Appendix Table DR1. Average composition of Early Cambrian sulfide marker bed (n=8) and black shale host sequence at the Huangjiawan mine, South China. Analysis by combined X-ray fluorescence spectrometry (XRF), gas chromatography (GC), neutron activation analysis (INA), inductively-coupled plasma spectrometry (ICPMS), inductively-coupled plasma mass spectometry (ICPMS), atomic absorption spectrometry/cold-vapor FIMA (AAS-H), prompt gamma neutron activation analysis (PGNA), thermal ion mass spectrometry (TIMS).

			Mo-Ni-rich sulfide marker bed										Black shale (n=10	
			ZH-1	ZH-2	ZH-5	Z-6	Z-11	Z-12	ZG-1	ZG-2	Mean	1SD	Mean	1SD
SiO2	XRF	%	16.8	20.8	21.7	13.9	17.0	22.4	21.2	20.8	19.3	3.0	63.0	7.5
TiO2	XRF	%	0.190	0.165	0.236	0.176	0.142	0.275	0.236	0.211	0.2	0.0	0.26	0.01
Al2O3	XRF	%	3.50	3.11	4.50	2.97	2.80	4.87	4.36	3.99	3.8	0.8	6.06	0.21
MnO	XRF	%	0.020	0.016	0.007	0.003	<0.001	0.091	0.024	0.037	0.0	0.0	0.02	0.01
MgO	XRF	%	1.35	0.830	1.48	0.300	0.930	4.95	1.79	2.99	1.8	1.5	1.79	0.17
CaO	XRF	%	2.34	4.71	5.82	4.78	3.54	10.6	4.25	6.08	5.3	2.5	2.45	0.30
Na2O	XRF	%	0.14	0.05	0.26	0.07	0.15	0.31	0.20	0.26	0.2	0.1	0.37	0.02
K2O	XRF	%	0.780	0.590	1.14	0.742	0.625	1.20	1.01	0.932	0.9	0.2	2.06	0.06
P2O5	XRF	%	0.920	3.52	3.35	3.52	1.95	2.66	1.74	1.95	2.4	1.0	0.14	0.07
C tot	GC	%	12.7	10.2	11.4	7.3	12.0	11.7	11.4	12.1	11.1	1.7	9.2	0.1
N	GC	%	0.18	0.13	0.19	0.12	0.20	0.17			0.2	0.0	0.14	0.03
H	GC	%	1.39	1.17	1.09	1.18	1.07	0.89			1.1	0.2		
FeS2	XRF	%	31.8	32.0	27.8	46.4	37.4	18.6	30.6	24.6	31.2	8.3	5.76	1.69
AsS	INA	%	3.23	1.66	1.83	2.00	1.86	1.27	2.00	2.17	2.0	0.6		
MoS2	XRF	%	11.85	4.84	8.14	6.41	10.86	6.37	7.04	9.03	8.1	2.4		
NiS	XRF	%	5.71	5.36	7.39	6.28	7.58	4.61	8.09	6.57	6.4	1.2		
ZnS	XRF	%	0.49	0.39	0.36	0.85	0.56	0.55	0.96	0.71	0.6	0.2		
Sum		%	93.33	89.57	96.63	96.97	98.65	91.49	94.85	92.43	94.2	3.1	91.3	
S	GC	%	22.50	20.60	19.40	29.20	25.60	13.40			21.8	5.4	3.53	0.77
Ag	ICP	ppm	87.2	66	54.5	49.5	75.3	39.1	60.5	61.6	61.7	15.0	0.98	0.41
As	INA	ppm	22600	11600	12800	14000	13000	8900	14000	15200	14013	3957	52	25
B	PGNA	ppm	12	15							13.5	2.1		
Ba	XRF	ppm	543	964	731	620	486	791	558	612	663	157.1	1577	1288
Be	ICP	ppm	<1	<1	<1	3	<1	<1	<1	1	2.0	1.4	1.9	0.3
Bi	ICP	ppm			36	43	58	27	52	46	43.7	11.1		
Cd	ICP	ppm	66.5	86.9	47.5	162.1	71.9	47.5	117	74.9	84.3	38.5	21	23
Co	INA	ppm	160	215	170	199	182	121	216	181	181	31.3	16	5
Cr	INA	ppm	90	124	66	62	53	71	83	56	75.6	23.3	47	10
Cs	ICPMS	ppm	8.10	4.41	7.19	6.79	9.57	6.72	6.41	7.45	7.1	1.5	5.1	0.9
Cu	XRF	ppm	2390	2420	2670	1800	2640	1960	3160	2680	2465	432	110	47
Ga	XRF	ppm			19	21	18	18	16	19	18.5	1.6	9.8	1.3
Hf	ICPMS	ppm	0.184	0.131	1.06	1.20	0.955	1.11	1.40	1.08	0.9	0.5	1.95	0.35
Hg	AAS-H	ppm	14.7	8.96	13.1	14.6	15.3	10.9	9.89	13.2	12.6	2.4	0.42	0.28
Mn	XRF	ppm	154	123	54	23	<10	701	185	285	218	230	195	150

