

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

- 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 CO₂ reference materials
- o 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'

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wbrand@bgc-jena.mpg.de

Outline:









Fig.1 Atmospheric CO₂ concentration and δ^{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:	$\sim 1.6~ppm$ / y $~\gg~3~Pg~C$ / y
Best (installed) measurement precision:	$\sim 0.1 \text{ ppm}$
Fossil Fuel emissions:	$\sim 6 \text{ Pg C} / \text{y}$
13 C of atmospheric CO ₂	\sim -7.8 ‰
¹³ C rate of change	\sim -0.023 ‰ / y
Best (reported) measurement precision	$\sim \pm 0.01$ ‰

Comparison:

Precision / Mixing ratio change : 0.1/1.6 = 0.063 or 6.3 % rel. Precision / ¹³C 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 ¹³C!





The CLASSIC experiment



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





CO₂ in two reference air cylinders







 δ^{13} C values for Westf 10-2000 vs. CA01656



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



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:

¹³C: 1.97 ‰; ¹⁸O: -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 CaCO₃ content of 98.0 % and 2.0 % MgCO₃. AI, 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 % CaCO₃ and 1.8 % MgCO₃. 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 CO₂ gas.

OMC-J1:

¹³C: -4.4 ‰; ¹⁸O: -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 % CaCO₃ and 0.9 % MgCO₃ 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 CO₂ 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





