

Δ_{47} Analysis Report – LGB-2 & DVH-2

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Number of analytical sessions	3
Number of samples (standards + unknowns)	6 (4 + 2)
Number of analyses (standards + unknowns)	112 (76+ 36)
Overall percentage of standard analyses	68 %
Nominal Δ_{47} of standard ETH-1:	0.2052 ‰
Nominal Δ_{47} of standard ETH-2:	0.2085 ‰
Nominal Δ_{47} of standard ETH-3:	0.6132 ‰
Nominal Δ_{47} of standard ETH-4:	0.4511 ‰
External reproducibility of $\delta^{13}\text{C}_{\text{VPDB}}$ measurements	5.6 ppm
External reproducibility of $\delta^{18}\text{O}_{\text{VSMOW}}$ measurements	17.2 ppm
External reproducibility of Δ_{47} measurements	9.1 ppm
Regression model degrees of freedom	101 ($t_{95\%} = 1.98$)

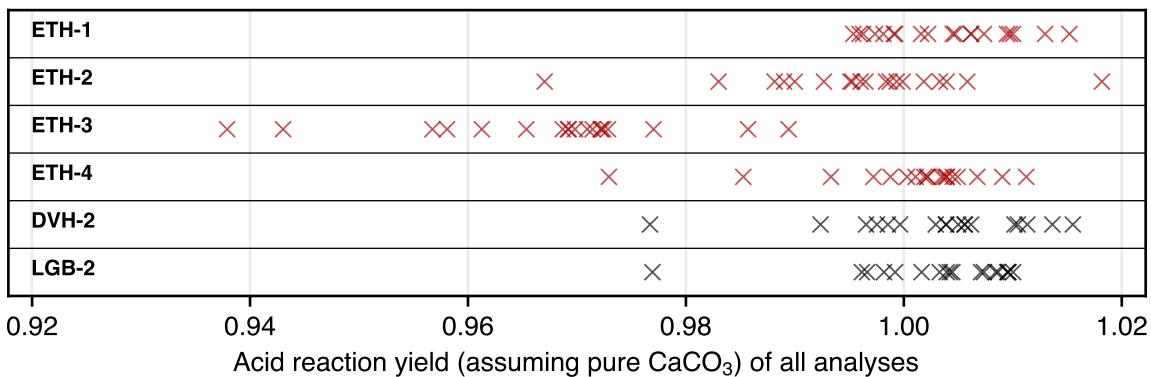
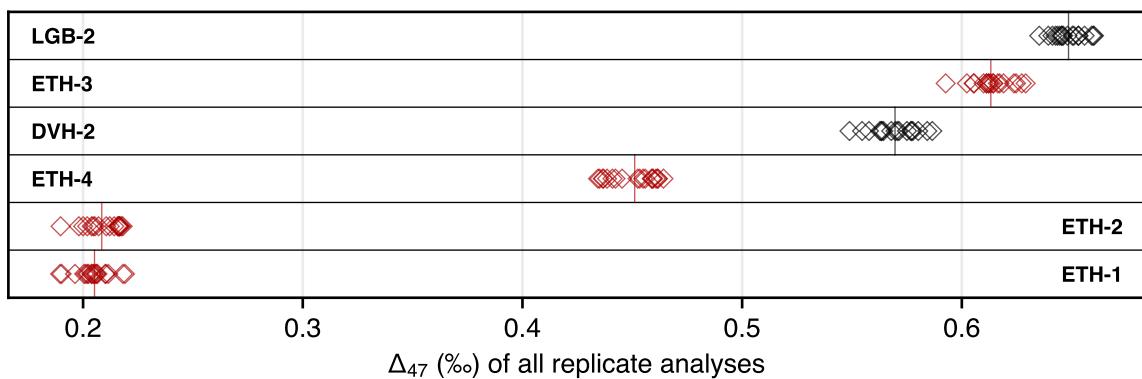
Analytical sessions

