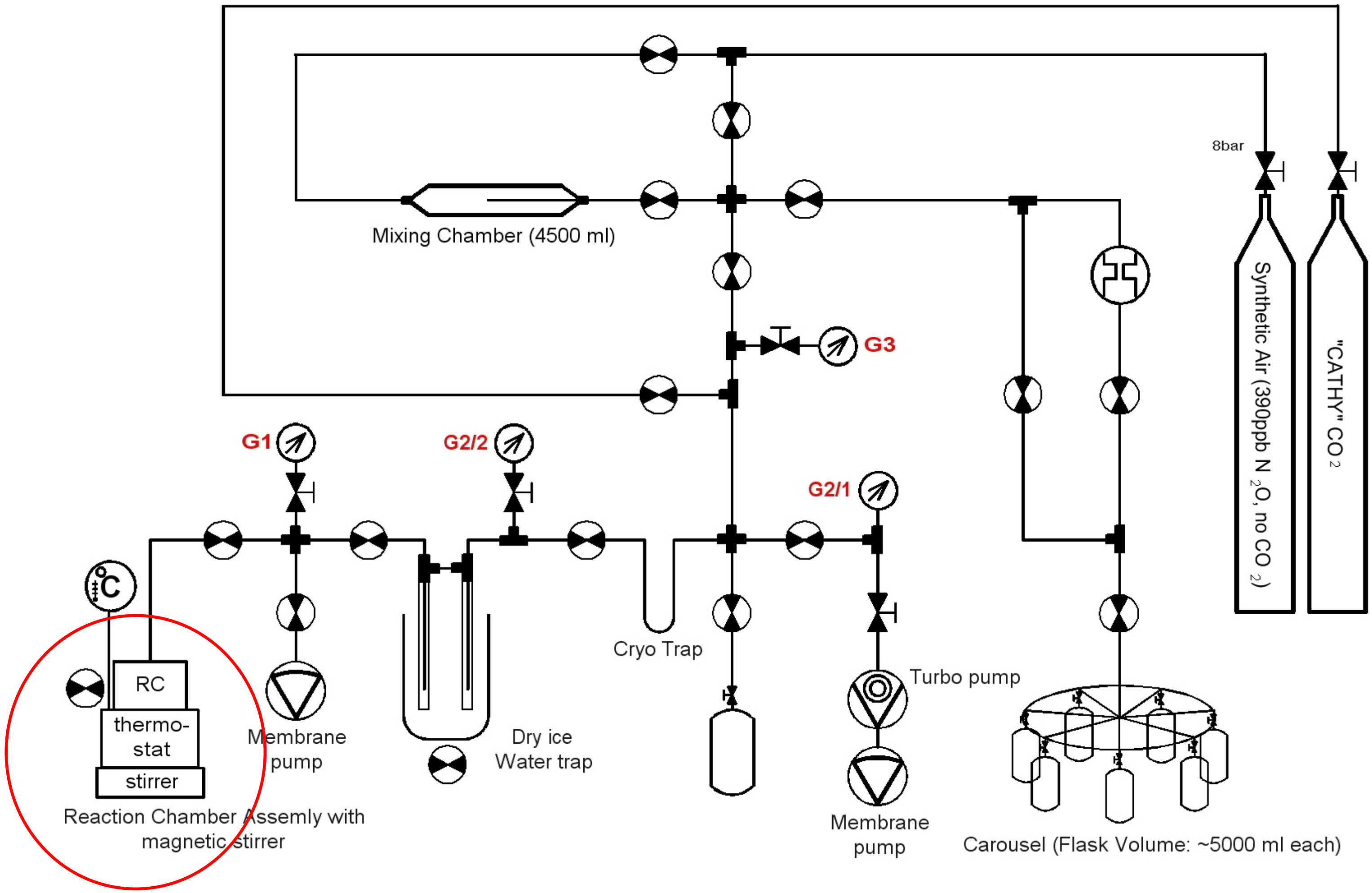


*One side for both preferred

Principle of Identical Treatment



Aramis layout for reacting carbonates



Automated dropping of carbonate

MAR-J1 and OMC-J1 Carbonates:

Laboratory carbonate reference materials were prepared from a (limestone) marble slab **('MAR-J1', Marble-Jena #1**) purchased from a local vendor and from a calcite slab from the Meieberg section of the Otavi platform in northern Namibia[i] **('OMC-J1'; Otavi Meieberg Calcite-Jena #1**), which was kindly provided by Paul Hoffmann. The slabs were broken into chips, crushed into fine grains, and sieved into fractions.

MAR-J1:

^{13}C: 1.97 ‰; ^{18}O: -2.02 ‰ VPDB

The <250 µ size fractions weighing about 900 g was labeled 'MAR-J1'. Texture and appearance of the powder is similar to NBS 19 carbonate material. Other fractions, 250-315 µ (~500 g) and 315-400 µ (~300 g), were designated as 'MAR-J2' and 'MAR-J3' and stored for future use. Quantitative analysis using ICP-MS and ICP-OES indicated an **average $CaCO_3$ content of 98.0 % and 2.0 % $MgCO_3$. Al, Fe, Cu, Mn, Na, K together were less than 0.1 %.** NBS 19 (TS limestone) is very similar: in line with literature XRF data[ii] we obtained 98.1 % $CaCO_3$ and 1.8 % $MgCO_3$. Other elements were 0.08 % in total. The similarity of the two materials is further confirmed by observing the carbonate reaction yield with NBS 19 and MAR-J1 resulting in the same amounts of CO_2 gas.

OMC-J1:

^{13}C: -4.4 ‰; ^{18}O: -8.4 ‰ VPDB (final batch, not 1st drill)

The composition analysis of the Otavi-Meieberg calcite using ICP-AES and ICP-OES has given **98.7 % $CaCO_3$ and 0.9 % $MgCO_3$ with non-carbonate cationic impurities summing up to 0.4 %.** The crushing, milling and sieving left us with 1270 g powder with a grain size <100 µ ('OMC-J0'), 700 g between 100 and 200 µ ('OMC-J1') and 1800g between 200 and 400 µ ('OMC-J2/3'). In order to avoid oxygen exchange with ambient moisture or CO_2 all fractions are kept in glass or PE jars topped with Ar.

