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Hg isotopes constrain metallogenic effects of the Wilson Cycle of the Paleo-Asian Ocean

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Supplementary Information

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Methods

The samples were processed using a double-stage tube furnace coupled with 40% anti aqua regia (HNO_3/HCl = 3/1, v/v) trapping solutions (Zerkle *et al.*, 2020). The trapping solutions were measured using an F732 atomic absorption spectroscopy for the total Hg (THg) concentrations of the samples. Measurements of GSS-4 standard reference material yielded THg recoveries of 90-110% and uncertainty of < 10% for sample triplicates. The trapping solutions were diluted to 1 ng/mL Hg and measured by a Neptune Plus multi-collector inductively-coupled plasma mass spectrometer for Hg isotope ratios (Yin *et al.*, 2016). Hg-MDF is expressed in δ^{202}Hg notation in units of ‰ referenced to the NIST-3133 Hg standard (analyzed before and after each sample):

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

MIF is reported in Δ notation, which describes the difference between the measured δ^{xxx}Hg and the theoretically predicted δ^{xxx}Hg value, in units of ‰:

$$\Delta^{xxx}\text{Hg} = \delta^{xxx}\text{Hg} - \delta^{202}\text{Hg} \times \beta \quad (2)$$

where β is 0.2520 for ^{199}Hg, 0.5024 for ^{200}Hg, and 0.7520 for ^{201}Hg. Analytical uncertainty was estimated based on the replication of the NIST-3177 standard solution. The average and uncertainty of NIST-3177 (δ^{202}Hg: -0.53 ± 0.06 ‰; Δ^{199}Hg: -0.01 ± 0.05 ‰; Δ^{200}Hg: 0.01 ± 0.04 ‰; Δ^{201}Hg: -0.02 ± 0.05 ‰, SD, n = 21) and GSS-4 (δ^{202}Hg: -1.63 ± 0.07 ‰; Δ^{199}Hg: -0.46 ± 0.04 ‰; Δ^{200}Hg: -0.02 ± 0.03 ‰; Δ^{201}Hg: -0.41± 0.05 ‰, SD, n = 7), agrees well with previous

results. The larger SD values for NIST-3177 and GSS-4 represent the analytical uncertainties of our samples (see Table S-3 for the Hg isotope data of Standard reference material).

Supplementary Tables

Table S-1 Description of samples used in this study.

Sample	Location	Type	Longitude	Latitude	Age (Ma)	Mineral assemblage	Wall rock
Deposit in oceanic subduction zone							
XRQZ24-1	Xiaorequanzi Cu-Zn deposit	Chalcopyrite	89.53	42.30	355	Ccp+Py+Sp	Tuff
XRQZ24-2	Xiaorequanzi Cu-Zn deposit	Chalcopyrite			355		
XRQZ24-3	Xiaorequanzi Cu-Zn deposit	Sphalerite			355		
XRQZ24-4	Xiaorequanzi Cu-Zn deposit	Sphalerite			355		
XRQZ24-5	Xiaorequanzi Cu-Zn deposit	Chalcopyrite			355		
9SCK-37	Sanchakou Cu deposit	Chalcopyrite	94.76	42.40	345	Ccp+Py+Mag	Quartz diorite
9SCK63	Sanchakou Cu deposit	Chalcopyrite			345		
TWZK1507	Tuwu Cu deposit	Plagiogranite porphyry	92.61	42.10	335	Pl+Qz+Chl+Ep+Bt+Ccp+Py+Mag+Mol	-
TWZK1507	Tuwu Cu deposit	Ore			335	Ccp+Py+Mag+Mol+Qz+Chl+Ep+Bt	Plagiogranite porphyry
FX22-1	Fuxing Cu deposit	Plagiogranite porphyry	92.33	42.08	332	Pl+Qz+Bt+Ccp+Py+Mag+Mol	-
YDZK008-297	Yandong Cu deposit	Quartz albite porphyry	92.53	42.10	325	Pl+Qz+Ab+Bt+Ccp+Py+Mag+Mol	-
YD23-1	Yandong Cu deposit	Ore			325	Ccp+Py+Mag+Mol+Qz+Ab+Chl+Ep+Bt	Quartz albite porphyry, plagiogranite porphyry
YD23-2	Yandong Cu deposit	Ore			325		
YD23-3	Yandong Cu deposit	Ore			325		
YD23-4	Yandong Cu deposit	Ore			325		
CH22-3	Chihu Cu deposit	Plagiogranite porphyry	93.03	42.17	322	Pl+Qz+Bt+Ccp+Py+Mag+Mol	-
Deposit in collisional settings							
11bst-M21	Xiaobaishitou W deposit	Molybdenite	95.17	41.5	245	Qz+Sch+Mol+Py+Grt+Cal	Limestone
11bst-M23	Xiaobaishitou W deposit	Molybdenite			245		

