

Supplement information for:

A Digestion-purging-trapping Method for Precise Stable Mercury Isotope Measurements of Natural Carbonates

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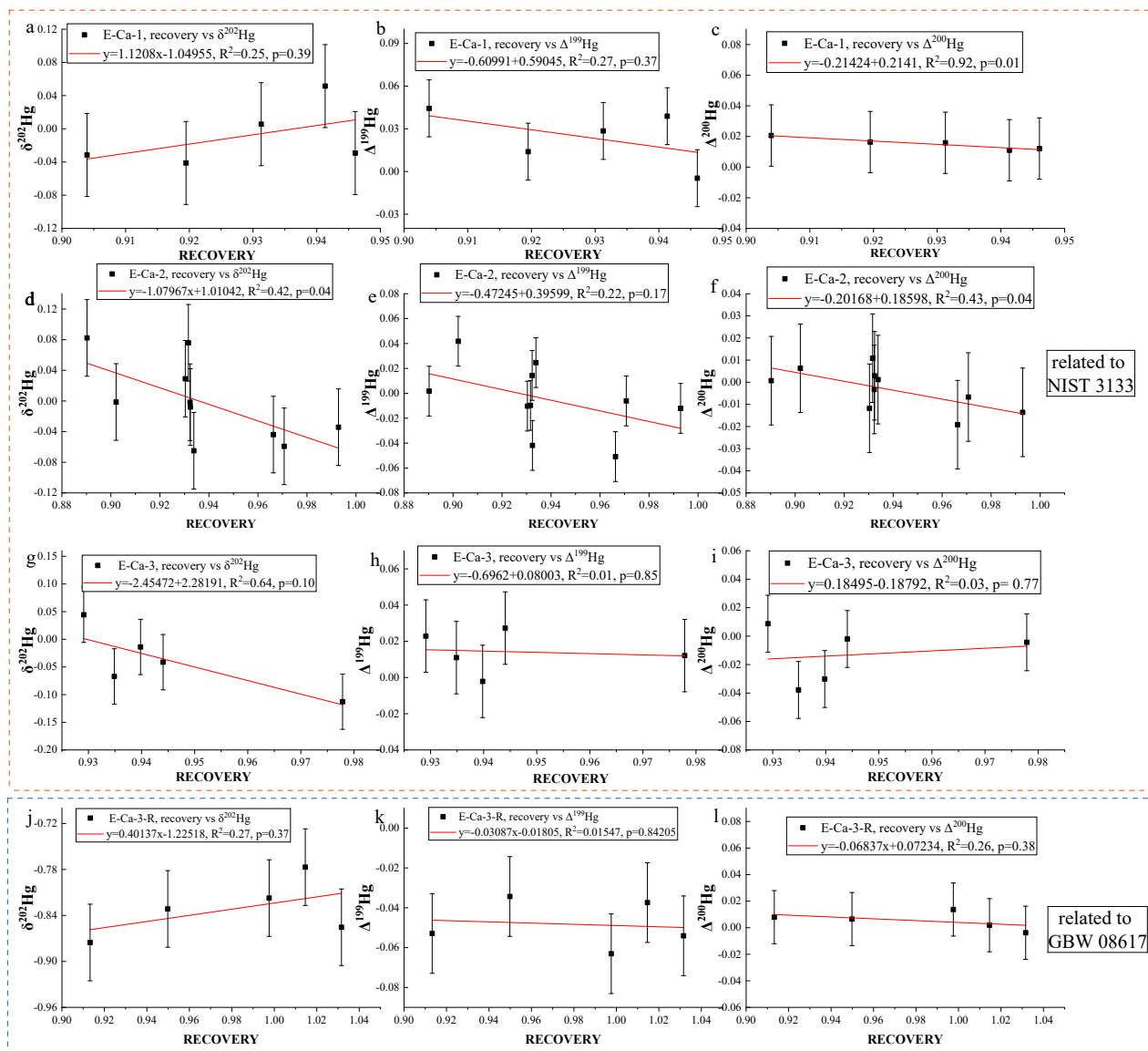


Figure SI-1 Linear regression between $\delta^{202}\text{Hg}$, $\Delta^{199}\text{Hg}$ and $\Delta^{200}\text{Hg}$ and Hg recovery of synthetic samples.

