GSA Data Repository 2017014

Supporting Information

Late Permian Extinction (LPE) samples from Meishan (China) and Buchanan Lake (Canada)

DR1. Total Hg concentration measurements

Meishan samples were analyzed for THg at the USGS-Wisconsin Mercury Research Laboratory using a direct combustion system (Nippon MA-2) and atomic absorbance detection (U.S. EPA Method 7473 SW-846). Recoveries for standard reference material (IAEA SL 1) were between 93 and 114%, and coefficients of variation (triplicate analyses) were less than 6%. Total mercury concentrations (THg) for Buchanan Lake samples were previously reported in Sanei et al. (2012), and replicated at University of Michigan using combustion/thermal decomposition and CV-AAS analysis (see below). THg concentrations of our measured samples are summarized in Table DR1.

DR2. Hg isotopic composition measurements

Buchanan Lake LPE section. Hg isotopic analyses of Permo-Triassic shales from Buchanan Lake (Axel Heiberg, Arctic Canada) were carried out at the University of Michigan using methods previously described in detail (Biswas et al., 2008; Lefticariu et al., 2011). Briefly, ~1 g of completely homogenized shale sample was placed in a two-stage combustion furnace equipped with quartz furnace tubes, and the temperature gradually increased to a maximum temperature of 750 °C over 6 hours. Hg(0) vapor was transported in a stream of Hg-clean O_2 through a second furnace held at 1,000 °C, and the gas stream was then bubbled into a solution of 1% $KMnO_4$, where Hg(0) was oxidized and retained as Hg(II). Following combustion, 1% $KMnO_4$ solutions were neutralized and reduced with NH_2OH and $SnCl_2$, and Hg(0) was sparged with Hg-clean air into a smaller volume of 1% $KMnO_4$ solution to accomplish a complete separation of Hg from the other combustion products. These $KMnO_4$ solutions were neutralized with NH_2OH, and Hg concentrations determined using a Nippon Instruments MA-2000 amalgamation–atomic absorption spectrometer to determine Hg separation yields. Replicate combustions of MESS-3 standard reference material (91 ng/g Hg, NRC, Canada) were carried out along with procedural blanks. For the MESS-3 Hg, combustion yields for total Hg averaged 97.4%, trap-to-trap transfer yields averaged 95.1%, and total Hg yields (combustion + trap-to-trap transfer) were > 90% (average 92.7%). Total process blanks were < 1 ng Hg, accounting for < 1% of total Hg processed per sample.

Hg isotopic compositions were determined at the University of Michigan on a Nu Instruments multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) using a continuous flow cold vapor introduction system. $KMnO_4$ sample solutions were diluted, using identical matrix, to 5 ng g^{-1}, and NIST SRM 3133 Hg isotope standard was prepared to match matrix and Hg concentrations. $KMnO_4$ run solutions were pre-neutralized with NH_2OH and then further reduced by $SnCl_2$ online. Reduced Hg(0) was separated from solution using an online gas-liquid phase separator and introduced to the MC-ICP-MS in a stream of Ar gas. Instrumental mass bias was corrected using both NIST SRM 997 Tl internal standard added as a dry aerosol to the gas stream, and sample-standard bracketing using NIST 3133. On-peak zero corrections were applied to all analyses. Replicate measurements of the UM-Almadén Hg intra-lab isotope reference standard (n = 4 analytical sessions) were as follows: δ^{202}Hg = -0.57 ± 0.08‰ (2sd); Δ^{199}Hg = -0.03 ± 0.02‰ (2sd); Δ^{200}Hg = 0.01 ± 0.04‰ (2sd); Δ^{201}Hg = -0.03 ± 0.02‰ (2sd).