11bst-G2	Xiaobaishitou W deposit	Biotite granite			242		-
11bst-G5	Xiaobaishitou W deposit	Biotite granite			242		-
11bst-G7	Xiaobaishitou W deposit	Biotite granite			242	Pl+Kfs+Qz+Bt	-
11bst-G9	Xiaobaishitou W deposit	Biotite granite			242		-
11bst-G10	Xiaobaishitou W deposit	Biotite granite			242		-
ZK0312-3	Donggebi Mo deposit	Porphyritic granite			236		-
ZK0312-4	Donggebi Mo deposit	Porphyritic granite			236		-
ZK0106-1	Donggebi Mo deposit	Porphyritic granite			236	Pl+Kfs+Qz+Bt	-
ZK0312	Donggebi Mo deposit	Porphyritic granite			236		-
ZK0106-2	Donggebi Mo deposit	Porphyritic granite			236		-
ZK03-47	Donggebi Mo deposit	Molybdenite	93.38	41.9	232		
ZK0408-2	Donggebi Mo deposit	Molybdenite			232		
ZK0408-3	Donggebi Mo deposit	Molybdenite			232	Qz+Mol+Py+Ccp	Sandstone
ZK0408-6	Donggebi Mo deposit	Molybdenite			232		
ZK0408-7	Donggebi Mo deposit	Molybdenite			232		
BS0408	Baishan Mo deposit	Pyrite			227		
19BS	Baishan Mo deposit	Molybdenite			227		
19BS-2	Baishan Mo deposit	Molybdenite	95.55	42.3	227	Qz+Kfs+Mol+Py	tuff, basalt, and shale
19BS-1	Baishan Mo deposit	Pyrite			227		

*Ccp = chalcopyrite; Py = pyrite; Sp = sphalerite; Mag = magnetite; Sch = scheelite; Grt = garnet; Ab = albite; Bt = biotite; Pl = plagioclase; Qz = quartz; Kfs = K-feldspar; Cal = calcite

Table S-2 The Hg isotope data of subduction to collisional ore systems in the CAOB.

Sample	Location	Type	Deposit type	THg (ng/g)	δ^{199}Hg	δ^{200}Hg	δ^{201}Hg	δ^{202}Hg	Δ^{199}Hg	Δ^{200}Hg	Δ^{201}Hg
Deposit in oceanic subduction zone											
XRQZ 24-1	Xiaorequanzi Cu-Zn deposit	Chalcopyrite	Volcanogenic massive sulfide (VMS) Cu-Zn deposit	962.69	-0.14	-0.16	-0.26	-0.52	0.00	0.10	0.13
XRQZ 24-2	Xiaorequanzi Cu-Zn deposit	Chalcopyrite	Volcanogenic massive sulfide (VMS) Cu-Zn deposit	8988.43	0.15	-0.09	0.00	-0.11	0.18	-0.03	0.08
XRQZ 24-3	Xiaorequanzi Cu-Zn deposit	Sphalerite	Volcanogenic massive sulfide (VMS) Cu-Zn deposit	530.50	-0.42	-1.41	-2.04	-3.14	0.37	0.17	0.32
XRQZ 24-4	Xiaorequanzi Cu-Zn deposit	Sphalerite	Volcanogenic massive sulfide (VMS) Cu-Zn deposit	1046.80	-0.26	-0.79	-0.99	-1.55	0.13	-0.01	0.17
XRQZ 24-5	Xiaorequanzi Cu-Zn deposit	Chalcopyrite	Volcanogenic massive sulfide (VMS) Cu-Zn deposit	315.39	-0.10	-0.37	-0.54	-0.96	0.14	0.11	0.18
9SCK-37	Sanchakou Cu deposit	Chalcopyrite	Porphyry Cu deposit	129.31	-0.23	-0.57	-0.83	-1.23	0.08	0.05	0.10
9SCK63	Sanchakou Cu deposit	Chalcopyrite	Porphyry Cu deposit	0.85	-0.20	-0.51	-0.56	-0.92	0.03	-0.05	0.13
TWZK 1507	Tuwu Cu deposit	Plagiogranite porphyry	Porphyry Cu deposit	4.90	0.19	0.29	0.48	0.37	0.10	0.10	0.20
TWZK 1507	Tuwu Cu deposit	Ore	Porphyry Cu deposit	2485.21	0.62	0.70	1.14	1.29	0.30	0.05	0.17
FX22-1	Fuxing Cu deposit	Plagiogranite porphyry	Porphyry Cu deposit	27.90	-0.01	-0.26	-0.39	-0.14	0.03	-0.19	-0.28
YDZK 008-297	Yandong Cu deposit	Quartz albite porphyry	Porphyry Cu deposit	7.80	-0.10	-0.25	-0.32	-0.68	0.07	0.09	0.18
YD23-1	Yandong Cu deposit	Ore	Porphyry Cu deposit	836.07	0.00	-0.46	-0.58	-1.17	0.30	0.13	0.31
YD23-2	Yandong Cu deposit	Ore	Porphyry Cu deposit	278.43	0.05	-0.22	-0.16	-0.41	0.15	-0.01	0.14

