

# $\Delta_{47}$ Analysis Report — N. Beaudoin (2021-07)

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## DEFINITIVE VERSION

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### Summary

Number of analytical sessions	1
Number of samples (anchors + unknowns)	14 (4 + 10)
Number of analyses (anchors + unknowns)	53 (23 + 30)
Overall percentage of anchor analyses	43 %
Nominal $\Delta_{47}$ of anchor ETH-1	0.2052 ‰
Nominal $\Delta_{47}$ of anchor ETH-2	0.2085 ‰
Nominal $\Delta_{47}$ of anchor ETH-3	0.6132 ‰
Nominal $\Delta_{47}$ of anchor ETH-4	0.4511 ‰
External reproducibility of $\delta^{13}\text{C}_{\text{VPDB}}$ measurements	13.0 ppm
External reproducibility of $\delta^{18}\text{O}_{\text{VSMOW}}$ measurements	23.5 ppm
External reproducibility of $\Delta_{47}$ measurements	8.1 ppm ( $N_f = 40$ )
External reproducibility of $\Delta_{47}$ for anchors	9.0 ppm ( $N_f = 20$ )
External reproducibility of $\Delta_{47}$ for unknowns	7.0 ppm ( $N_f = 20$ )
Regression model degrees of freedom	40 ( $t_{95\%} = 2.02$ )

### Analytical Sessions

Session	2021-07a
N of anchor analyses	23
N of unknown analyses	30
Working gas $\delta^{13}\text{C}$ (‰ VPDB)	−3.85
Working gas $\delta^{18}\text{O}$ (‰ VSMOW)	34.53
Working gas $\Delta_{47}$ (‰ $\pm$ SE)	$1.009 \pm 0.012$
Scrambling factor (a) ( $\pm$ SE)	$0.968 \pm 0.010$
Compositional slope (b) ( $\times 10^{-4} \pm$ SE)	$-0.0 \pm 1.2$
Working gas offset (c) ( $\pm$ SE)	$-0.976 \pm 0.005$
$\delta^{13}\text{C}_{\text{VPDB}}$ repeatability (ppm)	13.0
$\delta^{18}\text{O}_{\text{VSMOW}}$ repeatability (ppm)	23.5
$\Delta_{47}$ repeatability (ppm)	7.0

## Sample averages

Sample	N	Yield (%)	$\delta^{13}\text{C}_{\text{VPDB}}$	$\delta^{18}\text{O}_{\text{VSMOW}}$ (CO <sub>2</sub> )	$\delta^{18}\text{O}_{\text{VPDB}}$ (calcite*)	$\Delta_{47}$ (I-CDES)			p-value (Levene)
						$\pm$ SE	( $\pm$ 95 %)	SD	
ETH-1	4	100	2.03	37.03	-2.19	0.2052		0.0057	
ETH-2	4	101	-10.17	19.88	-18.69	0.2085		0.0087	
ETH-3	8	97	1.70	37.45	-1.78	0.6132		0.0092	
ETH-4	7	100	-10.22	19.79	-18.77	0.4511		0.0102	
REDACTED-1	3	96	-3.91	29.59	-9.34	0.4553	$\pm$ 0.0050	( $\pm$ 0.0100)	0.15
REDACTED-2	3	95	-3.70	25.50	-13.28	0.5100	$\pm$ 0.0051	( $\pm$ 0.0103)	0.42
REDACTED-3	3	95	-12.27	27.86	-11.01	0.4701	$\pm$ 0.0051	( $\pm$ 0.0104)	0.27
REDACTED-4	3	93	-14.08	29.80	-9.14	0.4886	$\pm$ 0.0052	( $\pm$ 0.0104)	0.90
REDACTED-5	3	101	-4.67	28.68	-10.22	0.4935	$\pm$ 0.0050	( $\pm$ 0.0101)	0.31
REDACTED-6	3	95	-7.87	22.97	-15.72	0.4693	$\pm$ 0.0052	( $\pm$ 0.0104)	0.17
S-01-A	3	100	-3.71	32.70	-6.35	0.5512	$\pm$ 0.0051	( $\pm$ 0.0103)	0.09
S-01-B	3	101	-2.47	33.07	-5.99	0.5639	$\pm$ 0.0051	( $\pm$ 0.0104)	0.85
S-28	3	100	-4.94	32.27	-6.77	0.5511	$\pm$ 0.0051	( $\pm$ 0.0103)	0.54
S-32-C	3	99	-3.60	33.05	-6.02	0.5350	$\pm$ 0.0051	( $\pm$ 0.0103)	0.15