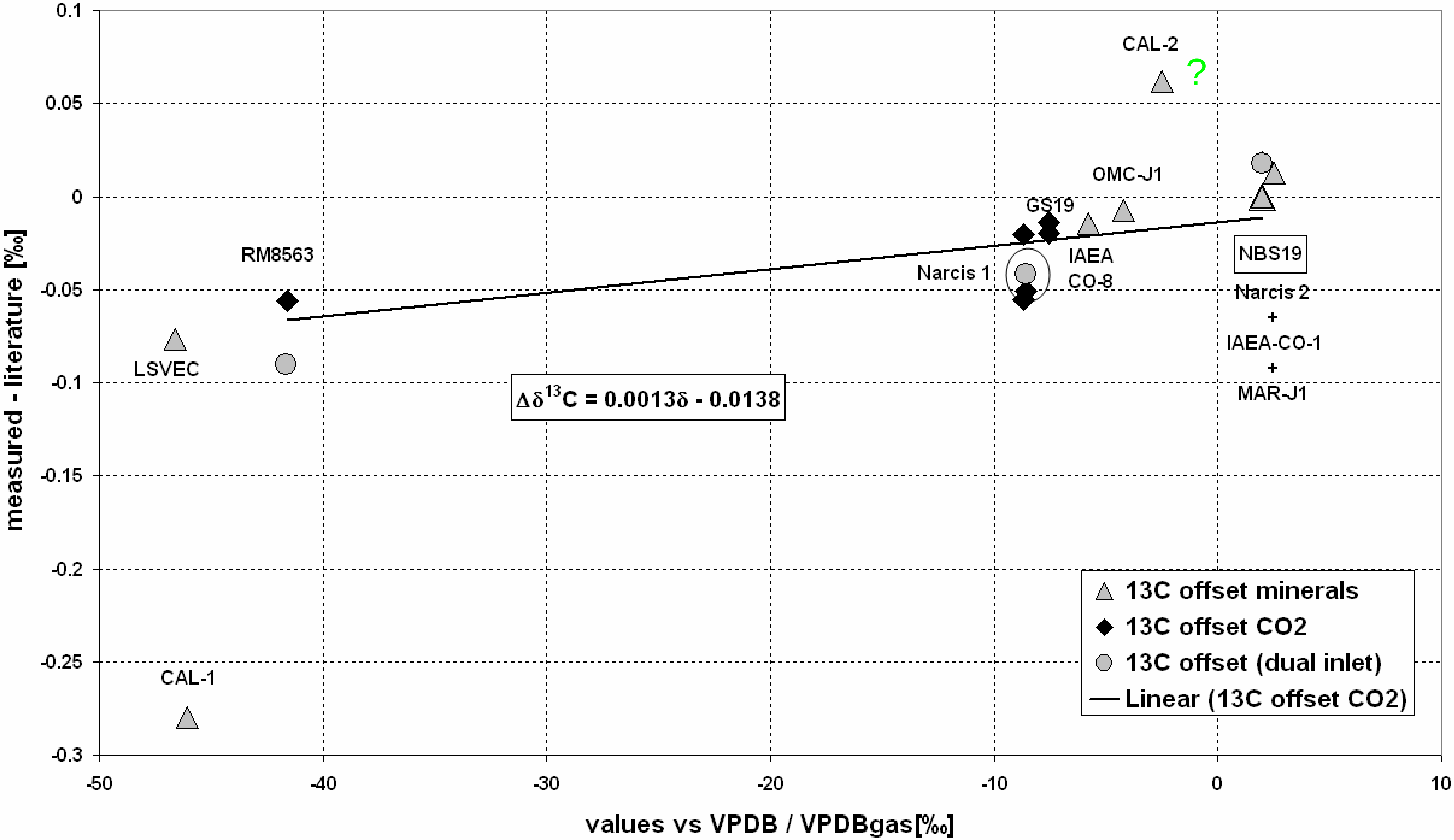
[i] Hoffmann PF and Schrag, D.P., Terra Nova 2002; **14**: 129-155

[ii] Ball JD, Crowley SF, Steele DF, Rapid Comm. Mass Spectrom. 1996; **10**: 987-995