YD23-3	Yandong Cu deposit	Ore	Porphyry Cu deposit	7855.67	0.07	-0.75	-0.90	-1.77	0.51	0.14	0.42
YD23-4	Yandong Cu deposit	Ore	Porphyry Cu deposit	176.33	0.08	0.11	0.13	0.28	0.00	-0.03	-0.08
CH22-3	Chihu Cu deposit	Plagiogranite porphyry	Porphyry Cu deposit	19.20	-0.32	-0.98	-1.34	-1.81	0.13	-0.07	0.02
Deposit in collisional settings											
11bst-M21	Xiaobaishitou W deposit	Molybdenite	Skarn W deposit	198.71	-0.46	-1.15	-1.69	-2.27	0.11	-0.01	0.02
11bst-M23	Xiaobaishitou W deposit	Molybdenite	Skarn W deposit	359.20	-0.44	-1.03	-1.51	-2.05	0.08	0.00	0.02
11bst-G2	Xiaobaishitou W deposit	Biotite granite	Skarn W deposit	20.70	-0.01	0.14	0.14	0.10	-0.04	0.09	0.06
11bst-G5	Xiaobaishitou W deposit	Biotite granite	Skarn W deposit	11.80	-0.02	0.06	-0.02	0.04	-0.03	0.04	-0.05
11bst-G7	Xiaobaishitou W deposit	Biotite granite	Skarn W deposit	4.30	-0.02	0.04	-0.10	0.18	-0.07	-0.05	-0.24
11bst-G9	Xiaobaishitou W deposit	Biotite granite	Skarn W deposit	10.30	-0.19	-0.19	-0.33	-0.33	-0.11	-0.03	-0.09
11bst-G10	Xiaobaishitou W deposit	Biotite granite	Skarn W deposit	33.90	-0.21	-0.16	-0.34	-0.57	-0.06	0.12	0.09
ZK0312-3	Donggebi Mo deposit	Porphyritic granite	Porphyry Mo deposit	1.20	-0.47	-0.82	-1.32	-1.71	-0.04	0.03	-0.03
ZK0312-4	Donggebi Mo deposit	Porphyritic granite	Porphyry Mo deposit	1.20	-0.47	-0.65	-1.07	-1.57	-0.07	0.13	0.11
ZK0106-1	Donggebi Mo deposit	Porphyritic granite	Porphyry Mo deposit	27.60	-0.12	-0.23	-0.36	-0.47	0.00	0.01	0.00
ZK0312	Donggebi Mo deposit	Porphyritic granite	Porphyry Mo deposit	19.00	-0.25	-0.39	-0.69	-0.78	-0.06	0.00	-0.11
ZK0106-2	Donggebi Mo deposit	Porphyritic granite	Porphyry Mo deposit	7.80	-0.16	-0.36	-0.61	-0.76	0.03	0.02	-0.04
ZK03-47	Donggebi Mo deposit	Molybdenite	Porphyry Mo deposit	114.94	-0.09	-0.19	-0.31	-0.44	0.02	0.03	0.02
ZK0408-2	Donggebi Mo deposit	Molybdenite	Porphyry Mo deposit	39.96	-0.34	-0.76	-1.12	-1.55	0.05	0.02	0.05
ZK0408-3	Donggebi Mo deposit	Molybdenite	Porphyry Mo deposit	68.97	-0.21	-0.18	-0.46	-0.44	-0.09	0.04	-0.13
ZK0408-6	Donggebi Mo deposit	Molybdenite	Porphyry Mo deposit	53.67	-0.27	-0.52	-0.84	-1.12	0.01	0.04	0.00
ZK0408-7	Donggebi Mo deposit	Molybdenite	Porphyry Mo deposit	38.31	-0.27	-0.23	-0.45	-0.62	-0.11	0.08	0.01
BS0408	Baishan Mo deposit	Pyrite	Porphyry Mo deposit	142.76	0.13	0.37	0.44	0.68	-0.04	0.03	-0.07
19BS	Baishan Mo deposit	Molybdenite	Porphyry Mo deposit	79.02	0.32	0.59	0.83	1.11	0.04	0.03	-0.01
19BS-2	Baishan Mo deposit	Molybdenite	Porphyry Mo deposit	46.42	-0.33	-0.89	-1.34	-1.89	0.15	0.06	0.08
19BS-1	Baishan Mo deposit	Pyrite	Porphyry Mo deposit	105.13	-0.38	-0.66	-0.92	-1.32	-0.04	0.00	0.08