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

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

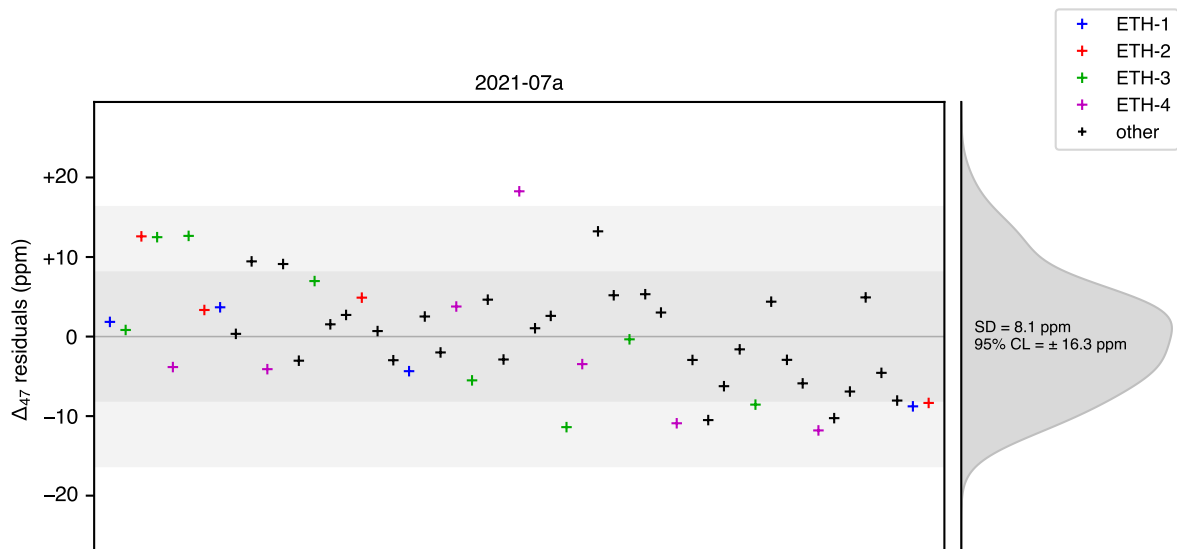
Based on Kim et al. [2007b], at 90 °C:  $\delta^{18}\text{O}_{\text{arag}} = (1000 + \delta^{18}\text{O}_{\text{calcite}}) / 1.00041 - 1000$

## Temperature and water $\delta^{18}\text{O}$ reconstructions

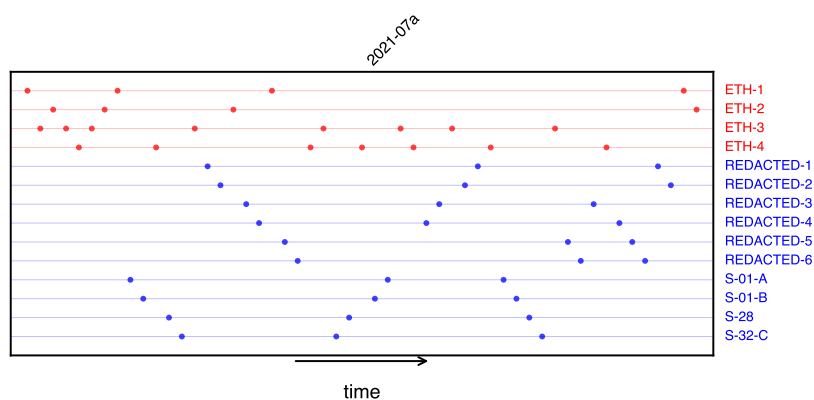
Sample	N	$\Delta_{47}$	$T_{47}$	Water $\delta^{18}\text{O}_{\text{VSMOW}}$ (‰ $\pm$ 95 %)	
		(‰ $\pm$ 95 %)	(°C $\pm$ 95 %)	Kim & O'Neil [1997]	Daëron et al. [2019]
S-01-A	3	$0.5512 \pm 0.0103$	$40.1 \pm 4.0$	$-1.1 \pm 0.7$	$-2.9 \pm 0.7$
S-01-B	3	$0.5639 \pm 0.0104$	$35.3 \pm 3.8$	$-1.6 \pm 0.7$	$-3.4 \pm 0.7$
S-28	3	$0.5511 \pm 0.0103$	$40.1 \pm 4.0$	$-1.5 \pm 0.7$	$-3.3 \pm 0.7$
S-32-C	3	$0.5350 \pm 0.0103$	$46.6 \pm 4.2$	$+0.4 \pm 0.7$	$-1.4 \pm 0.7$