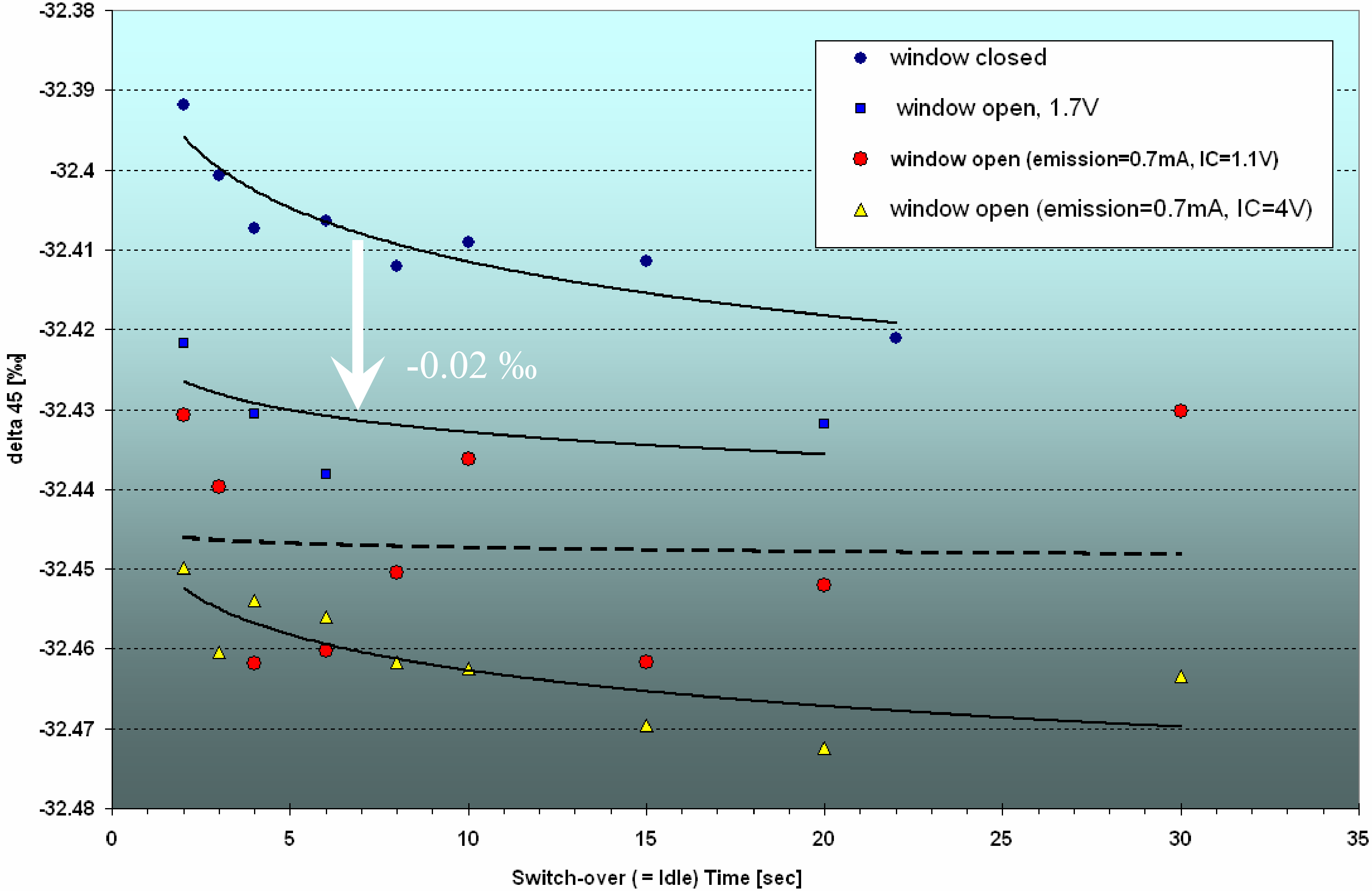
Table 1; Summary table for isotopic measurements of calcite and CO_2 reference materials; all values in [‰]

Minerals (reacted with H3PO4 and mixed into CO2-free air)										
Material	# of batches	# of 5-L flasks	δ13C [CG99-J]	std.dev (interbatch)	std.dev (intrabatch)	δ18O [CG99-J]	std.dev (interbatch)	std.dev (intrabatch)	**δ13C [VPDB]**	**δ18O [VPDB]**
NBS-19*	7	21	2.026	0.012	0.010	-2.159	0.015	0.023	***1.950***	**-2.200**
MAR-J1	29	88	2.050	0.015	0.011	-1.979	0.025	0.020	**1.974**	**-2.020**
IAEA-LSVEC	3	9	-46.535	0.029	0.018	-26.426	0.010	0.033	**-46.607**	**-26.466**
IAEA-C01	3	9	2.568	0.020	0.007	-2.287	0.038	0.017	**2.492**	**-2.328**
IAEA-C08	2	6	-5.689	0.025	0.009	-22.895	0.043	0.021	**-5.764**	**-22.935**
CAL1	1	2	-45.972		0.01	-22.286		0.011	**-46.044**	**-22.327**
CAL2	1	3	-2.421		0.012	-12.581		0.053	**-2.496**	**-12.622**
OMC-J1 (test drill)	3	9	-4.165	0.017	0.018	-8.664	0.012	0.029	**-4.241**	**-8.705**
CO2-gases (mixed into CO2-free air)										
Material	# of batches	# of 5-L flasks	δ13C [CG99-J]	std.dev (interbatch)	std.dev (intrabatch)	δ18O [CG99-J]	std.dev (interbatch)	std.dev (intrabatch)	**δ13C [VPDB]**	**δ18O [VPDBgas]**
Narcis I	2	3	-8.525	0.008	0.009	-0.668	0.020	0.008	**-8.601**	**-0.709**
Narcis II	2	2	2.030	0.003		-2.557	0.020		**1.954**	**-2.598**
NIST RM 8563	1	2	-41.541		0.017	-33.708		0.025	**-41.616**	**-33.749**
GS19 (M)	2	4	-7.489	0.020	0.014	-0.094	0.010	0.023	**-7.564**	**-0.135**
GS19 (D)	2	3	-7.494	0.006	0.020	-0.068	0.047	0.029	**-7.569**	**-0.109**
GS20 (M)	2	4	-8.640	0.010	0.008	-0.902	0.004	0.023	**-8.716**	**-0.943**
GS20 (D)	1	2	-8.605		0.001	-0.854		0.003	**-8.680**	**-0.895**
Eire (D)	1	2	-6.499		0.003	-17.651		0.013	**-6.574**	**-17.692**
Rose (D)	2	4	-7.381	0.016	0.011	-1.848	0.035	0.025	**-7.457**	**-1.889**
Yaka (D)	1	2	-6.698		0.005	-18.057		0.005	**-6.773**	**-18.098**
HC453 (BM504,enr.)	2	4	-6.072	0.001	0.011	-12.681	0.015	0.006	**-6.147**	**-12.722**
HC453 (recalc st set)	2	6	-6.324		0.023	-13.280		0.015	**-6.399**	**-13.239**
CO2-gases (directly measured on dual inlet)										
	# of inlets	# of runs								
Narcis I	1	2						0.001	**-8.592**	**-0.679**
Narcis II**	1	2						0.005	***1.954***	**-2.598**
NIST RM 8563	2	8		0.002	0.013		0.001	0.065	**-41.650**	**-33.517**
(* the isotopic results for NBS-19 on the CG99-J scale are used for correcting all subsequent results to the VPDB scale)										
(** difference between Narcis II and I measured and VPDB values for Narcis II adopted from above)										

δ^{13}C Offset measured vs. literature data



η-Effect: $\delta^{45}CO_2$ values as a function of the switch-over time



MPI-BGC Jena

NEW: Scaling of $\delta^{13}C$ for the VPDB scale:

Press release IUPAC Commission on Isotopic Abundances and Atomic Weights, Beijing Aug. 11 (2005):

It is recommended that delta carbon-13 values of all carbon-bearing materials be measured and expressed relative to VPDB on a scale normalized by assigning values of -46.6 parts per thousand relative to L-SVEC lithium carbonate and +1.95 parts per thousand relative to NBS 19 calcium carbonate...