Mo	XRF	ppm	71000	29000	48800	38400	65100	38200	42200	54100	48350	14348	111	21
Nb	ICPMS	ppm			4.44	3.08	2.84	5.03	4.59	3.89	4.0	0.9	5.54	0.62
Ni	XRF	ppm	36900	34700	47800	40600	49000	29800	52300	42500	41700	7731	166	89
Pb	XRF	ppm	679	329	432	241	506	311	386	444	416	135	53.7	21.7
Rb	ICPMS	ppm	27.4	21.0	40.4	27.6	24.0	41.8	36.6	33.6	31.5	7.7	50.1	7.5
Re	NTIMS	ppm									*11.2*	*0.9*	*0.2*	
Sb	INA	ppm	650	365	404	369	573	332	487	594	472	121		
Sc	ICPMS	ppm	4.1	4.8	5.5	4.8	3.2	5.9	5.8	5.6	5.0	0.9	6.17	0.61
Se	INA	ppm	1500	1810	1650	1830	2120	1210	1960	2130	1776	315	9.1	8.6
Sn	XRF	ppm			6	9	5	9	11	7	7.8	2.2	1.2	0.2
Sr	ICPMS	ppm	140	344	236	208	140	287	153	176	211	74.4	50.4	28.1
Ta	INA/ICP	ppm	<0.5	<0.5	0.23	0.18	0.14	0.22	0.19	0.16	0.2	0.0	0.35	0.19
Th	ICPMS	ppm	4.34	4.82	5.01	3.65	3.08	5.37	3.96	3.58	4.2	0.8	7.42	0.91
U	ICPMS	ppm	71.0	320	221	293	126	187	116	108	180	91.3	46.4	9.9
V	XRF	ppm	373	363	1269	508	904	545	469	467	612	315	580	316
W	XRF	ppm	37	<3	35	31	55	29	45	38	38.6	8.9	4.0	3.9
Y	ICPMS	ppm	25.2	234	109	199	63.8	110	62.1	77.7	110	71.6	25.2	5.63
Zn	XRF	ppm	3260	2650	2410	5690	3730	3710	6430	4730	4076	1429	260	239
Zr	XRF/IC	ppm	51	34	53.1	52.6	40.4	58.7	59.2	50.6	50.0	8.7	60.4	13.6
La	ICPMS	ppm	33.5	178	57.7	106	37.3	65.4	37.2	61.4	72.1	48.8	17.9	3.21
Ce	ICPMS	ppm	44.4	244	96.4	138	63.1	105	65.5	85.9	105	63.0	38.7	7.08
Pr	ICPMS	ppm	4.43	32.2	11.8	21.5	7.59	12.7	7.55	9.70	13.4	9.2	4.45	0.87
Nd	ICPMS	ppm	17.0	133	50.4	92.0	32.2	54.5	31.9	39.3	56.3	38.1	18.5	3.69
Sm	ICPMS	ppm	3.25	24.0	9.93	17.0	6.27	10.4	6.23	7.15	10.5	6.8	3.57	0.74
Eu	ICPMS	ppm	0.663	4.99	2.68	3.80	1.74	2.65	1.61	1.84	2.5	1.4	0.91	0.26
Gd	ICPMS	ppm	2.84	26.6	10.9	19.5	6.86	11.2	6.65	8.08	11.6	7.8	4.18	0.99
Tb	ICPMS	ppm	0.394	3.45	1.50	2.63	0.949	1.53	0.904	1.07	1.6	1.0	0.77	0.18
Dy	ICPMS	ppm	2.44	20.4	9.26	16.3	5.90	9.51	5.60	6.52	9.5	6.0	3.99	0.86
Ho	ICPMS	ppm	0.490	4.03	1.88	3.37	1.23	1.98	1.13	1.35	1.9	1.2	0.80	0.19
Er	ICPMS	ppm	1.37	10.4	5.17	8.86	3.28	5.28	3.02	3.62	5.1	3.1	2.40	0.48
Tm	ICPMS	ppm	0.177	1.10	0.606	0.984	0.384	0.617	0.364	0.422	0.6	0.3	0.43	0.08
Yb	ICPMS	ppm	1.05	5.51	3.32	4.87	2.02	3.37	1.93	2.33	3.1	1.5	2.27	0.40
Lu	ICPMS	ppm	0.149	0.665	0.422	0.612	0.255	0.453	0.250	0.323	0.4	0.2	0.36	0.08
Ir	ICPMS	ppb	5.38	4.03	4.07	3.75	3.58	2.40	4.03	4.37	4.0	0.8	*<1*	
Pd	ICPMS	ppb	419	412	421	379	421	267	463	385	396	58.0	*28*	
Pt	ICPMS	ppb	358	347	337	340	349	226	405	383	343	52.7	*30*	
Rh	ICPMS	ppb	17.3	16.4	16.7	15.4	16.7	10.6	18.7	14.3	15.8	2.5	*<1*	
Ru	ICPMS	ppb	12.0	8.92	5.78	7.00	9.63	3.78	7.12	4.36	7.3	2.8	*<1*	
Os	ICPMS	ppb	135	109	127	115	130	114	157	147	129	16.8	*3*	
Au	INA	ppb	280	360	282	529	432	269	540	457	394	112	*10*	