Table S1 Results of the recovery and isotope ratio of 24 natural carbonate samples, .

sample	Hg_Conc. ng g ⁻¹	Recovery %	$\delta^{202}\text{Hg}$ ‰	1SD	$\Delta^{199}\text{Hg}$ ‰	1SD	$\Delta^{200}\text{Hg}$ ‰	1SD	$\Delta^{201}\text{Hg}$ ‰	1SD	$\Delta^{204}\text{Hg}$ ‰	1SD
Coral subsamples												
coral-1-I	1.07	98%	-2.44	0.04	0.02	0.02	0.04	0.02	-0.04	0.03	0.01	0.06
coral-1-II	1.07	100%	-2.38	0.04	0.01	0.02	0.02	0.02	0.01	0.03	-0.05	0.06
coral-2-I	12.1	94%	-2.60	0.04	0.07	0.02	0.02	0.02	0.06	0.03	0.02	0.06
coral-2-II	12.1	99%	—	—	—	—	—	—	—	—	—	—
coral-2-III	12.1	109%	—	—	—	—	—	—	—	—	—	—
coral-3-I	1.72	92%	-2.83	0.04	0.06	0.02	0.02	0.02	0.03	0.03	0.00	0.06
coral-3-II	1.72	106%	-2.87	0.04	0.01	0.02	0.01	0.02	0.04	0.03	0.04	0.06
coral-3-III	1.72	91%	-2.77	0.04	-0.01	0.02	-0.01	0.02	0.00	0.03	0.03	0.06
coral-3-IV	1.72	109%	—	—	—	—	—	—	—	—	—	—
coral-4-I	3.44	103%	—	—	—	—	—	—	—	—	—	—
coal-DL-a ~ h subsamples are divided according to average growth rate after removing the outermost layer.												
coral-DL-a	0.57	104%	-2.12	0.04	0.04	0.02	0.05	0.02	-0.07	0.03	-0.17	0.06
coral-DL-b	0.25	98%	—	—	—	—	—	—	—	—	—	—
coral-DL-c	0.26	—	—	—	—	—	—	—	—	—	—	—
coral-DL-d	0.44	—	—	—	—	—	—	—	—	—	—	—
coral-DL-e	0.36	108%	-2.65	0.04	-0.07	0.02	0.00	0.02	-0.07	0.03	0.03	0.06
coral-DL-f	0.67	91%	-2.02	0.04	0.10	0.02	-0.01	0.02	-0.25	0.03	-0.48	0.06
coral-DL-g	0.73	95%	-2.15	0.04	-0.01	0.02	0.01	0.02	-0.05	0.03	-0.03	0.06
coral-DL-h	1.27	106%	-2.51	0.04	-0.03	0.02	0.00	0.02	-0.08	0.03	-0.05	0.06
Stalagmites subsamples												
SS-YS-I	8.39	103%	-1.20	0.04	-0.18	0.02	-0.02	0.02	-0.16	0.03	-0.04	0.06
SS-YS-II	8.39	99%	-1.29	0.04	-0.14	0.02	0.02	0.02	-0.23	0.03	0.03	0.06
SS-YS-III	8.39	92%	—	—	—	—	—	—	—	—	—	—
SS-YS-IV	8.39	94%	—	—	—	—	—	—	—	—	—	—
Standard reference materials												
GBW07129-I	5.00	95.96%	-1.82	0.04	-0.22	0.02	-0.04	0.02	-0.23	0.03	0.06	0.06
GBW07129-II	5.00	102.50%	-1.82	0.04	-0.22	0.02	-0.04	0.02	-0.29	0.03	0.00	0.06
GBW07129-III	5.00	104.7%	-1.95	0.04	-0.23	0.02	-0.02	0.02	-0.27	0.03	—	—
GBW07129-IV	5.00	91.4%	-1.84	0.04	-0.26	0.02	0.00	0.02	-0.26	0.03	—	—
GBW07129-V	5.00	98.3%	-1.75	0.04	-0.26	0.02	0.00	0.02	-0.25	0.03	—	—
GBW07134-I	25.9	100.0%	-1.05	0.04	0.02	0.02	0.01	0.02	-0.07	0.03	-0.11	0.06
GBW07134-II	25.9	100.1%	-1.20	0.04	-0.02	0.02	0.01	0.02	-0.04	0.03	0.00	0.06
GBW07134-III	25.9	102.0%	-1.16	0.04	0.00	0.02	-0.01	0.02	-0.10	0.03	-0.11	0.06
GBW07134-IV	25.9	102.7%	-1.25	0.04	-0.09	0.02	-0.01	0.02	-0.09	0.03	0.01	0.06

GBW07134-V	25.9	101.6%	-1.23	0.04	-0.08	0.02	-0.01	0.02	-0.11	0.03	-0.02	0.06
GBW07134-VI	25.9	98.0%	-1.15	0.04	-0.01	0.02	0.00	0.02	-0.08	0.03	—	—

Coral-1 and coral-2 are from inner and outermost sections of the same slab, respectively, with coral-1 representing the inner portion after removing the outermost layer (coral-2). Coral-3 and coral-4 are different bulk slab samples, where I~V represents the sample replicates (i.e., different aliquots of the same subsample). Coral-DL a~h consists of subsamples prepared based on annual growth rates of coral.“—” indicates that the sample concentration was too low for isotope analysis or that the analysis was unsuccessful.