Material # of batches # of 5 L flasis 6132 [C G99-J] std.dev 6180 [C G99-J] std.dev fidt.dev fidt.dev <th< th=""><th colspan="4">Minerals (reacted with H3PO4 and mixed into CO2-free air)</th></th<>	Minerals (reacted with H3PO4 and mixed into CO2-free air)										
Matchin # of balaches # of balaches	Material	# of batches	# of 51 fleeke	843C1 CC99 II	atd day	atd day	5480 (CC99_1]	atd day	atd day	\$43C IVDDB1	5480 IVDDB1
NBS-19* 7 21 2.026 0.012 0.010 -2.158 0.0025 0.023 7.956 -2.200 MARI 28 88 2.050 0.011 0.010 -2.158 0.0025 0.020 0.020 1.974 -2.200 MARI 28 48 2.050 0.018 -2.846 0.010 0.033 -4.667 2.846 MARLOT 3 9 -2.588 0.025 0.009 -2.286 0.001 0.033 -4.667 2.846 MARLOT 1 2 -4.537 0.001 -2.2286 0.001 -4.804 -2.237 CAL 1 3 -2.421 0.012 -1.2581 0.0025 -2.486 -2.846 CAL 9 -4.165 0.017 0.018 -8.684 0.012 0.025 -4.421 8.705 Material # of batches # of 5L fissis 6130 [CO99-J] std.dev 6180 [CO99-J] std.dev 6180 [CO99-J] std.dev	Matcallar	# Of balcries	# 01 J-L lidshs	0100[0000-0]	(interbatch)	(intrahatch)	0100 [0033-0]	(interhetch)	(introbatch)	OISC [VEDD]	
MAR_J1 23 68 2.050 0.011 1179 0.012 0.002 0.003 7.300 7.2.200 IAEA_LSVEC 3 9 4.6.535 0.020 0.011 -1179 0.023 0.003 4.6.607 -2.2.20 IAEA_LSVEC 3 9 2.568 0.020 0.007 -2.2.85 0.043 0.021 -5.764 -22.328 IAEA_C08 2 6 -5.689 0.022 0.001 -22.895 0.043 0.021 -5.764 -22.328 IAEA_C08 2 1 3 -2.421 0.012 -12.581 0.023 -4.464 -42.329 CAL2 1 3 -2.421 0.017 0.018 -8.664 0.012 0.029 -4.241 -8.765 Material # of 54.C[C699-J] std dev std	NBS_19*	7	21	2.026	0.012	0.010	-2.159	0.015	0.023	1 050	-2 200
Material # of batches # of SL flasts 6132 (CG99-J) ctd.dev 6130 (VPDBgas) Material # of batches # of SL flasts 613 (C G99-J) std.dev 6130 (CG99-J) std.dev 6130 (VPDBgas) 6130 (VPDBgas) Marcis I 2 3 -8525 0.000 0.009 -0.688 0.020 0.002 -0.098 -0.023 -1.669 -1.669 S51 (00) 2 -7.489 0.000 -0.029	MAR- 11	, 29	88	2.020	0.012	0.010	-2.133	0.015	0.020	1 974	-2.200
Act-Colu 3 9 2.668 0.020 0.007 2.287 0.038 0.001 4.492 2.232 AEA-C08 2 6 -5.689 0.022 0.007 -2.287 0.038 0.001 -5.764 -22.395 CAL1 1 2 -45.972 0.01 -2.2286 0.001 4.6.044 -2.328 CMC-J1 (test drill) 3 9 -4.165 0.017 0.018 -8.664 0.012 0.029 -4.241 -4.6.044 -2.328 OMC-J1 (test drill) 3 9 -4.165 0.017 0.018 -8.664 0.012 0.029 -4.241 -4.6.04 -2.328 Material # of batches # of sL (test drill) 6130 [CVPBg] 513C [VPDg] 5	IAFA-L SVEC	3	900	-46 535	0.010	0.011	-26.426	0.020	0.020	-46 607	-26.466
Attract Ob 2 0 <th0< th=""><th>IAFA-C01</th><th>3</th><th>9</th><th>2 568</th><th>0.020</th><th>0.007</th><th>-20.420</th><th>0.010</th><th>0.000</th><th>2 492</th><th>-20.400</th></th0<>	IAFA-C01	3	9	2 568	0.020	0.007	-20.420	0.010	0.000	2 492	-20.400
Action a b<	IAFA-C08	2	6	-5.689	0.025	0.009	-22.895	0.000	0.011	-5.764	-22.925
CAL2 1 3 -2.421 0.012 -1.2.581 0.053 -2.436 -1.2.622 OMC-J1 (test drill) 3 9 -4.165 0.017 0.018 -8.664 0.012 0.029 -4.241 -8.705 Material # of batches # of 5L flasks 613C [C099-J] std.dev std.dev 6180 [C099-J] std.dev 6180 [C099-J] std.dev 613C [VPDB] 6180 [VPDBgas] Material # of batches # of 5L flasks 613C [C099-J] std.dev std.dev std.dev std.dev 613C [VPDB] 6180 [VPDBgas] Narcis I 2 3 -8.525 0.000 0.009 -0.688 0.020 0.001 -0.709 Narcis I 2 3 -8.525 0.000 0.009 -0.688 0.020 1.954 -2.598 NST RM 8563 1 2 -41.541 0.017 -33.708 0.010 0.002 -7.684 -0.019 GS19 (0) 2 3 -7.484 0.0010 <	CAL1	1	2	-6.888	0.020	0.000	-22.000	0.040	0.021	-46.044	-22,300
OMC-J1 (test drill) 3 9 4.165 0.017 0.018 1.866 0.012 0.029 4.241 6.705 Material # of batches # of 5L flasks 613C [CG99-J] std.dev std.dev 6180 [CG99-J] std.dev 613C [VPDB] 613C [VPDB]<	CAL2	. 1	3	-2 421		0.012	-12.581		0.053	-2.496	-12.622
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CO2-gases (mixed into CO2-free air) Material # of 5L flasks δi3C [C G99-J] (Si3C [C G99-J] std.dev (intrebatch) std.dev (0.011	0.010	0.001	0.012	0.020		01100
Material # of batches # of 5-L flasks 613C [CG99-J] std.dev (interbatch) st					CO2-gases	(mixed into CO)2-free air)				
Material # of batches # of 5L flashs 613C [C G99-J] std.dev 618O [C G99-J] std.dev (intrabatch)											
Image: Name of the stand of the st	Material	# of batches	# of 5-L flasks	δ13C [CG99-J]	std.dev	std.dev	δ18O [CG99-J]	std.dev	std.dev	δ13C [VPDB]	δ180 [VPDBgas]