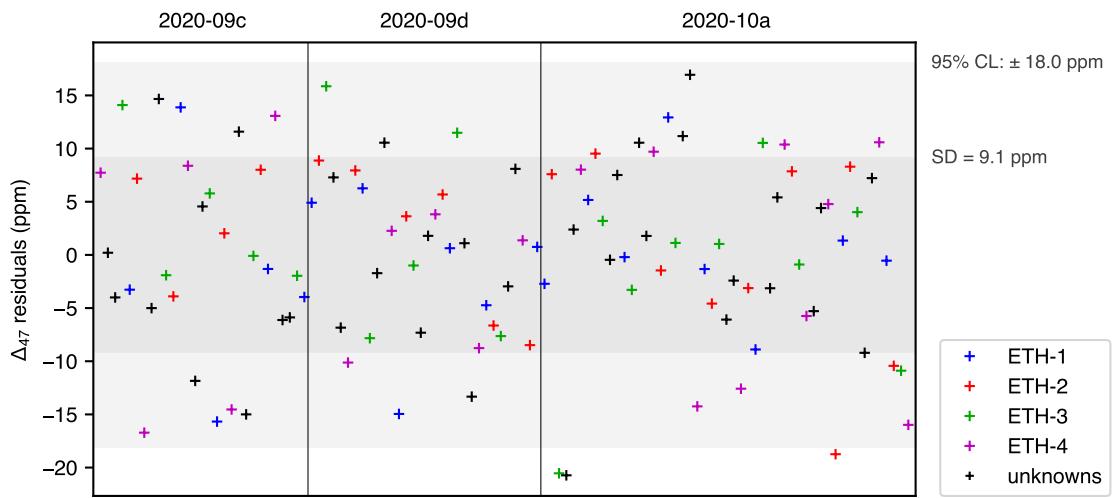
Session	2020-09c	2020-09d	2020-10a
N of standard analyses	19	22	35
N of unknown analyses	10	10	16
Working gas $\delta^{13}\text{C}$ (%) VPDB	-3.81	-3.81	-3.80
Working gas $\delta^{18}\text{O}$ (%) VSMOW	35.16	35.12	35.16
Working gas Δ_{47} (‰ ± SE)	0.964 ± 0.011	0.961 ± 0.010	0.964 ± 0.009
Scrambling factor (a) (± SE)	0.918 ± 0.010	0.924 ± 0.009	0.921 ± 0.008
Compositional slope (b) ($\times 10^{-4}$ ± SE)	0.5 ± 1.3	0.4 ± 1.2	0.3 ± 1.0
Working gas offset (c) (± SE)	-0.885 ± 0.005	-0.888 ± 0.004	-0.888 ± 0.004
$\delta^{13}\text{C}_{\text{VPDB}}$ repeatability (ppm)	3.2	5.0	7.2
$\delta^{18}\text{O}_{\text{VSMOW}}$ repeatability (ppm)	13.6	18.6	18.2
Δ_{47} repeatability (ppm)	10.0	8.2	9.4

Sample	N	Yield	$\delta^{13}\text{C}_{\text{VPDB}}$	$\delta^{18}\text{O}_{\text{VSMOW}}$	$\delta^{18}\text{O}_{\text{VPDB}}$	Δ_{47}			p-value (Levene)	
			(%)	(CO ₂)	(calcite*)	$\pm \text{SE}$	($\pm 95\%$)	SD		
ETH-1	19	100	2.03	37.03	-2.19	0.2052			0.0077	
ETH-2	19	100	-10.17	19.88	-18.69	0.2085			0.0081	
ETH-3	19	97	1.70	37.44	-1.79	0.6132			0.0089	
ETH-4	19	100	-10.21	19.77	-18.79	0.4511			0.0106	
DVH-2	18	100	-1.97	22.88	-15.80	0.5696	± 0.0027	(± 0.0054)	0.0102	0.395
LGB-2	18	100	0.09	34.82	-4.31	0.6486	± 0.0030	(± 0.0059)	0.0072	0.744

* computed assuming the sample is pure calcite; adjust accordingly for different mineralogies.