Reconstructions based on the OGLS23 calibration of Daëron & Vermeesch [2024]. Temperature confidence intervals account for analytical error in  $\Delta_{47}$  but not for calibration uncertainties, which remain below  $\pm 1$  °C (95 % CL) in the range 0–50 °C.

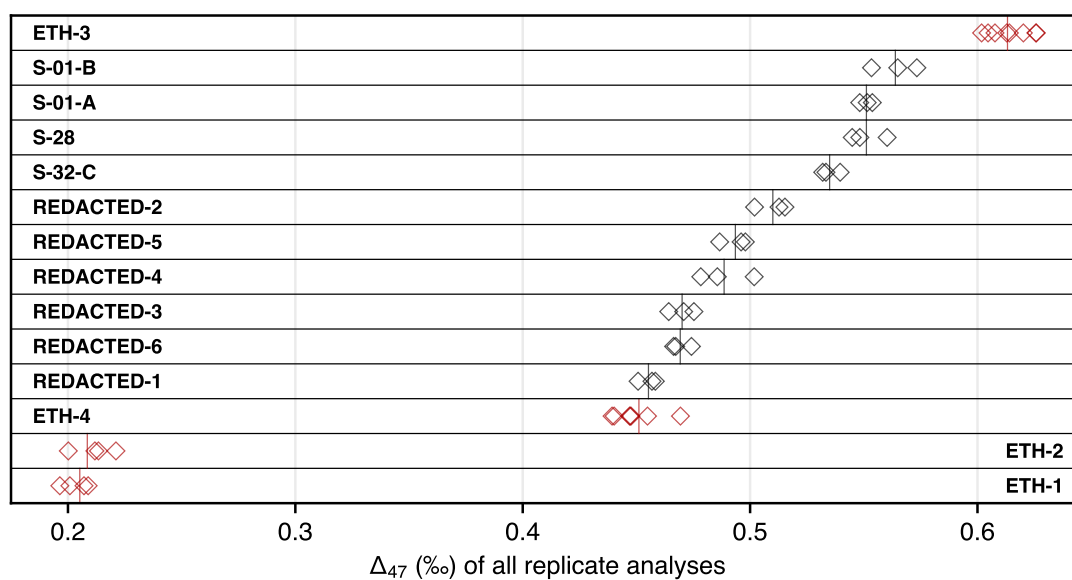
## Residuals



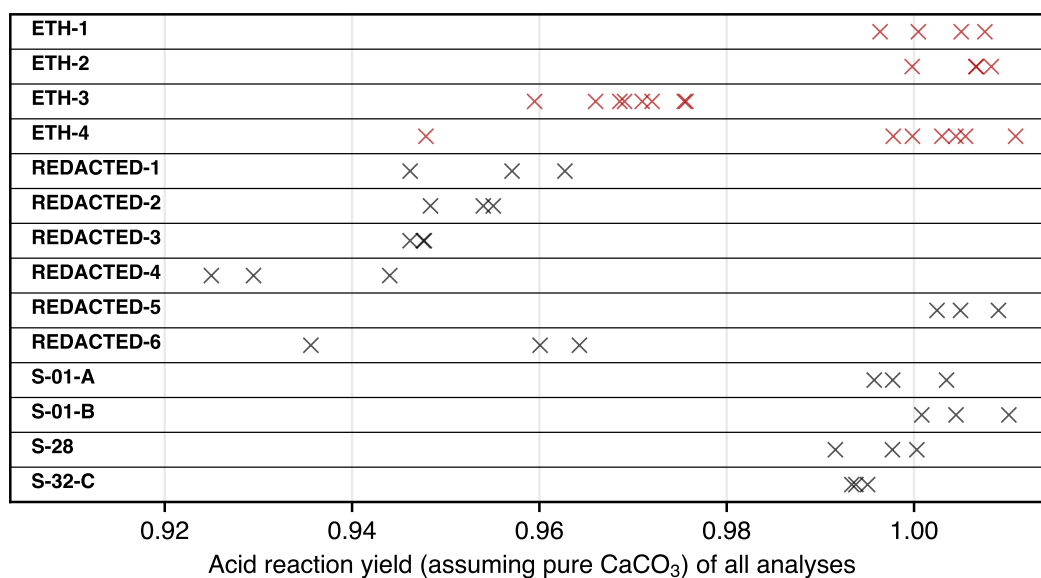
## Temporal distribution of analyses



## Distribution of $\Delta_{47}$ results



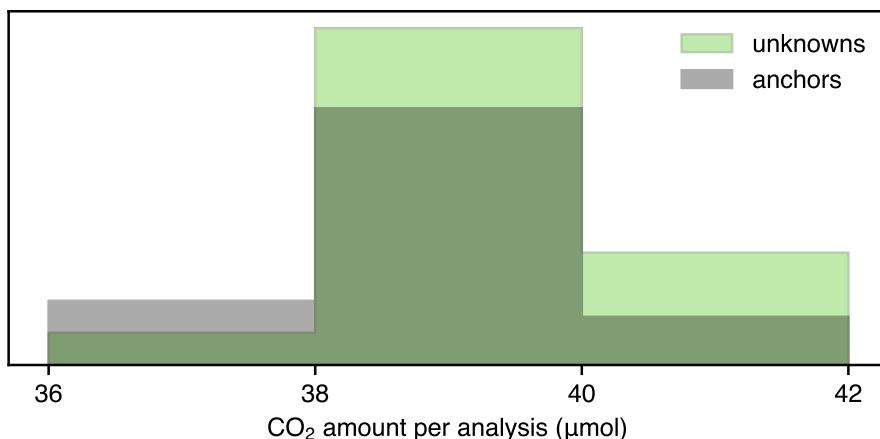
## CO<sub>2</sub> yields



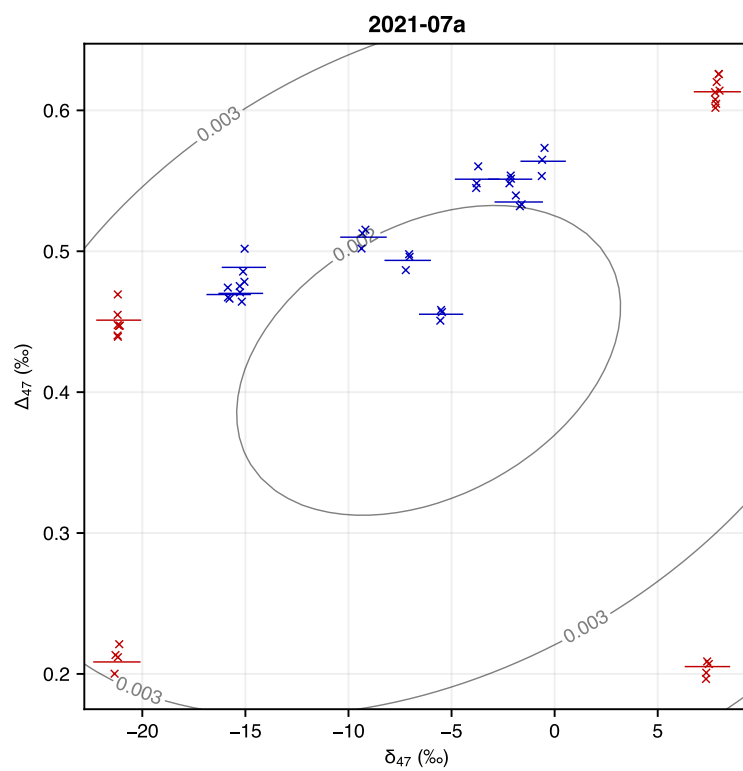
## Methods

Carbonate samples were converted to CO<sub>2</sub> 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/cm<sup>3</sup>) and each batch of acid was used for 7 days. After cryogenic removal of water, the evolved CO<sub>2</sub> was helium-flushed at 25 mL/min 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 recollectd by cryogenic trapping and transferred into an Isoprime 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 ion beam 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 within ±6 hours of any given analysis were used to determine a mass-specific relationship for that analysis, linking electrical background ( $Z_m$ ), total m/z = 44 amperage ( $I_{44}$ ), and time ( $t$ ):  $Z_m = a \cdot I_{44} + P(t)$ , with  $P$  being a polynomial of degree 2 to 4. Background-corrected ion current ratios ( $\delta_{45}$  to  $\delta_{49}$ ) were converted to  $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ , and “raw”  $\Delta_{47}$  values as described by *Daëron et al.* [2016] using the IUPAC oxygen-17 correction parameters [Brand et al., 2010]. The isotopic composition ( $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ ) of our working reference gas was computed based on the nominal isotopic composition of all ETH carbonate standards [Bernasconi et al., 2018] and an oxygen-18 acid fractionation factor of 1.00813 [Kim et al., 2007a]. Raw  $\Delta_{47}$  values were then converted to the I-CDES reference frame [Bernasconi et al., 2021] using a pooled regression approach [Daëron, 2021] as implemented by the *D47crunch* Python library (v2.4.1). Full analytical errors are derived from the external reproducibility of unknowns and standards ( $N_f = 40$ ) and conservatively account for the uncertainties in raw  $\Delta_{47}$  measurements as well as those associated with the conversion to the I-CDES reference frame [Daëron, 2021].