Consistency of $\delta^{13}C$ Data Improved

T. B. Coplen, W. A. Brand, M. Gehre, M. Groening, H. A. J. Meijer, B. Toman, and R. M. Verkouteren

to be submitted (2005)

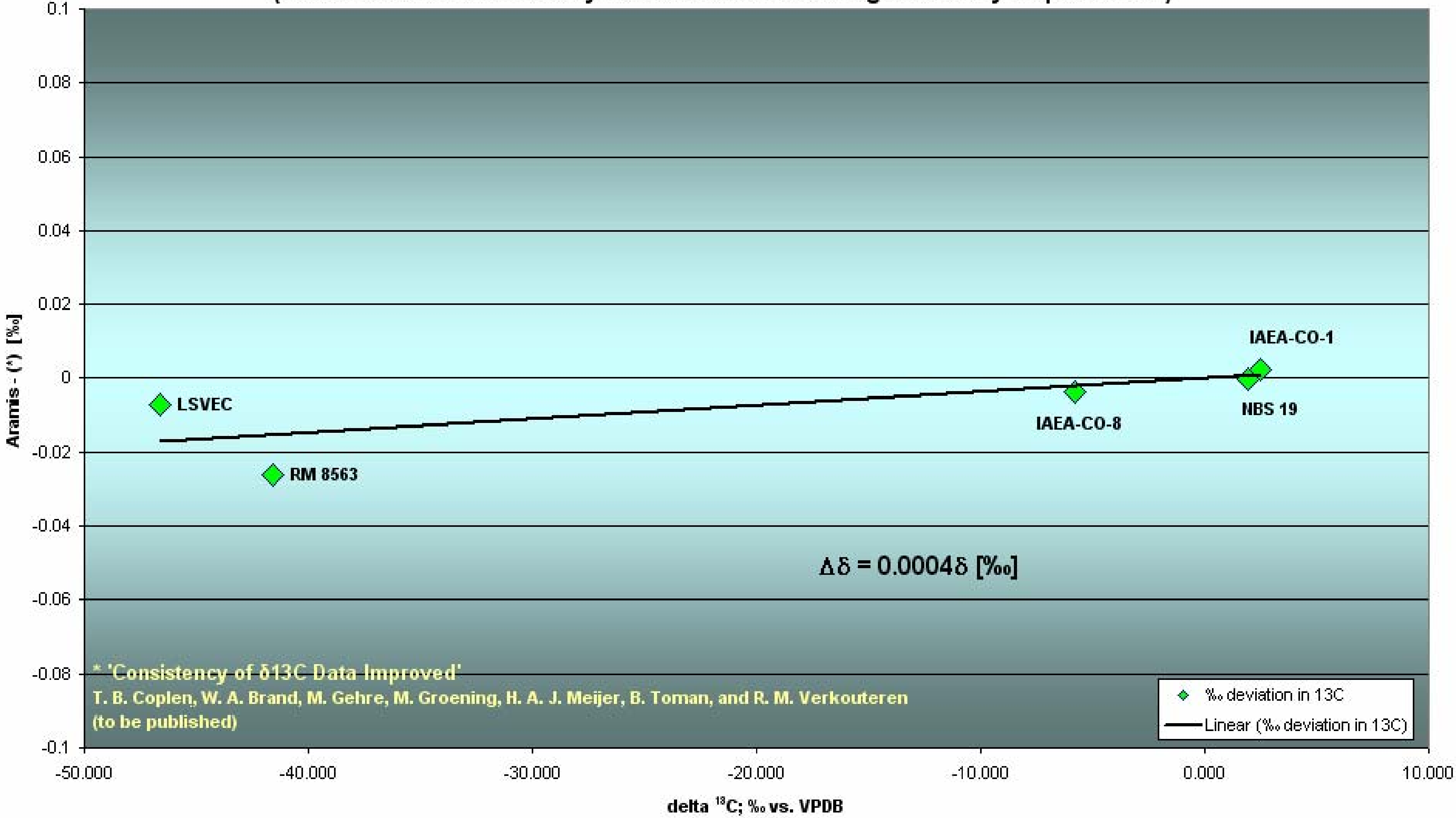
Recommended $\delta^{13}C$ Values of Carbon Stable Isotopic Reference Materials[a,b]

Name	$\delta^{13}C$ [‰]
USGS41 L-glutamic acid	**+37.63**
IAEA-CO-1 calcium carbonate	**+2.49 (+2.48)**
NBS 19 calcium carbonate	**+1.95**
RM 8562 carbon dioxide	**-3.72 (-3.76)**
NBS 18 calcium carbonate	**-5.01 (-5.0)**
IAEA-CO-8 calcium carbonate	**-5.76 (-5.75)**
IAEA-CH-6 sucrose	**-10.45 (-10.4)**
RM 8564 carbon dioxide	**-10.45 (-10.45)**
USGS24 graphite	**-16.05 (-15.99)**
IAEA-CH-3 cellulose	**-24.72 (-24.9)**
USGS40 L-glutamic acid	**-26.39**
IAEA-600 caffeine	**-27.77**
IAEA-601 benzoic acid	**-28.81**
NBS 22 oil	**-30.03 (-29.78)**
IAEA-CH-7 polyethylene	**-32.15 (-31.8)**
RM 8563 carbon dioxide	**-41.59 (-41.56)**
L-SVEC lithium carbonate	**-46.6 (-46.44)**
IAEA-CO-9 barium carbonate	**-47.32 (-47.13)**

[a] Recommendations from a Consultants Meeting of the International Atomic Energy Agency. Analytical data and estimates of uncertainty are available (*3*).
[b] $\delta^{13}C$ values expressed relative to VPDB (NBS 19 ≡ +1.95 ‰) and normalized to LSVEC ≡ –46.6 ‰.