Narcis I 2 3 -8.525 0.008 0.009 -0.668 0.020 0.008 -8.601 -0.709 Narcis I 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 (W) 2 4 -7.488 0.020 -0.068 0.047 0.029 -7.569 -0.109 GS19 (W) 2 4 -8.640 0.010 0.008 -0.902 0.004 0.023 -7.769 -0.189 GS20 (M) 2 4 -8.640 0.010 0.008 -0.902 0.004 0.023 -7.769 -0.189 GS20 (D) 1 2 -8.605 0.001 -0.854 0.003 -8.680 -0.893 Erre (D) 1 2 -6.499 0.003 -17.651 0.013 -6.574 -17.992 Rose (D) 1 2 -6.638 <td></td> <td></td> <td></td> <td></td> <td>(interbatch)</td> <td>(intrabatch)</td> <td></td> <td>(interbatch)</td> <td>(intrabatch)</td> <td></td> <td></td>					(interbatch)	(intrabatch)		(interbatch)	(intrabatch)		
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NIST RM 8563 1 2 -41.541 0.017 -33.708 0.025 -41.616 -33.749 GST9 (M) 2 4 -7.499 0.020 0.014 -0.039 0.010 0.023 -7.564 -0.135 GS19 (M) 2 3 -7.494 0.006 0.020 -0.068 0.047 0.029 -7.569 -0.019 GS20 (M) 2 4 -8.640 0.010 0.008 -0.902 0.004 0.023 -8.680 -0.049 GS20 (D) 1 2 -8.680 0.010 0.008 -0.902 0.004 0.023 -8.680 -0.943 GS20 (D) 1 2 -6.649 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 -6.173 -18.098 HC453 (Precis" *set) 2 4 -6.324 0.023 -13.280 0	Narcis II	2	2	2.030	0.003		-2.557	0.020		1.954	-2.598
GS19 (M) 2 4 -7.489 0.020 0.014 -0.094 0.010 0.023 -7.564 -0.136 GS19 (D) 2 3 -7.494 0.006 0.020 -0.068 0.047 0.023 -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 -0.885 Eire (D) 1 2 -6.639 0.001 -0.854 0.003 -6.674 -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 -6.638 0.001 0.011 -1.848 0.005 -6.773 -1.809 Yaka (D) 2 4 -6.072 0.001 0.011 -1.2681 0.015 0.006 -6.1414 -1.272 <td>NIST RM 8563</td> <td>1</td> <td>2</td> <td>-41.541</td> <td></td> <td>0.017</td> <td>-33.708</td> <td></td> <td>0.025</td> <td>-41.616</td> <td>-33.749</td>	NIST RM 8563	1	2	-41.541		0.017	-33.708		0.025	-41.616	-33.749
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 -6.674 -17.692 Rose (D) 2 4 -7.381 0.016 0.011 -1.848 0.035 0.025 -7.457 -1.809 Rose (D) 1 2 -6.698 0.005 -18.087 0.005 -6.713 -18.098 HC453 (IM504,enr.) 2 4 -6.072 0.001 0.011 -12.681 0.015 0.006 -6.147 -12.72 HC453 (Im504,enr.) 2 6 -6.324 0.023 -13.280 0.015 -6.399 -13.239 Marcis I <td>GS19 (M)</td> <td>2</td> <td>4</td> <td>-7.489</td> <td>0.020</td> <td>0.014</td> <td>-0.094</td> <td>0.010</td> <td>0.023</td> <td>-7.564</td> <td>-0.135</td>	GS19 (M)	2	4	-7.489	0.020	0.014	-0.094	0.010	0.023	-7.564	-0.135
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 44 -7.381 0.016 0.011 -1.889 0.035 0.025 -7.457 -1.889 Yaka (D) 1 2 -6.698 0.005 -18.057 0.005 -6.713 -1.889 Yaka (D) 2 4 -6.072 0.001 0.011 -1.2881 0.015 0.005 -6.717 -1.889 Yaka (D) 2 4 -6.072 0.001 0.011 -1.281 0.015 0.005 -6.747 -1.272 HC453 (recalc ¹⁵ set) 2 6 -6.324 0.023 -13.280 0.015 6.6147 -1.272 Narcis I	GS19 (D)	2	3	-7.494	0.006	0.020	-0.068	0.047	0.029	-7.569	-0.109
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 *i set) 2 6 -6.324 0.023 -13.280 0.015 0.006 -6.147 -12.722 HC453 (recalc *i set) 2 6 -6.324 0.023 -13.280 0.015 0.005 -6.399 -13.239 Marcis I 1 2 CO2-gases (directry measured or dual inlet) 0.001 -8.592 -0.679 Narcis I 1	GS20 (M)	2	4	-8.640	0.010	0.008	-0.902	0.004	0.023	-8.716	-0.943
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 (BM504,enr.) 2 6 6.324 0.023 13.280 0.015 0.006 6.147 -12.722 HC453 (recalc "set) 2 6 6.324 0.023 -13.280 0.015 0.005 6.399 13.239 HC453 (recalc "set) 2 6 6.324 0.023 -13.280 0.015 0.001 6.399 3.239 HC453 (recalc "set) # of runs # of runs # of runs # of runs	GS20 (D)	1	2	-8.605		0.001	-0.854		0.003	-8.680	-0.895
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 HC453 (recalc st set) 2 6 -6.324 0.023 -13.280 0.015 -6.399 -13.239 HC453 (recalc st set) 2 6 -6.324 0.023 -13.280 0.015 -6.399 -13.239 HC453 (recalc st set) # of runs KCU-gases (directly measured on dual inlet) KCU-gases (directly measured on dual inlet) KCU-gases (directly measured on dual inlet) Narcis I 1 2 C C C C C C C C C C	Eire (D)	1	2	-6.499		0.003	-17.651		0.013	-6.574	-17.692