### Amount of CO<sub>2</sub> per analytical replicate



### Session plots



# Replicate-level data

UID	Session	Sample	Mass (mg)	CO <sub>2</sub> yield (if CaCO <sub>3</sub> )	δ45 (‰ WG)	δ46 (‰ WG)	δ47 (‰ WG)	δ48 (‰ WG)	δ49 (‰ WG)	δ <sup>13</sup> C <sub>V_PDB</sub> (‰)	δ <sup>18</sup> O <sub>VSMOW</sub> (‰)	Δ <sub>47</sub> <sup>raw</sup> (‰)	Δ <sub>47</sub> <sup>abs</sup> (‰)
I161	2021-07a	ETH-1	3.84	1.01	5.599739	2.510782	7.478248	4.580221	0.118210	2.040	36.986	-0.775748	0.207045
I162	2021-07a	ETH-3	3.83	0.97	5.316907	2.931577	7.998746	5.561845	0.604954	1.722	37.457	-0.381883	0.614028
I163	2021-07a	ETH-2	3.83	1.01	-6.390494	-14.108205	-21.119487	-28.476767	-0.527404	-10.149	19.900	-0.762020	0.221099
I164	2021-07a	ETH-3	3.83	0.97	5.313179	2.885237	7.960485	5.388564	0.342314	1.720	37.452	-0.370591	0.625696
I165	2021-07a	ETH-4	3.81	1.01	-6.447878	-14.236971	-21.089122	-28.623074	-0.301308	-10.206	19.798	-0.543142	0.447265
I166	2021-07a	ETH-3	3.87	0.98	5.305963	2.893625	7.961466	5.490234	-0.639908	1.712	37.485	-0.370436	0.625856
I167	2021-07a	ETH-2	3.78	1.01	-6.394490	-14.161336	-21.184187	-28.641158	-0.644265	-10.152	19.897	-0.770978	0.211841
I168	2021-07a	ETH-1	3.92	1.01	5.593562	2.434428	7.398212	4.533522	-0.047906	2.036	37.026	-0.773972	0.208880
I169	2021-07a	S-01-A	3.86	1.00	0.050785	-1.760507	-2.120118	-3.899950	-0.353061	-3.729	32.709	-0.442358	0.551492
I170	2021-07a	S-01-B	3.97	1.00	1.258531	-1.389821	-0.490861	-3.110836	-0.835399	-2.452	33.095	-0.421225	0.573336
I171	2021-07a	ETH-4	4.01	1.00	-6.456911	-14.268441	-21.129277	-28.814628	-0.942148	-10.214	19.808	-0.543396	0.447002
I172	2021-07a	S-28	3.80	1.00	-1.092926	-2.186951	-3.707688	-4.738599	-0.934256	-4.935	32.286	-0.433856	0.560270
I173	2021-07a	S-32-C	3.97	0.99	0.206821	-1.463564	-1.686513	-3.364500	-0.667195	-3.573	33.035	-0.461288	0.531934
I174	2021-07a	ETH-3	3.91	0.97	5.290099	2.813373	7.860216	5.364057	-0.451237	1.698	37.444	-0.375931	0.620178
I175	2021-07a	REDACTED-1	3.99	0.96	-0.220627	-4.790399	-5.467650	-9.931931	-0.439244	-3.906	29.602	-0.533948	0.456837
I176	2021-07a	REDACTED-2	4.08	0.95	-0.200570	-8.790969	-9.324255	-18.024572	-0.835256	-3.736	25.471	-0.479854	0.512714