Calibration of international ^{13}C reference materials

(Data from the Aramis study vs. new reference assignments by Coplen et al.*)



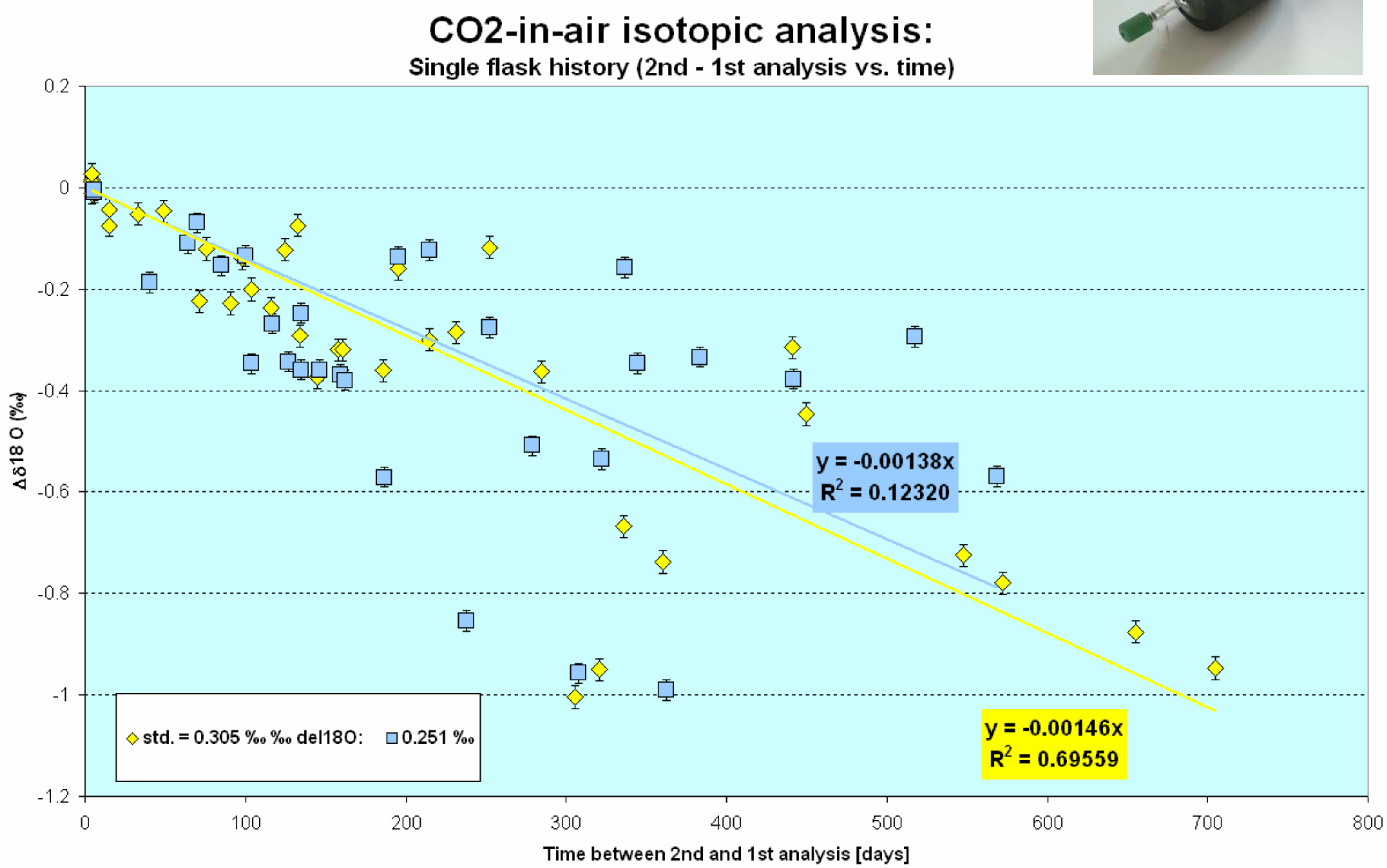
MPI-BGC Jena

J-RAS: (Jena-Reference-Air-Set)

- o pair of 5-L glass flasks
- o pressure = ~ 1.5 Bar
- o single valve, PCTFE seat
- o fits to most sample ports
- o transport friendly Al- case
- o refill possible
- o 12 months guarantee for $\delta^{18}O$