Table S-3 Hg isotope data of standard reference materials used to calculate analytical uncertainty.

Sample	$\delta^{199}Hg$	$\delta^{200}Hg$	$\delta^{201}Hg$	$\delta^{202}Hg$	$\Delta^{199}Hg$	$\Delta^{200}Hg$	$\Delta^{201}Hg$
GSS-4-1	-0.84	-0.87	-1.64	-1.61	-0.43	-0.06	-0.43
GSS-4-2	-0.88	-0.82	-1.57	-1.65	-0.46	0.01	-0.33
GSS-4-3	-0.92	-0.86	-1.75	-1.72	-0.49	0.00	-0.46
GSS-4-4	-0.85	-0.83	-1.65	-1.64	-0.43	-0.01	-0.42
GSS-4-5	-0.86	-0.91	-1.64	-1.68	-0.43	-0.06	-0.38
GSS-4-6	-0.92	-0.84	-1.64	-1.55	-0.53	-0.06	-0.47
GSS-4-7	-0.84	-0.76	-1.51	-1.54	-0.45	0.01	-0.35
NIST-3177-1	-0.20	-0.29	-0.39	-0.56	-0.06	-0.01	0.03
NIST-3177-2	-0.07	-0.20	-0.41	-0.56	0.07	0.08	0.01
NIST-3177-3	-0.19	-0.21	-0.34	-0.44	-0.08	0.01	-0.01
NIST-3177-4	-0.20	-0.26	-0.51	-0.56	-0.06	0.02	-0.09
NIST-3177-5	-0.03	-0.23	-0.39	-0.44	0.08	-0.01	-0.05
NIST-3177-6	-0.15	-0.23	-0.41	-0.50	-0.02	0.03	-0.03
NIST-3177-7	-0.16	-0.28	-0.43	-0.45	-0.05	-0.05	-0.08
NIST-3177-8	-0.14	-0.21	-0.38	-0.49	-0.01	0.04	-0.02
NIST-3177-9	-0.09	-0.21	-0.30	-0.44	0.02	0.01	0.03
NIST-3177-10	-0.07	-0.28	-0.49	-0.54	0.06	-0.01	-0.08
NIST-3177-11	-0.11	-0.26	-0.46	-0.56	0.03	0.02	-0.04
NIST-3177-12	-0.15	-0.24	-0.40	-0.59	0.00	0.06	0.05
NIST-3177-13	-0.21	-0.35	-0.50	-0.58	-0.07	-0.06	-0.07
NIST-3177-14	-0.19	-0.29	-0.45	-0.60	-0.04	0.01	0.01
NIST-3177-15	-0.07	-0.32	-0.46	-0.54	0.06	-0.05	-0.05
NIST-3177-16	-0.22	-0.30	-0.45	-0.67	-0.05	0.04	0.06
NIST-3177-17	-0.20	-0.26	-0.48	-0.56	-0.06	0.03	-0.06
NIST-3177-18	-0.12	-0.21	-0.36	-0.50	0.00	0.04	0.01
NIST-3177-19	-0.13	-0.24	-0.33	-0.53	0.00	0.02	0.07
NIST-3177-20	-0.18	-0.37	-0.52	-0.62	-0.02	-0.06	-0.05
NIST-3177-21	-0.19	-0.20	-0.36	-0.46	-0.07	0.03	-0.01

Supplementary Information References

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