For example, for aragonite samples, $\delta^{18}\text{O}_{\text{arag}} = (1000 + \delta^{18}\text{O}_{\text{calcite}}) \times 1.00813 / {}^{18}\alpha_{\text{arag}} - 1000$



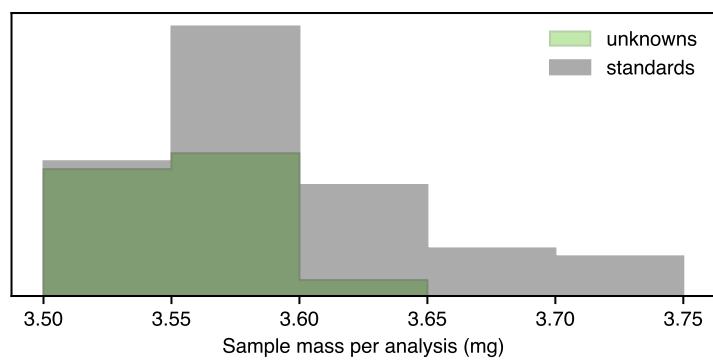


Methods

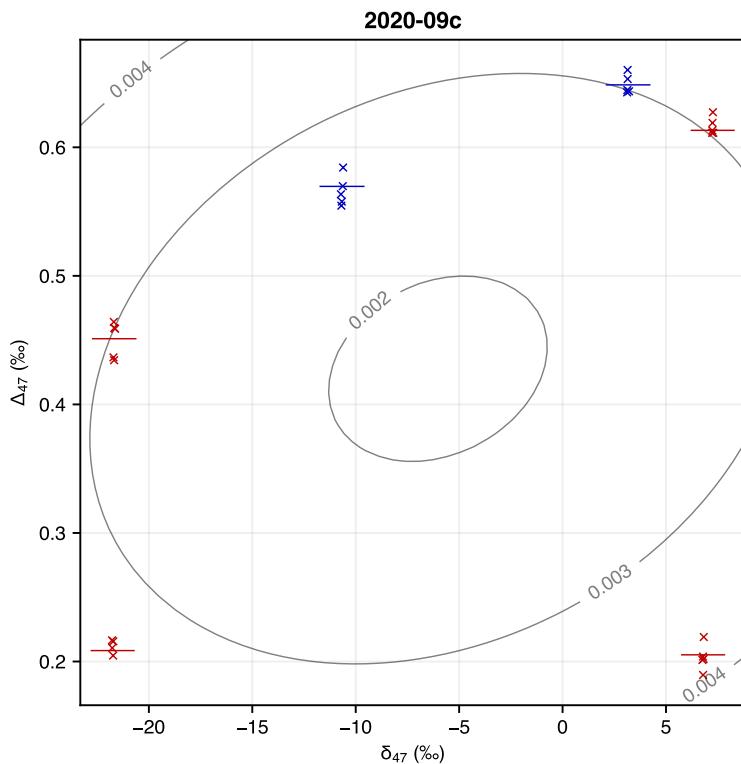
Carbonate samples were converted to CO₂ by phosphoric acid reaction at 90 °C in a common, stirred acid bath for 15 minutes. Initial phosphoric acid concentration was 103 % (1.91 g/cm³) and each batch of acid was used for 7 days. After cryogenic removal of water, the evolved CO₂ was helium-flushed at 25 mL/mn through a purification column packed with Porapak Q (50/80 mesh, 1 m length, 2.1 mm ID) and held at -20 °C, then quantitatively recollected by cryogenic trapping and transferred into an Isopprime 100 dual-inlet mass spectrometer equipped with six Faraday collectors (m/z 44–49). Each analysis took about 2.5 hours, during which analyte gas and working reference gas were allowed to flow from matching, 10 mL reservoirs into the source through deactivated fused silica capillaries (65 cm length, 110 µm ID). Every 20 minutes, gas pressures were adjusted to achieve m/z = 44 current of 80 nA, with differences between analyte gas and working gas generally below 0.1 nA. Pressure-dependent background current corrections were measured 12 times for each analysis. All background measurements from a given session are then used to determine a mass-specific relationship linking background intensity (Z_m), total m/z = 44 intensity (I_{44}), and time (t): $Z_m = a + bI_{44} + ct + dt^2$. Background-corrected ion current ratios (δ_{45} to δ_{49}) were converted to δ¹³C, δ¹⁸O, and “raw” Δ₄₇ values as described by Daëron *et al.* [2016], using the IUPAC oxygen-17 correction parameters. The isotopic composition (δ¹³C, δ¹⁸O) of our working reference gas was computed based on the nominal isotopic composition of carbonate standard ETH-3 [Bernasconi, Müller, *et al.*, 2018] and an oxygen-18 acid fractionation factor of 1.00813 [Kim *et al.*, 2007]. Raw Δ₄₇ values were then converted to the I-CDES Δ₄₇ reference frame by comparison with four “ETH” carbonate standards [Bernasconi, Daëron, *et al.*, 2021] using a pooled regression approach [Daëron, 2021]. Full analytical errors are derived from the external reproducibility of unknowns and standards (N_f = 101) and conservatively account for the uncertainties in raw Δ₄₇ measurements as well as those associated with the conversion to the “absolute” Δ₄₇ reference frame.