in italics:
Re data from sample set by Mao et al. (2002)
PGE+Au data on black shales from Li and Gao (2000)

Reference data on seawater and bulk continental crust in Figures 1 and 2 from Nozaki (1997) and Taylor and McLennan (1985), respectively.

Appendix Table DR2.

Molybdenum data of five samples of the Early Cambrian sulfide marker bed from the Huangjiawan mine in Guizhou (Mao et al., 2002), six black shale samples from the host sequence of the sulfide marker bed at Ganziping, 350 km NE of Huangjiawan (Pan et al., 2004), and two black shale samples from Yuanling, 300 km ENE of Huangjiawan (Zhu et al., 2004), where the sulfide marker bed is not developed.
Mo isotope analytical procedures followed Siebert et al. (2001). The external standard reproducibility is at or better than 0.1 ‰ for the $^{98}Mo/^{95}Mo$ ratio (2 σ).
See main text for discussion.

Sample	stratigraphic position [m][a]	$\delta^{98/95}Mo$ MOMO[b]	$\delta^{98/95}Mo$ standard[c]	2σ std.err.[d]	$\delta^{97/95}Mo$ standard[e]	Mo [ppm]
Huangjiawan sulfide marker bed						
ZG-1	0	-1.36	0.94	0.04	0.62	42200
ZG-2	0	-1.25	1.05	0.02	0.69	54100
ZH-1	0	-1.17	1.13	0.04	0.75	29000
ZH-2	0	-1.33	0.97	0.02	0.64	71000
ZH-5	0	-1.10	1.20	0.04	0.79	48800
Niutitang Formation (black shales at Ganziping)						
ZG-3	-0.7	-0.80	1.50	0.04	1.00	209
ZG-7	1.5	-0.40	1.90	0.04	1.25	115
"		-0.43	1.87	0.04	1.23	
ZG-11	1.8	-1.05	1.25	0.04	0.83	102
ZG-17	4.5	-1.49	0.81	0.04	0.53	293
"		-1.36	0.94	0.06	0.62	
ZG-26	46.5	-1.08	1.22	0.04	0.81	54
ZG-29	61	-1.24	1.06	0.04	0.71	35
Niutitang Formation (black shales at Yuanling)						
L-60	0	-1.20	1.10	0.04	0.73	22
L-66	6	-1.82	0.48	0.04	0.32	12

[a] Stratigraphic position in m relative to the sulfide marker bed.
[b] Deviations of $^{98}Mo/^{95}Mo$ in permil from Mean Ocean Molybdenum (MOMO) (Siebert et al., 2003).
[c] Ditto, but relative to the Bern Laboratory standard as in Siebert et al. (2003) and McManus et al. (2002).
[d] In-run errors denoting stability of the measurement. A better assessment of the real uncertainty is the 2σ external standard reproducibility of samples (± 0.1 ‰). The latter is used in text and figure.
[e] Deviations of $^{97}Mo/^{95}Mo$ in permil from Rochester Laboratory standard as in Barling et al. (2001) and Arnold et al. (2004). The intercalibration of the latter two is approximated by comparable samples (seawater, recent Fe-Mn crusts).

Additional references besides main text:

Li, S.R., and Gao, Z.M., 2000, Source tracing of noble metal elements in Lower Cambrian black rock series of Guizhou-Hunan provinces, China: Science in China (ser. D), v. 43, p. 1051-1061.

Taylor, S.R., and McLennan, S.M., 1985, The continental crust: its composition and evolution. Blackwell, 312 pp.

McManus, J., Nägler, T.F., Siebert, C., Wheat, C.G., and Hammond, D.E., 2002, Oceanic molybdenum isotope fractionation: Diagenesis and hydrothermal ridge-flank alteration: Geochem., Geophys., Geosyst., v. 3, no. 2, 19 Dec 2002, DOI: 10.1029/2002GC000356.

Siebert, C., Nägler, T.F., and Kramers, J., 2001, Determination of molybdenum isotope fractionation by double-spike multicollector inductively coupled plasma mass spectrometry: Geochem., Geophys., Geosyst., v. 2, 3 July 2002, Paper number 2000GC000124.