I177	2021-07a	ETH-2	3.83	1.00	-6.434001	-14.241240	-21.300867	-28.873506	-1.148261	-10.191	19.856	-0.769476	0.213393
I178	2021-07a	REDACTED-3	3.88	0.95	-8.134263	-6.520465	-15.261625	-13.448391	-1.496466	-12.295	27.841	-0.520402	0.470789
I179	2021-07a	REDACTED-4	3.95	0.94	-9.764200	-4.664300	-15.112028	-9.651459	-0.764370	-14.105	29.765	-0.506075	0.485594
I180	2021-07a	ETH-1	4.00	1.00	5.587815	2.404864	7.355227	4.325611	0.082732	2.031	37.036	-0.781744	0.200850
I181	2021-07a	REDACTED-5	3.96	1.00	-0.952566	-5.661088	-7.035906	-11.648930	-0.331494	-4.656	28.718	-0.495997	0.496045
I182	2021-07a	REDACTED-6	4.25	0.96	-4.176191	-11.257010	-15.844650	-22.877153	-0.657672	-7.890	22.944	-0.523794	0.467281
I183	2021-07a	ETH-4	4.04	1.00	-6.468215	-14.333950	-21.197256	-28.929424	-0.884809	-10.224	19.771	-0.535772	0.454879
I184	2021-07a	ETH-3	3.97	0.97	5.278662	2.768970	7.792333	5.255769	-0.427032	1.687	37.419	-0.388012	0.607694
I185	2021-07a	S-32-C	3.94	0.99	0.032775	-1.485757	-1.880135	-3.382197	-0.249570	-3.758	33.037	-0.453861	0.539607
I186	2021-07a	S-28	3.89	0.99	-1.109222	-2.232795	-3.781036	-4.874435	-1.138154	-4.950	32.270	-0.445473	0.548266
I187	2021-07a	ETH-4	3.86	1.00	-6.465048	-14.343047	-21.189191	-29.028473	-1.007875	-10.220	19.768	-0.521755	0.469363
I188	2021-07a	S-01-B	3.80	1.00	1.224775	-1.466209	-0.608925	-3.295276	-0.140037	-2.486	33.058	-0.429359	0.564931
I189	2021-07a	S-01-A	3.84	1.00	0.082821	-1.808028	-2.131659	-3.969617	-1.046367	-3.693	32.709	-0.440172	0.553751
I190	2021-07a	ETH-3	3.97	0.96	5.285000	2.774471	7.798585	5.293822	-0.526604	1.694	37.434	-0.393703	0.601814
I193	2021-07a	ETH-4	3.88	1.00	-6.466889	-14.322346	-21.191443	-29.044582	-1.037867	-10.223	19.798	-0.542780	0.447638
I194	2021-07a	REDACTED-4	4.34	0.93	-9.783090	-4.582898	-15.036791	-9.498464	-0.529675	-14.128	29.869	-0.490394	0.501797
I195	2021-07a	REDACTED-3	4.17	0.95	-8.120589	-6.552190	-15.274243	-13.475958	-0.922828	-12.279	27.832	-0.516048	0.475288
I196	2021-07a	ETH-3	3.97	0.97	5.275525	2.759584	7.784847	5.300708	-0.791934	1.684	37.424	-0.383018	0.612854
I197	2021-07a	REDACTED-2	4.22	0.95	-0.229424	-8.615081	-9.178415	-17.625322	-0.818990	-3.773	25.683	-0.477332	0.515322