Figure SI-2 coral-DL-a~h, a slab divided into 8 parts.

This figure is coral DL(a ~ h, from the bottom to upper layer). After removing non-coral skeleton and altered areas, and following the cleaning process, the remaining sample mass was insufficient to perform duplicate isotope tests. The coral-DL-b sample was even too small for a single isotope measurement.

Table S2 Summary of experiments investigating the effects of the inorganic matrix on Hg recovery and isotopic ratios in synthetic carbonate samples.

SAMPLE	Recovery %	CaCO ₃ _g	Hg ²⁺ ng g ⁻¹	Ca ²⁺ %	LAR mL	Hg/Ca ng g ⁻¹	LAR/CaCO ₃ mL g ⁻¹	Cl ⁻ mol L ⁻¹	SnCl ₂ %	Hg/Sn ng g ⁻¹	MQ _mL	Vol _mL	δ ²⁰² Hg ‰	1SD	Δ ¹⁹⁹ Hg ‰	1SD	Δ ²⁰⁰ Hg ‰	1SD	Δ ²⁰¹ Hg ‰	1SD	Δ ²⁰⁴ Hg ‰	1SD
E-Ca-1, varying the amount of LAR at fixed ratio of Hg (NIST 3133) and CaCO ₃																						
E-Ca-1-1	94.6%	5.00	0.14	0.07	10.00	2.02	2.0	0.47	0.07	10.1	60	70	-0.03	0.04	0.00	0.02	0.01	0.00	0.01	0.01	0.02	0.04
E-Ca-1-2	91.9%	5.00	0.14	0.07	15.00	2.01	3.0	0.71	0.07	10.1	55	70	-0.04	0.04	0.01	0.02	0.02	0.00	-0.01	0.01	0.00	0.04
E-Ca-1-3	93.1%	5.00	0.14	0.07	20.00	2.02	4.0	0.94	0.07	10.1	50	70	0.01	0.04	0.03	0.02	0.02	0.00	0.01	0.01	-0.04	0.04
E-Ca-1-4	90.4%	5.00	0.14	0.07	25.00	2.02	5.0	1.18	0.07	10.1	45	70	-0.03	0.04	0.04	0.02	0.02	0.00	0.00	0.01	-0.09	0.04
E-Ca-1-5	94.1%	5.00	0.14	0.07	30.00	2.02	6.0	1.41	0.07	10.1	40	70	0.05	0.04	0.04	0.02	0.01	0.00	0.01	0.01	-0.01	0.04
E-Ca-2_related to NIST 3133, varying the Hg concentrations at fixed concentrations of Ca ²⁺ and H ⁺ /Ca ²⁺																						
E-Ca-2-1	96.6%	10.02	0.08	0.15	20.00	0.50	2.0	1.02	0.08	5.0	40	65	-0.04	0.05	-0.05	0.03	-0.02	0.01	0.01	0.02	0.04	0.03
E-Ca-2-2	93.2%	10.02	0.15	0.15	20.00	0.99	2.0	1.02	0.08	9.9	40	65	0.08	0.05	-0.01	0.03	0.01	0.01	0.01	0.02	-0.08	0.03
E-Ca-2-3	93.4%	10.02	0.25	0.15	20.00	1.62	2.0	1.02	0.08	16.2	40	65	-0.06	0.05	0.02	0.03	0.00	0.01	0.02	0.02	0.01	0.03
E-Ca-2-4	97.1%	10.01	0.33	0.15	20.00	2.74	2.0	1.02	0.08	21.2	40	65	-0.06	0.05	-0.01	0.03	-0.01	0.01	-0.02	0.02	0.03	0.03
E-Ca-2-5	89.0%	10.01	0.37	0.15	20.00	2.61	2.0	1.02	0.08	23.8	40	65	0.08	0.05	0.00	0.03	0.00	0.01	0.02	0.02	0.03	0.03
E-Ca-2-6	93.2%	10.00	0.42	0.15	20.00	3.08	2.0	1.02	0.08	27.4	40	65	-0.01	0.05	-0.04	0.03	0.00	0.01	0.00	0.02	0.00	0.03
E-Ca-2-7	99.3%	10.01	0.47	0.15	20.00	3.73	2.0	1.02	0.08	30.8	40	65	-0.03	0.05	-0.01	0.03	-0.01	0.01	0.02	0.02	0.00	0.03
E-Ca-2-8	93.0%	10.01	0.58	0.15	20.00	3.82	2.0	1.02	0.08	37.4	40	65	0.03	0.05	-0.01	0.03	-0.01	0.01	-0.03	0.02	0.00	0.03
E-Ca-2-9	90.2%	10.02	0.59	0.15	20.00	4.26	2.0	1.02	0.08	38.2	40	65	0.00	0.05	0.04	0.03	0.01	0.01	-0.01	0.02	-0.01	0.03
E-Ca-2-10	93.2%	10.02	0.66	0.15	20.00	1.61	2.0	1.02	0.08	42.7	40	65	0.00	0.05	0.01	0.03	0.00	0.01	0.04	0.02	-0.02	0.03
E-Ca-3_related to NIST 3133, varying the Ca concentrations at fixed concentrations of Hg ²⁺ and H ⁺ /Ca ²⁺																						
E-Ca-3-1	94.0%	5.02	0.13	0.06	5.00	1.99	1.0	0.21	0.06	10.0	75	80	-0.01	0.06	0.00	0.01	-0.03	0.02	-0.01	0.02	-0.05	0.02
E-Ca-3-2	97.8%	10.01	0.13	0.13	10.00	1.00	1.0	0.41	0.06	10.0	70	80	-0.11	0.06	0.01	0.01	0.00	0.02	0.00	0.02	-0.01	0.02
E-Ca-3-3	94.4%	15.01	0.12	0.19	15.00	0.66	1.0	0.62	0.06	10.0	65	80	-0.04	0.06	0.03	0.01	0.00	0.02	-0.03	0.02	0.01	0.02