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 ^{s1} set) 2 6 -6.324 0.023 -13.280 0.015 0.015 -6.399 -13.239 HC453 (recalc ^{s1} set) 2 6 -6.324 0.023 -13.280 0.015 -6.399 -13.239 HC453 (recalc ^{s1} set) 2 6 -6.324 0.023 -13.280 0.015 -6.399 -13.239 HC453 (recalc ^{s1} set) 2 6 -6.324 0.023 -13.280 0.015 -6.399 -13.239 HC453 (recalc ^{s1} set) # of inlets # of fruns CO2-gases (directly measured on dual inlet) 0.001 -8.592 -0.679 Narcis I 1 2 6 -6.002 0.001 0.005 1.954 -2.598 Narcis I ^M 1 2	Rose (D)	2	4	-7.381	0.016	0.011	-1.848	0.035	0.025	-7.457	-1.889
HC 453 (BM504,enr.) 2 4 -6.072 0.001 0.011 -12.681 0.015 0.006 -6.147 -12.722 HC 453 (recalc ⁵¹ set) 2 6 -6.324 0.023 -13.280 0.015 0.005 -6.399 -13.239 HC 453 (recalc ⁵¹ set) 2 6 -6.324 0.023 -13.280 0.015 -6.399 -13.239 HC 453 (recalc ⁵¹ set) 2 6 -6.324 0.023 -13.280 0.015 -6.399 -13.239 HC 453 (recalc ⁵¹ set) 4 of inlets # of runs CO2-gases (directly measured on dual inlet) 0.001 0.001 -6.592 -0.679 Narcis I 1 2 0 0.002 0.013 0.001 0.005 1.954 -2.598 Narcis II** 1 2 0.002 0.013 0.001 0.065 -41.650 -33.517 Narcis II** 1 2 0.002 0.013 0.001 0.065 -41.650 -33.517 Narcis II** 1 2 1 1 2 1 1 <th< td=""><td>Yaka (D)</td><td>1</td><td>2</td><td>-6.698</td><td></td><td>0.005</td><td>-18.057</td><td></td><td>0.005</td><td>-6.773</td><td>-18.098</td></th<>	Yaka (D)	1	2	-6.698		0.005	-18.057		0.005	-6.773	-18.098
HC453 (recalc ** set) 2 6 -6.324 0.023 -13.280 0.015 -6.399 -13.239 HC453 (recalc ** set) 2 6 -6.324 0.023 -13.280 0.015 -6.399 -13.239 HC453 (recalc ** set) 4 0 0 0 0 0 0 0 HC453 (recalc ** set) # of inlets # of runs CO2-gases (directly measured on dual inlet) 0 0 0 0 Marcis I # of inlets # of runs CO2-gases (directly measured on dual inlet) 0.001 0.001 -8.592 -0.679 Narcis I 1 2 Co Co 0.001 -8.592 -0.679 Narcis I** 1 2 Co 0.002 0.013 0.001 0.005 1.954 -2.598 NIST RM 8563 2 8 0.002 0.013 0.001 0.005 -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) Co Co Co	HC453 (BM504,enr.)	2	4	-6.072	0.001	0.011	-12.681	0.015	0.006	-6.147	-12.722
Image: state stat	HC453 (recalc ^{si} set)	2	6	-6.324		0.023	-13.280		0.015	-6.399	-13.239
Image: Coll gases (directly measured on dual inlet) # of inlets # of runs Image: Coll gases (directly measured on dual inlet) Narcis I # of runs Image: Coll gases (directly measured on dual inlet) Narcis I # of inlets # of runs Image: Coll gases (directly measured on dual inlet) Narcis I 1 2 Image: Coll gases (directly measured on dual inlet) Image: Coll gases (directly measured on dual inlet) Narcis I 1 2 Image: Coll gase (directly measured on dual inlet) Image: Coll gase (directly measured on dual inlet) Narcis I 1 2 Image: Coll gase (directly measured on dual inlet) Image: Coll gase (directly measured on dual inlet) Narcis I 1 2 Image: Coll gase (directly measured on dual inlet) Image: Coll gase (directly measured on dual inlet) NIST RM 8563 2 8 0.002 0.013 0.001 0.065 -441.650 -33.517 Image: Coll gase (directly measured for correcting all subsequent results to the VPDB scale) Image: Coll gase (directly measured directly measured for correcting all subsequent results to the VPDB scale) Image: Coll gase (directly measured directly measured directly measured directly measured directly measured directly measured directly											
# of inlets # of runs # of runs Image: Comparison of the compari		41 - 4 - 1 - 4 -		C	02-gases (dre	ectly measured	i on dual inlet)				
rearcisit 1 2 -0.679 Narcisit 1 2 -0.679 Narcisit 1 2 -0.679 Nist RM 8563 2 8 0.002 0.013 0.001 0.065 -41.650 -33.517 Image: State	Manaia	# of inlets	#otruns						0.004	0 500	0.070
rear cris m 1 2 Image: Constraint of the constraint of th	Narcis I Narcis IIII	1	2						0.001	-8.592	-0.679
Initial RM 8503 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) <	Narcis II**	1	2		0.000	0.010		0.001	0.005	1.954	-2.598
(* the isotopic results for NBS-19 on the CG99-J scale are used for correcting all subsequent results to the VPDB scale)	NIST RM 8563	2	8		0.002	0.013		0.001	0.065	-41.650	-33.517
(" the isotopic results for NDS-13 on the CO33-3 scale are used for correcting all subsequent results to the VPDB scale)	/* the isstenic used the A		L COOR Leaste er				(DDD acata)				
(77 difference between Never Never Never and MDD values for Never Never Never Never	(* trie isotopic results t	UT NOS-19 ON IN	ie CG99-J SCale al	re used for correcting	y an subsequer	it results to the '	veud scalej				