References

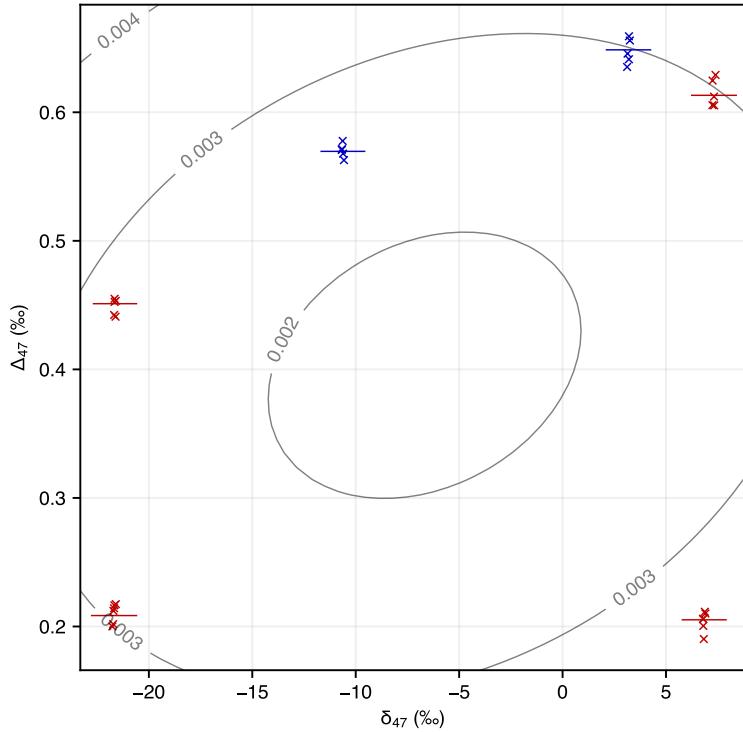
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UID	Session	Sample	Mass (mg)	CO ₂ yield (if CaCO ₃)	δ_{45} (‰ WG)	δ_{46} (‰ WG)	δ_{47} (‰ WG)	δ_{48} (‰ WG)	δ_{49} (‰ WG)	$\delta^{13}\text{C}_{\text{VPDB}}$ (‰)	$\delta^{18}\text{O}_{\text{VSMOW}}$ (‰)	$\Delta_{\text{raw}}^{\text{abs}}$ (‰)	$\Delta_{\text{abs}}^{\text{abs}}$ (‰)
H641	2020-10a	ETH-1	3.53	1.00	5.516252	1.788352	6.747919	3.454205	-0.109589	2.028	37.026	-0.706597	0.196308
H642	2020-10a	ETH-3	3.64	0.94	5.225713	2.206539	7.257580	4.396562	-1.085496	1.702	37.462	-0.312895	0.623735
H643	2020-10a	LGB-2	3.59	1.00	3.616443	-0.341946	3.099858	-0.853224	-0.145425	0.077	34.823	-0.293045	0.645437
H644	2020-10a	DVH-2	3.55	1.00	1.298057	-11.852316	-10.685241	-24.822203	-0.703626	-1.973	22.887	-0.358377	0.575009
H645	2020-10a	ETH-4	3.57	1.00	-6.518208	-14.880430	-21.710635	-31.079731	0.080367	-10.215	19.764	-0.463312	0.461481
H646	2020-10a	ETH-2	3.52	1.00	-6.473328	-14.764691	-21.773045	-31.048959	-0.449448	-10.171	19.886	-0.689085	0.216360
H647	2020-10a	ETH-3	3.62	0.97	5.222127	2.181394	7.218410	4.358154	-0.619736	1.699	37.443	-0.323430	0.612298
H648	2020-10a	ETH-4	3.59	1.00	-6.519390	-14.877375	-21.723391	-31.118875	-0.173233	-10.216	19.772	-0.478167	0.445354
H649	2020-10a	DVH-2	3.57	1.01	1.294257	-11.870220	-10.716492	-24.836185	-0.483831	-1.976	22.875	-0.368233	0.564309