Meishan LPE section. Hg isotopic analyses of samples from Meishan were measured at the Wisconsin State Laboratory of Hygiene (WSLH) using methods previously described in detail (Lepak et al., 2015; Yin et al., 2016). Specifically, about 0.5 g of ground sample was digested (95 °C, 1 hour) in a 5 mL aqua regia ($HCl:HNO_3$ = 3:1, v:v). Certified reference materials (NIST SRM 2711 Montana soil II and MESS-1 estuary sediment) were similarly prepared in 10% of the sample count. The digest solutions of samples were diluted to 0.3, 0.5 and 1 ng mL^{-1} based on THg values measured in Table S1. All sample solutions have acid concentrations of < 20% (v/v). Duplicate UM-Almadén secondary solutions were prepared into 0.3, 0.5 and 1.0 ng mL^{-1} Hg using 10% (v/v) aqua regia solutions. The bracketing NIST SRM 3133 Hg standard solutions with Hg concentrations of 0.3, 0.5 and 1 ng mL^{-1}, were also prepared in 10% (v/v) aqua regia.

Isotopic compositions were measured by the Neptune Plus MC-ICP-MS at Wisconsin with the high sensitivity X skimmer cone. NIST SRM 997 Tl standard was used as an internal standard for simultaneous instrumental mass bias correction of Hg. The instrument was equipped with a gas-liquid phase separator and an Apex-Q desolvation unit (Elemental Scientific Inc., USA) for Hg and thallium (Tl) introduction, respectively. Briefly, stannous chloride ($SnCl_2$) was continually pumped along with Hg solutions onto a frosted glass phase separator, producing gaseous elemental Hg(0) which was mixed with the dry Tl aerosol generated by the Apex-Q nebulizer, before being introduced into the plasma. The concentrations of Hg and acid matrices in the bracketing NIST SRM 3133 solutions were matched with neighbour samples. THg in sample digests was monitored by MC-ICP-MS using ^{202}Hg signals as shown in Table S1. The signals for ^{202}Hg were <0.011 V for acid blanks. The sensitivity for ^{202}Hg during Hg isotope analysis was ~1.3 V per ng mL^{-1} Hg. The THg values estimated by ^{202}Hg signals were 90 to 118% to that measured in Section S1.

DR3. Reporting of Hg isotope data

Hg isotopic composition is expressed in δ^{202}Hg notation in units of permil (‰) referenced to the NIST-3133 Hg standard (analyzed before and after each sample):

$$\delta^{202}\mathrm{Hg}(‰)= [(^{202}\mathrm{Hg}/^{198}\mathrm{Hg}_{sample})/(^{202}\mathrm{Hg}/^{198}\mathrm{Hg}_{standard}) -1]\times 1000 \qquad (1)$$

Mass independent fractionation of Hg isotopes is reported in Δ notation (Δ^{xxx}Hg), and it describes difference between the measured δ^{xxx}Hg and the theoretically predicted δ^{xxx}Hg value, in units of permil (‰), using the following formula:

$$\Delta^{xxx}\mathrm{Hg} \approx \delta^{xxx}\mathrm{Hg} - \delta^{202}\mathrm{Hg}\times\beta \qquad (2)$$

β is equal to 0.2520 for ^{199}Hg, 0.5024 for ^{200}Hg, and 0.7520 for ^{201}Hg (Blum and Bergquist, 2007).

Analytical uncertainty at both Wisconsin and Michigan was estimated based on replication of the UM-Almadén standard solution, and full procedural analyses of standard reference materials (MESS-3, MESS-1 and NIST SRM 2711). As shown in Table S2, our results agree well with previous studies (Blum and Bergquist, 2007; Biswas et al., 2008; Lefticariu et al., 2011; Donovan et al., 2013;Yin et al., 2014; Lepak et al., 2015).

References

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TableDR1. Hg concentrations and Hg isotopic composition for samples. For Buchanan Lake additional data from Sanei et al. 2012 are provided for Hg concentration and total organic carbon (TOC). These data are plotted in Figure 2 and were used to select a representative subset of samples for Hg isotope analyses in this study.