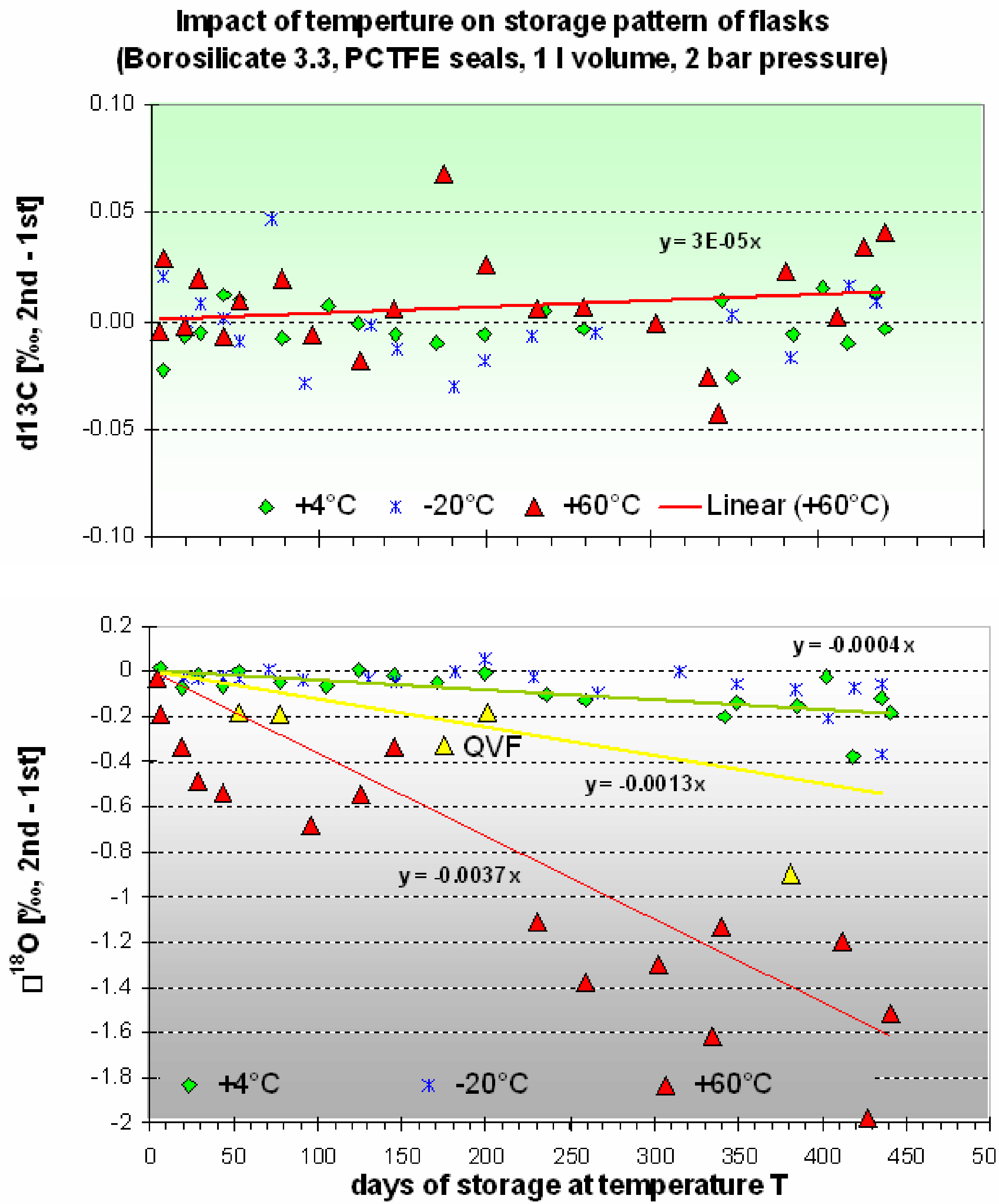
MPI-BGC Jena

Storage effects in glass flasks (1 L)

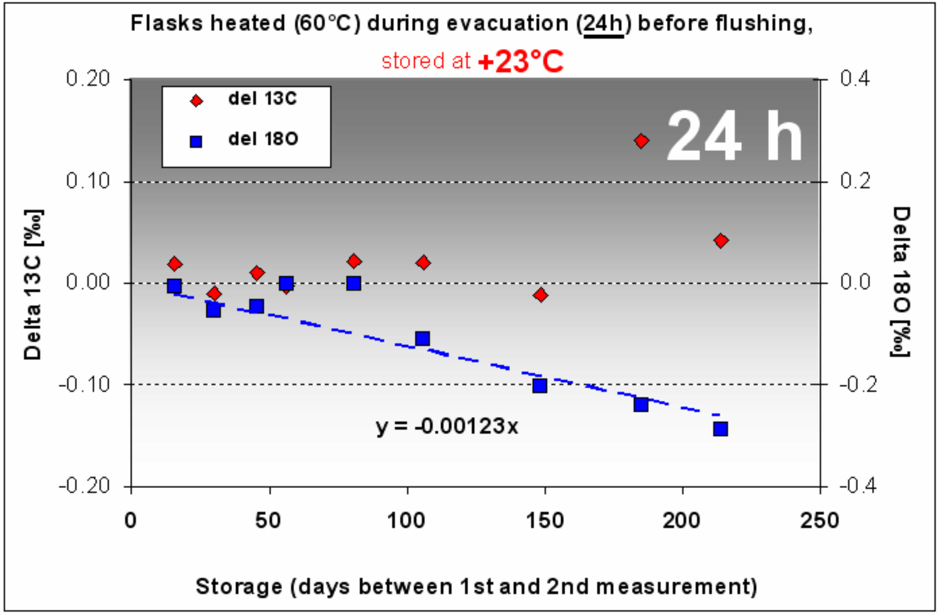


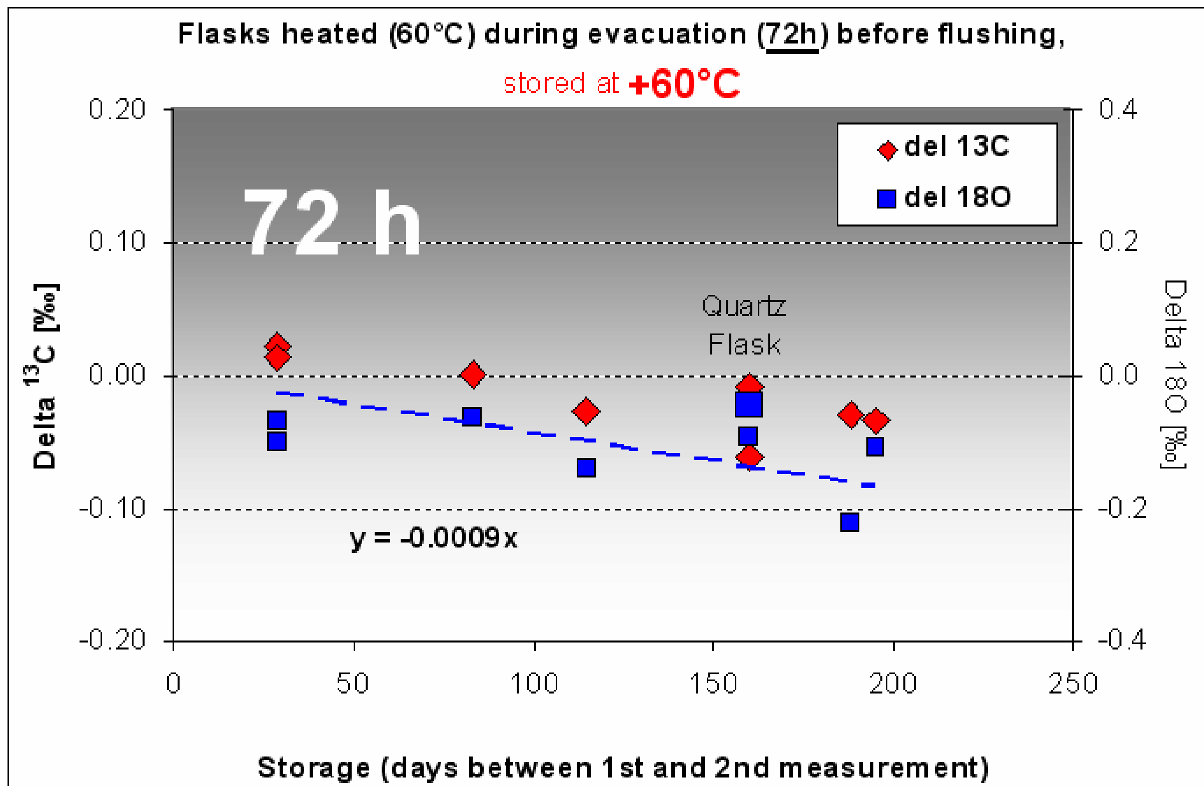
MPI-BGC Jena

Storage effects in glass flasks (1 L)