E-Ca-3-4	93.5%	20.00	0.13	0.25	20.00	0.50	1.0	0.83	0.06	10.0	60	80	-0.07	0.06	0.01	0.01	-0.04	0.02	0.00	0.02	0.01	0.02
E-Ca-3-5	92.9%	25.01	0.12	0.31	25.00	0.40	1.0	1.03	0.06	10.0	55	80	0.04	0.06	0.02	0.01	0.01	0.02	-0.05	0.02	-0.02	0.02
E-Ca-3-R_ replicate of E-Ca-3_ related to GBW 08617, varying the Ca concentrations at fixed concentrations of Hg²⁺ and H⁺/Ca²⁺																						
E-Ca-3-R-1	101.5%	5.02	0.12	0.06	5.00	1.85	1.0	0.21	0.06	9.3	75	80	-0.78	0.04	-0.04	0.01	0.00	0.01	-0.07	0.03	-0.08	0.04
E-Ca-3-R-2	103.2%	10.01	0.11	0.13	10.00	0.92	1.0	0.41	0.06	9.2	70	80	-0.86	0.04	-0.05	0.01	0.00	0.01	-0.07	0.03	-0.04	0.04
E-Ca-3-R-3	99.8%	15.01	0.12	0.19	15.00	0.62	1.0	0.62	0.06	9.3	65	80	-0.82	0.04	-0.06	0.01	0.01	0.01	-0.04	0.03	-0.01	0.04
E-Ca-3-R-4	95.0%	20.00	0.12	0.25	20.00	0.46	1.0	0.83	0.06	9.2	60	80	-0.83	0.04	-0.03	0.01	0.01	0.01	-0.08	0.03	-0.04	0.04
E-Ca-3-R-5	91.3%	25.01	0.1	0.3	25.0	0.4	1.0	1.0	0.1	9.2	55	80	-0.88	0.04	-0.05	0.01	0.01	0.01	-0.01	0.03	0.04	0.04
E-Ca-4_ related to NIST 3133, varying the amount of diluted MQ used to reduce																						
E-Ca-4-1	93.2%	10.02	9.91	0.15	20.00	0.99	2.0	1.02	0.08	9.9	60	65	0.08	0.05	-0.01	0.01	0.01	0.02	0.01	0.01	-0.08	0.07
E-Ca-4-2	94.6%	5.00	10.12	0.07	10.00	2.02	2.0	0.47	0.07	10.1	40	70	-0.03	0.05	0.00	0.01	0.01	0.02	0.01	0.01	0.02	0.07
E-Ca-4-3	92.3%	10.02	11.12	0.13	20.00	1.11	2.0	0.88	0.07	11.1	50	75										
E-Ca-4-4	102.5%	15.00	11.05	0.14	30.00	0.74	2.0	0.90	0.05	11.0	75	110	0.01	0.05	0.02	0.01	-0.02	0.02	0.00	0.01	0.05	0.07
E-Ca-4-5	94.8%	20.00	10.9	0.1	40.0	0.5	2.0	0.9	0.0	10.9	100	145										
Calcined coral_ related to NIST 3133, used for initial method validation																						
Calcined coral	96.0%	10.02			20.0		2.0				40	65	-0.02	0.04	-0.02	0.02	-0.02	0.02	-0.03	0.02		

Table S3 Results for linear relative contribution analysis of recovery and isotope ratio in simulated samples.