Sample No.	THg*	Formation	Depth rel. to LPE	Total Hg**	δ^{202}Hg	Δ^{199}Hg	Δ^{200}Hg	Δ^{201}Hg	TOC	Hg/TOC
	ng g^{-1}	Name	cm	ng g^{-1}	‰	‰	‰	‰	%	ng/g/%
Meishan										
MSC30-1	26	Yinkeng	58.2	28.3	-0.58	0.03	0.03	-0.04	0.49	0.58
MSC29	27	Yinkeng	39	27.3	-1.07	-0.02	-0.06	0.01	0.86	0.32
MSC28	65	Yinkeng	26.2	60.1	-1.47	-0.03	0.01	-0.07	-	-
MSC27cd	22	Yinkeng	20.7	20.6	-1.10	-0.07	0.07	-0.06	0.14	1.47
MSC27ab	20	Yinkeng	13.7	19.4	-0.93	-0.08	-0.03	-0.07	0.16	1.21
MSC26e	114	Yinkeng	8.7	103.2	-1.14	-0.04	0.01	-0.08	0.56	1.84
MSC26d	135	Yinkeng	7.1	139	-1.55	-0.05	0.02	-0.08	0.94	1.48
MSC26c	142	Yinkeng	5.9	129.4	-1.54	-0.12	0.02	-0.14	1.16	1.12
MSC26b	146	Yinkeng	4.9	140.4	-1.36	-0.05	0.04	-0.10	0.81	1.73
MSC26a	155	Yinkeng	3.4	156.8	-1.29	-0.04	0.02	-0.02	0.82	1.91
MSC25g	125	Yinkeng	2.9	115.2	-1.41	-0.03	0.02	-0.03	0.82	1.40
MSC25f	78	Yinkeng	2.1	71.7	-1.72	0.02	0.02	0.02	0.54	1.33
MSC25de	64	Yinkeng	0.9	61.4	-2.08	-0.03	-0.04	-0.03	0.34	1.81
MSC25bc	84	Yinkeng	0.3	75.5	-1.73	-0.01	0.00	-0.04	0.18	4.19
MSC25a	61	Yinkeng	0	59.5	-1.95	0.12	0.05	0.08	0.09	6.61
MSC24fo	190	Changxing	-0.8	176	-1.67	0.09	0.01	0.02	0.19	9.26
MSC24ec	24	Changxing	-5.8	27.5	-1.34	0.09	0.06	0.05	0.97	0.28
MSC24ea	13	Changxing	-9.8	15.3	-1.14	0.03	0.02	0.05	0.44	0.35
MSC24d	54	Changxing	-40.9	61.5	-0.65	0.09	0.04	0.08	0.56	1.10