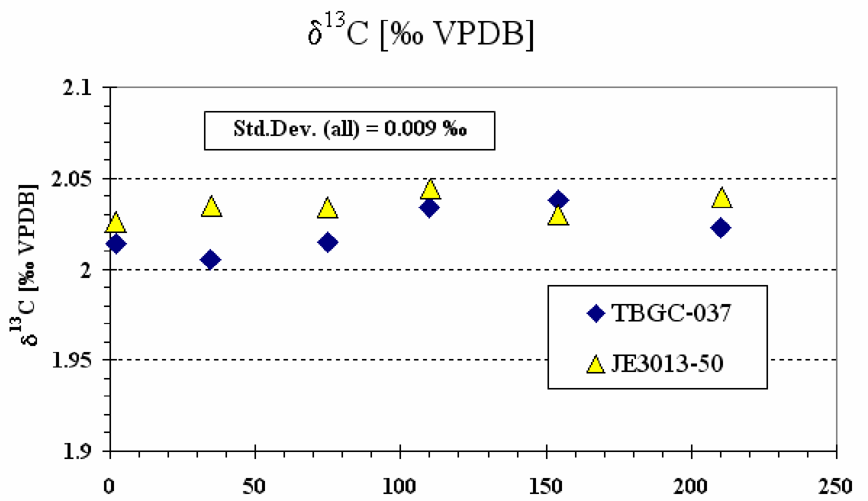
Storage effects in glass flasks (1 L)