Factors	Recovery*		$\delta^{202}\text{Hg}^*$	
	relative contribution %	p-value	relative contribution %	p-value
H^+	2.31	0.22	10.09	0.040
Ca^{2+} _%	1.86	0.33	5.72	0.18
H^+/Ca _%	1.39	0.51	2.78	0.28
MQ_mL	0.15	0.43	2.24	0.35
Vol_mL	0.38	0.56	1.31	0.46
Hg^{2+} _ng/g	0.40	0.56	1.23	0.34
Hg/Ca _ng/g	2.56	0.94	0.31	0.61
Cl^- _mol/L	3.11	0.96	0.48	0.66
SnCl_2 _%	5.30	0.98	3.95	0.90
Hg/Sn _ng g ⁻¹	5.53	0.95	5.20	0.93

* In this study, a linear model was conducted using “rfPermute” package in R v.4.3.2 to explore the relative influence of inorganic component of DPT system on samples recovery and $\delta^{202}\text{Hg}$. Briefly, this model is aimed to analyze relative contribution and correlation of 10 variables of purging directly from digestion solution.

Table S4 Results of the loss of organic components analysis for corals. Coral-1 represents low organic coral and coral-2 represents high organic coral.

sample	weight		Loss of organic*	ratio	Hg_Con c._ng g ⁻¹
	initial weight_g	after ignition_g			
coral-1	0.1128	0.1075	0.0053	4.699%	1.072
coral-2	0.11	0.1034	0.0066	6.000%	12.07

* In this study, we conducted three rounds of combustion in DMA-80 under an oxygen flow, with the temperature set as 650°C, each lasting 15 mins, to estimate organic components in coral.

Table S5 Results of cumulative recovery for different types of carbonate samples.

calcined coral					Hg_ng		Hg_ng		cumulative Hg_ng	cumulative Recovery_%	cumulative purge time_min
LAR	LAR/Ca	MQ	Vol	Added	Hg/Ca	Trapped					
11.02	30	2.72	60	95	32.99	3.0	30.5		30.5	92.3%	10
11.02	30	2.72	60	95		3.0	0.71		31.2	94.5%	20
11.02	30	2.7	60	95		3.0	0.40		31.6	95.7%	30
11.02	30	2.72	60	95		3.0	0.34		31.9	96.7%	40
11.02	30	2.72	60	95		3.0	0.24		32.2	97.5%	50

11.02	30	2.72	60	95		3.0	0.20	32.4	98.1%	60
calcined CaCO3										
10.02	30	2.99	60	95	32.89	3.3	32.3	32.3	98.1%	10
10.02	30	2.99	60	95		3.3	0.51	32.8	99.6%	20
10.02	30	2.99	60	95		3.3	0.18	32.9	100.2%	30
10.02	30	2.99	60	95		3.3	0.11	33.1	100.5%	40
10.02	30	2.99	60	95		3.3	0.14	33.2	100.9%	50
10.02	30	2.99	60	95		3.3	0.08	33.3	101.2%	60
High organic coral_coral-2										
10.02	30	2.99	60	95	32.68	3.3	0.79	0.79	2.4%	10
10.02	30	2.99	60	95		3.3	0.50	1.29	3.9%	20
10.02	30	2.99	60	95		3.3	0.09	1.37	4.2%	30
10.02	30	2.99	60	95		3.3	0.08	1.46	4.5%	40
10.02	30	2.99	60	95		3.3	0.11	1.57	4.8%	50
10.02	30	2.99	60	95		3.3	0.12	1.69	5.2%	60
Low organic coral_coral-1										
10.01	30	3.00	60	95	32.78	3.3	7.43	7.43	22.7%	10
10.01	30	3.00	60	95		3.3	0.22	7.65	23.4%	20
10.01	30	3.00	60	95		3.3	0.13	7.78	23.8%	30
10.01	30	3.00	60	95		3.3	0.14	7.92	24.2%	40
10.01	30	3.00	60	95		3.3	0.23	8.15	24.9%	50
10.01	30	3.00	60	95		3.3	0.19	8.34	25.5%	60