Table 1; Summary table for isotopic measurements of calcite and CO₂ reference materials; all values in [‰]

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





GASIR annual meeting, Jena, Oct. 2005



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





GASIR annual meeting, Jena, Oct. 2005



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 δ^{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)

^a Recommendations from a Consultants Meeting of the International Atomic Energy Agency. Analytical data and estimates of uncertainty are available (3). ^b δ^{13} C values expressed relative to VPDB (NBS 19 = +1.95 ‰) and normalized to LSVEC = -46.6 ‰.

Recommended δ^{13} C Values of Carbon Stable Isotopic Reference Materials^{a,b}

Name	δ 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)





Calibration of international ¹³C reference materials





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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
δ¹⁸O





Storage effects in glass flasks (1 L)







Storage effects in glass flasks (1 L)







-2

0

50

100

150

200

250

days of storage at temperature T

(Borosilicate 3.3, PCTFE seals, 1 | volume, 2 bar pressure) 0.10 d13C [‰, 2nd - 1st] 0.05 $y = 3E_{-}05x$ 0.00 ¥ ж ж -0.05 x -20°C ▲ +60°C — Linear (+60°C) ♦ +4°C -0.10 0.2 y = -0.0004 xΟ -0.2 -0.4 □¹⁸O [‰, 2nd - 1st] v = -0.0013x-0.6 -0.8 $y = -0.0037 \times$ -1 -1.2 -1.4 -1.6 -1.8 ★ -20°C ▲ +60°C

500

450

350

400

300

Impact of temperture on storage pattern of flasks

Storage effects in glass flasks (1 L)









Storage effects in glass flasks (5-L)



Jena



J-RAS 1st intercomparison

Unified ¹⁷O correction data:

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

Original data:	$\delta^{13}\mathbf{C}$	$\delta^{18}O$
avg	-0.019	0.181
std.dev	0.019	0.141





MPI-BGC

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avg

std.dev

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δ¹³C

-0.0022

0.020

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