H650	2020-10a	LGB-2	3.54	1.00	3.646725	-0.340563	3.139417	-0.927881	-0.435047	0.109	34.835	-0.286098	0.652979
H651	2020-10a	ETH-4	3.53	1.00	-6.517652	-14.857396	-21.692630	-31.156060	-0.320568	-10.215	19.797	-0.468470	0.455880
H652	2020-10a	ETH-2	3.58	1.00	-6.475480	-14.776517	-21.810761	-31.012601	-0.015817	-10.173	19.882	-0.713588	0.189758
H653	2020-10a	ETH-1	3.52	1.00	5.515617	1.763527	6.732236	3.408943	0.026852	2.029	37.018	-0.697166	0.206548
H654	2020-10a	ETH-2	3.54	1.00	-6.467506	-14.769788	-30.951659	-0.069631	-10.165	19.893	-0.688680	0.216799	
H655	2020-10a	ETH-3	3.68	0.96	5.207206	2.163462	7.189838	4.279251	-0.463398	1.684	37.436	-0.318895	0.617223
H656	2020-10a	LGB-2	3.56	1.00	3.606419	-0.365537	3.060636	-0.794630	0.630412	0.067	34.817	-0.298639	0.639366
H657	2020-10a	DVH-2	3.56	1.00	1.293573	-11.880853	-10.716253	-25.105367	-0.519266	-1.977	22.875	-0.356710	0.576819
H658	2020-10a	ETH-4	3.57	0.99	-6.525434	-14.906905	-21.743635	-31.205247	-0.319452	-10.222	19.754	-0.463119	0.461692
H659	2020-10a	ETH-1	3.55	1.00	5.515215	1.753373	6.720034	3.320187	0.071257	2.028	37.015	-0.698906	0.204659
H660	2020-10a	ETH-2	3.58	0.99	-6.482778	-14.818288	-21.851455	-31.049533	-0.903483	-10.179	19.849	-0.705935	0.198069
H661	2020-10a	ETH-3	3.69	0.94	5.205862	2.156336	7.167568	4.139230	-0.971826	1.683	37.435	-0.332631	0.602311
H662	2020-10a	ETH-4	3.58	0.97	-6.525007	-14.878852	-21.739769	-31.253280	-1.584380	-10.222	19.788	-0.487596	0.435117



2020-09d



2020-10a