Sample No.	THg*	Formation	Depth rel. to LPE	Total Hg**	$\delta^{202}Hg$	$\Delta^{199}Hg$	$\Delta^{200}Hg$	$\Delta^{201}Hg$	TOC	Hg/TOC
	ng g^{-1}	Name	metres	ng g^{-1}	‰	‰	‰	‰	%	ng/g/%
Buchanan Lake										
C-445076	174	Blind Fiord	34.8	166	-0.83	0.12	0.03	0.09	-	-
C-445074	63	Blind Fiord	33.8	-	-	-	-	-	0.30	210
C-445071	23	Blind Fiord	32.3	-	-	-	-	-	0.15	153
C-445066	180	Blind Fiord	29.8	-	-	-	-	-	0.44	409
C-445062	83	Blind Fiord	27.8	-	-	-	-	-	-	-
C-445059	125	Blind Fiord	26.3	-	-	-	-	-	0.40	313
C-445057	183	Blind Fiord	25.3	-	-	-	-	-	0.52	352
C-445055	149	Blind Fiord	24.3	133	-0.96	0.08	0.01	0.10	0.22	677
C-445053	67	Blind Fiord	23.2	-	-	-	-	-	-	-
C-445051	147	Blind Fiord	22.2	-	-	-	-	-	0.54	272
C-445049	173	Blind Fiord	21.2	-	-	-	-	-	0.32	541
C-445048	107	Blind Fiord	20.7	-	-	-	-	-	0.23	465
C-411533-a	227	Blind Fiord	19.4	-	-	-	-	-	0.47	483
C-411531-a	132	Blind Fiord	17.4	-	-	-	-	-	0.34	388
C-411530-a	196	Blind Fiord	16.4	-	-	-	-	-	0.47	417
C-411529-a	419	Blind Fiord	15.4	-	-	-	-	-	0.93	451
C-411528-a	377	Blind Fiord	14.4	-	-	-	-	-	1.22	309
C-411527-a	306	Blind Fiord	13.4	-	-	-	-	-	0.70	437
C-411526a	606	Blind Fiord	12.4	762	-1.04	0.13	0.03	0.14	0.32	1894
C-411525-a	366	Blind Fiord	11.4	-	-	-	-	-	0.89	411
C-411524-a	308	Blind Fiord	10.4	-	-	-	-	-	0.85	362
C-411523-a	393	Blind Fiord	9.4	-	-	-	-	-	1.04	378
C-411522-a	134	Blind Fiord	8.4	139	-0.98	0.12	0.04	0.10	0.42	319
C-411520-a	239	Blind Fiord	6.9	-	-	-	-	-	0.59	405

C-411519-a	257	Blind Fiord	6.4	-	-	-	-	-	0.69	372
C-411518-a	404	Blind Fiord	5.9	-	-	-	-	-	1.03	392
C-411517-a	412	Blind Fiord	5.4	-	-	-	-	-	0.81	509
C-411516-a	368	Blind Fiord	4.9	-	-	-	-	-	1.10	335
C-411515-a	339	Blind Fiord	4.7	-	-	-	-	-	0.66	514
C-411514-a	309	Blind Fiord	4.4	-	-	-	-	-	0.68	454
C-411513-a	325	Blind Fiord	4.2	-	-	-	-	-	0.99	328
C-411512-a	493	Blind Fiord	4.0	-	-	-	-	-	0.81	609
C-411511-a	173	Blind Fiord	3.8	-	-	-	-	-	0.52	333
C-411508-a	244	Blind Fiord	3.2	247	-0.96	0.14	0.06	0.08	0.32	763
C-411507a	400	Blind Fiord	3.0	492	-0.96	0.10	-0.05	0.07	0.99	404
C-411505-a	203	Blind Fiord	2.6	-	-	-	-	-	0.71	286
C-411503a	390	Blind Fiord	2.1	482	-0.95	0.12	0.00	0.09	0.68	574
C-411501-a	397	Blind Fiord	1.7	-	-	-	-	-	0.59	673
C-411499	450	Blind Fiord	1.3	-	-	-	-	-	0.64	703
C-411497	458	Blind Fiord	0.9	-	-	-	-	-	0.65	705
C-411495	565	Blind Fiord	0.5	-	-	-	-	-	0.67	843
C-411485	515	Blind Fiord	0.3	-	-	-	-	-	0.63	817
C-411481	520	Blind Fiord	0.2						0.54	963
C-411484	641	Blind Fiord	0.1	614	-1.02	0.15	0.00	0.10	0.42	1530
C-411480	412	Blind Fiord	0.0	-	-	-	-	-	0.39	1060
C-411479	613	Black Stripe	-0.2	-	-	-	-	-	0.49	1250
C-411478	155	Black Stripe	-0.4	-	-	-	-	-	3.10	50
C-411477	182	Black Stripe	-0.6	-	-	-	-	-	4.33	42
C-411476	211	Black Stripe	-0.8	-	-	-	-	-	1.92	110
C-411475	238	Black Stripe	-1.0	-	-	-	-	-	1.53	156
C-411469	248	Black Stripe	-2.2	-	-	-	-	-	2.98	83