I198	2021-07a	REDACTED-1	4.11	0.96	-0.210698	-4.843330	-5.508036	-10.105720	-0.146234	-3.894	29.581	-0.532512	0.458320
I199	2021-07a	ETH-4	3.97	1.01	-6.464566	-14.327092	-21.200765	-29.098328	-0.851472	-10.220	19.796	-0.549979	0.440199
I200	2021-07a	S-01-A	3.90	1.00	0.063463	-1.844424	-2.192709	-4.062893	-0.895714	-3.712	32.681	-0.445534	0.548211
I201	2021-07a	S-01-B	3.92	1.01	1.229424	-1.474604	-0.623570	-3.313809	-0.322691	-2.480	33.061	-0.440534	0.553384
I202	2021-07a	S-28	3.82	1.00	-1.092829	-2.273487	-3.807348	-4.862846	-0.183308	-4.931	32.242	-0.448720	0.544911
I203	2021-07a	S-32-C	4.05	1.00	0.295566	-1.470543	-1.600607	-3.277047	-0.391728	-3.478	33.070	-0.459909	0.533359
I204	2021-07a	ETH-3	4.04	0.98	5.293136	2.800089	7.835075	5.407427	-0.988990	1.702	37.471	-0.390963	0.604645
I205	2021-07a	REDACTED-5	4.03	1.00	-0.947344	-5.691297	-7.058420	-11.956637	-1.153892	-4.649	28.711	-0.494193	0.497908
I206	2021-07a	REDACTED-6	4.14	0.94	-4.140683	-11.214695	-15.767923	-22.912035	-0.986916	-7.854	23.012	-0.524696	0.466350
I207	2021-07a	REDACTED-3	4.14	0.95	-8.078932	-6.482037	-15.173768	-13.469197	-0.826435	-12.237	27.912	-0.526766	0.464213
I208	2021-07a	ETH-4	4.08	0.95	-6.466457	-14.308039	-21.184938	-28.996542	-1.330998	-10.223	19.822	-0.550849	0.439301
I209	2021-07a	REDACTED-4	4.27	0.92	-9.676372	-4.682512	-15.046534	-9.878680	-0.890528	-14.010	29.777	-0.513122	0.478312
I210	2021-07a	REDACTED-5	3.98	1.01	-1.005459	-5.782947	-7.218844	-12.075688	-1.025506	-4.708	28.620	-0.505125	0.486612
I211	2021-07a	REDACTED-6	4.07	0.96	-4.165875	-11.282699	-15.852678	-23.013937	-1.523564	-7.878	22.945	-0.517099	0.474200
I212	2021-07a	REDACTED-1	4.03	0.95	-0.239286	-4.842965	-5.544318	-10.271176	-1.018358	-3.924	29.591	-0.539852	0.450736
I213	2021-07a	REDACTED-2	4.23	0.96	-0.082368	-8.946703	-9.366805	-18.352647	-1.046793	-3.604	25.350	-0.490268	0.501953
I214	2021-07a	ETH-1	3.96	1.00	5.587485	2.397341	7.343138	4.326362	-0.692786	2.031	37.060	-0.786024	0.196427
I215	2021-07a	ETH-2	3.80	1.01	-6.431239	-14.277420	-21.345922	-29.173095	-1.827011	-10.186	19.857	-0.782288	0.200155

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