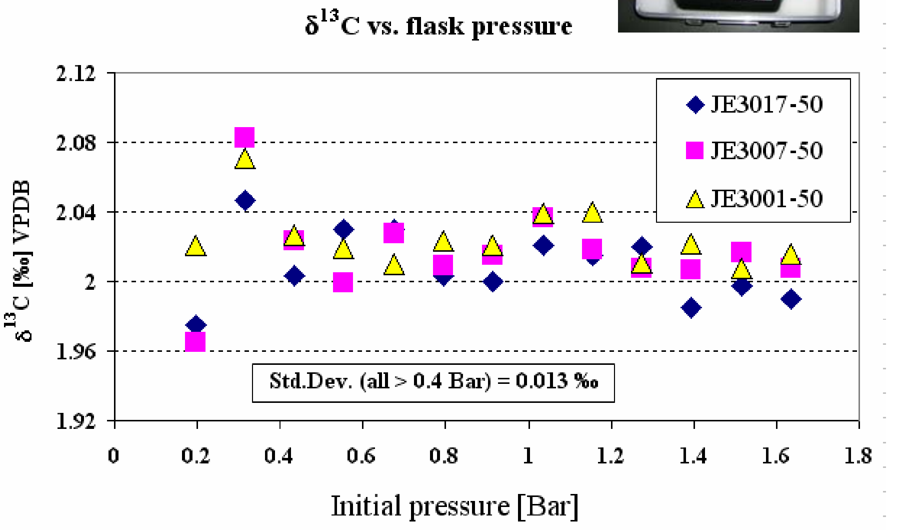


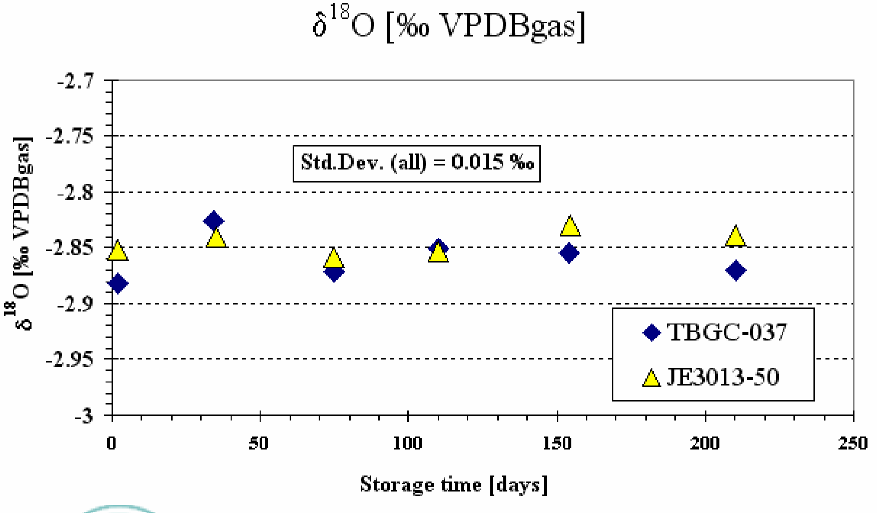


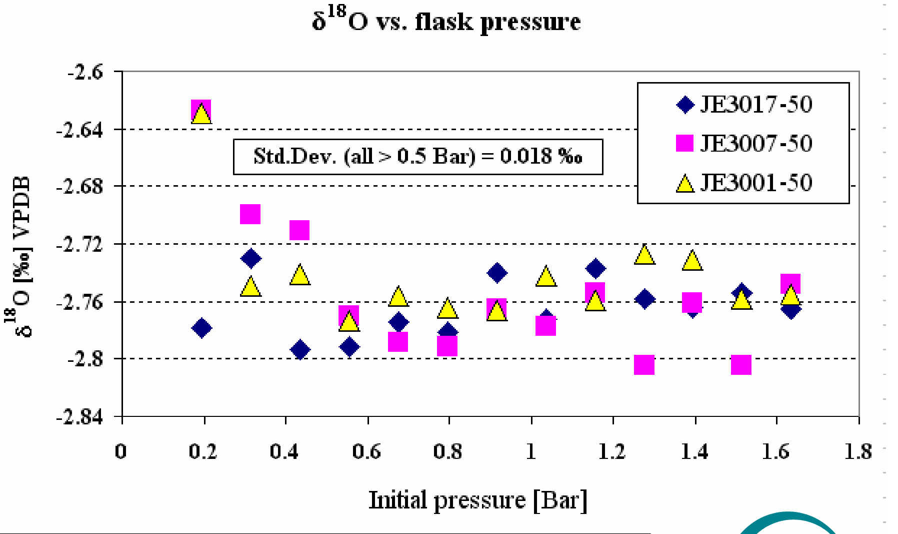
MPI-BGC Jena

Storage effects in glass flasks (5-L)



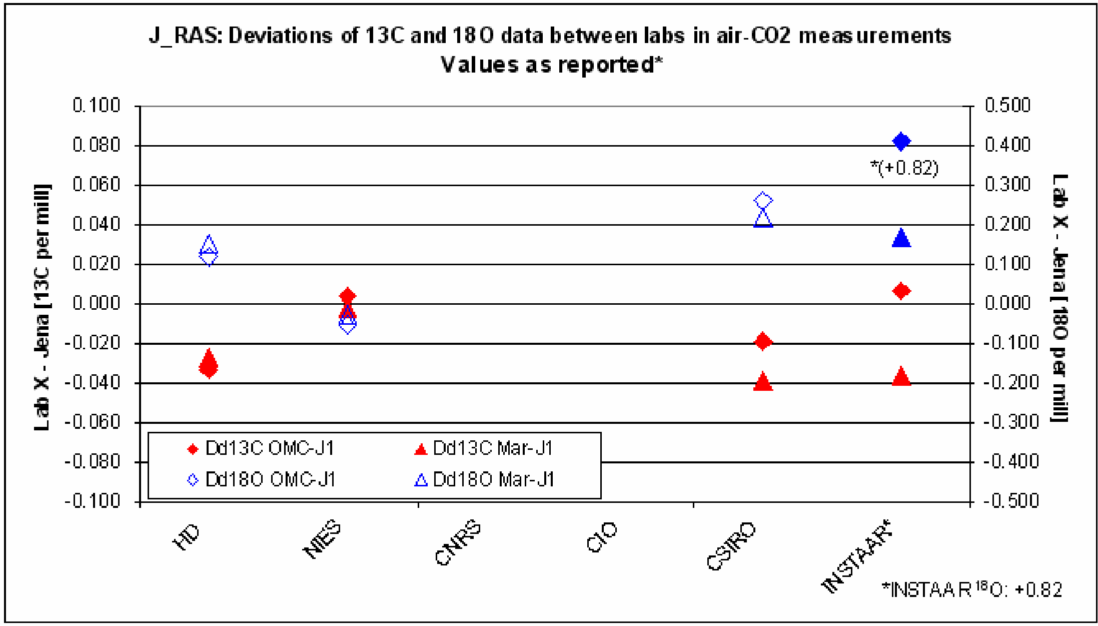






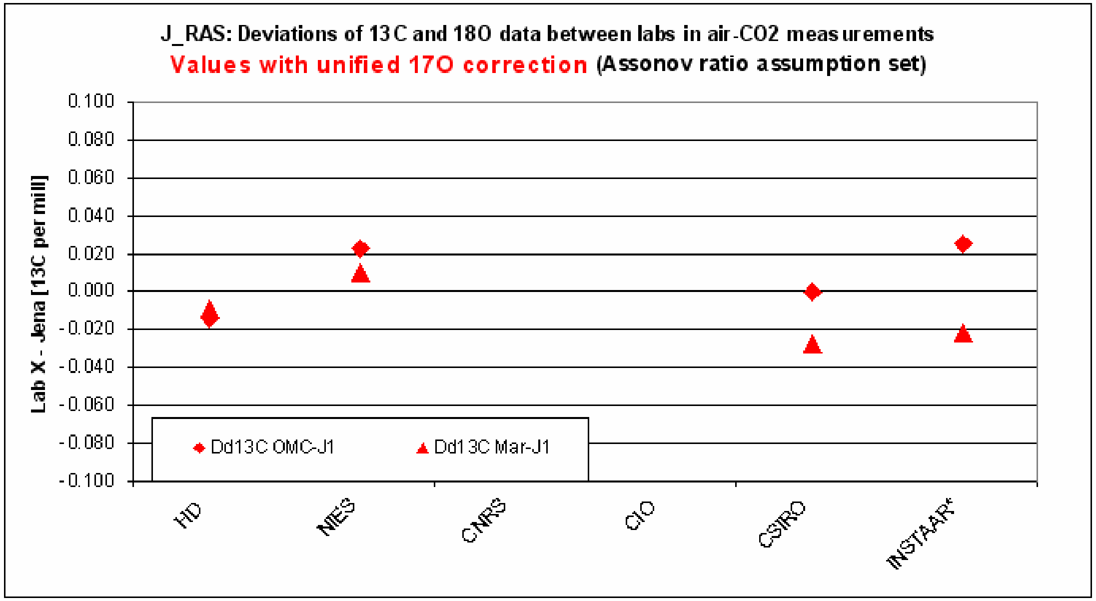
J-RAS 1st intercomparison

(I. Levin, H. Mukai, C. Allison, J. White)



Original data: $\delta^{13}C$ $\delta^{18}O$

avg		-0.019		0.181
std.dev		0.019		0.141



Unified ^{17}O correction data: $\delta^{13}C$

avg		-0.0022
std.dev		0.020

Acknowledgments:

Prosenjit Ghosh
Michael Rothe
Michael Patecki
Jürgen Richter
Colin Allison
Lin Huang
Paul Hoffmann
Manfred Gröning
Jim White

Armin Jordan
Hitoshi Mukai
Harro Meijer
Marc Delmotte
Robert Lippmann
Ingeborg Levin

& TACOS