C-411467	271	Black Stripe	-2.6	-	-	-	-	-	1.98	137
C-411465	250	Black Stripe	-3.0	247	-0.87	0.13	0.00	0.07	0.36	694
C-411464	544	Black Stripe	-3.2	508	-0.94	0.18	0.00	0.07	1.89	288
C-411463	287	Black Stripe	-3.4	-	-	-	-	-	3.72	77
C-411458	241	Black Stripe	-4.7	-	-	-	-	-	2.65	91
C-411457	150	Black Stripe	-5.2	149	-0.97	0.13	0.03	0.10	0.32	469
C-411455b	174	Black Stripe	-6.2	167	-0.88	0.17	-0.02	0.10	1.79	97
C-411453	210	Black Stripe	-7.2	224	-0.99	0.17	0.03	0.10	0.61	344
C-411449	180	Black Stripe	-9.2	164	-0.96	0.16	0.02	0.07	-	-
C-411447	179	Black Stripe	-10.2	176	-0.94	0.18	0.02	0.10	-	-
C-445083	163	Black Stripe	-13.0	-	-	-	-	-	1.62	101
C-445084	155	Black Stripe	-14.0	184	-0.9	0.12	0.00	0.13	1.76	88
C-445085	164	Black Stripe	-15.0	-	-	-	-	-	2.59	63
C-445086	212	Black Stripe	-16.0	-	-	-	-	-	3.82	55
C-445087	294	Black Stripe	-17.0	-	-	-	-	-	6.41	46
C-445088	352	Black Stripe	-18.0	-	-	-	-	-	4.91	72
C-445089	286	Black Stripe	-19.0	-	-	-	-	-	2.92	98
C-445090	465	Black Stripe	-20.0	499	-0.69	0.12	-0.01	0.07	4.31	108

C-445094	155	Black Stripe	-24.0	-	-	-	-	-	2.62	59
C-445096	135	Black Stripe	-26.0	-	-	-	-	-	2.22	61
C-445098	169	Black Stripe	-28.0	-	-	-	-	-	1.80	94
C-445100	200	Black Stripe	-30.0	-	-	-	-	-	1.24	161
C-445102	139	Black Stripe	-32.0	-	-	-	-	-	1.70	82
C-445104	138	Black Stripe	-34.0	-	-	-	-	-	1.71	81
C-445105	145	Black Stripe	-35.0	-	-	-	-	-	1.54	94
C-445107	89	Black Stripe	-38.0	-	-	-	-	-	1.77	50
C-445109	93	Black Stripe	-40.0	186	-0.53	0.14	-0.01	0.09	1.62	57
C-445111	129	Black Stripe	-42.0	-	-	-	-	-	1.88	69
C-445113	186	Black Stripe	-44.0	-	-	-	-	-	2.25	83
C-445115	182	Black Stripe	-46.0	-	-	-	-	-	1.97	92
C-445117	303	Black Stripe	-48.0	-	-	-	-	-	4.17	73
C-445119	257	Black Stripe	-50.0	-	-	-	-	-	5.99	43
C-445121	148	Black Stripe	-52.0	-	-	-	-	-	2.04	73
C-445123	98	Black Stripe	-54.0	-	-	-	-	-	1.56	63
C-445125	150	Black Stripe	-56.0	-	-	-	-	-	1.74	86
C-445127	128	Black Stripe	-58.0	-	-	-	-	-	1.33	96

C-445129	154	Black Stripe	-60.0	163	-0.39	0.16	0.02	0.06	1.43	108

*****Known Hg concentrations prior to processing for Hg isotopic analysis (see Section S1).

******Hg concentrations determined either by a) MC-ICP-MS at Wisconsin (Meishan samples), or b) CV-AAS at Michigan (Buchanan Lake samples)