

Supplementary Material

Molybdenum isotope fractionation mechanism of metal sulfides in magmatic hydrothermal systems: Constraints from the Pulang porphyry Cu deposit, Yunnan, Southwest China

Wanli Tang, Jifeng Xu^{*}, Kang Cao, Jie Li, Jianlin Chen

* Corresponding author: Jifeng Xu

E-mail addresses: jifengxu@gig.ac.cn (J.-F. Xu)

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1. Supplementary Tables:

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2. Supplementary Figures:

Fig. S1. Modelled isotopic fractionation $\epsilon^{98}\text{Mo}$ fluid-mineral between oxidized molybdate and different magmatic-hydrothermal phases as a function of temperature were calculated according to Young et al. (2015). These curves depict the combined effect of valence, coordination, and anion (O vs. S) changes.

Fig. S2. Quantitative model of Rayleigh fractionation between ore-forming fluids and molybdenite at 332°C. The light bands illustrate the variation of the fractionation curve in the temperature range of 350–550°C.

3. Supplementary Text: The Rayleigh fractionation modelling.

4. References

Table S1. Trace element (ppm) of metal sulfides and whole rocks in Pulang deposit

Mineralization stage	Epidote-chlorite									Chlorite-illite		
Sample	0102-156	0315-169	0408-103	0408-253	0408-74	0416-397.5	17PLT-3	18PL-14	18PL-29	0102-88-1	0408-232	0102-156-2
Major mineral	Py	Py	Py	Py	Py	Py	Ccp	Ccp	Ccp	Py	Py	Ccp
	Qz-Chl-Ilt-Py-Ccp	Qz-Chl-Ep-Ilt-Py-Ccp	Qz-Ilt-Chl-Py	Qz-Chl-Ep-Ilt-Py-Ccp	Qz-Ep-Chl-Ilt-Py	Qz-Ep-Chl-Ilt-Py	Qz-Ep-Chl-Ilt-Py-Ccp	Qz-Chl-Ep-Ccp	Qz-Chl-Ep-Ccp	Qz-Chl-Ilt-Py-Ccp	Qz-Ilt-Chl-Ep-Py	Qz-Ep-Chl-Py-Ccp
Trace element (ppm)												
Mo	11.4	20.0	7.62	1.18	2.45	5.65	9.36	0.13	3.56	8.38	0.16	8.18
Cu	6200	714	1120	2430	499	769	13100	>50000	>50000	>10000	1530	>50000
Fe	43.6	42.6	41.4	40.9	44.2	42.8	40.2	30.3	38.4	41.8	41.8	30.5
Ag	30.7	1.64	0.33	0.90	0.15	0.86	2.0	17.3	28.8	3.99	0.47	27.2
Al	0.02	0.07	0.21	0.26	0.02	0.09	<0.1	<0.1	0.1	0.10	0.06	<0.1
As	27.0	94.8	3.5	29.8	4.0	2.9	<2	<2	12	6.8	22.5	<2
Ba	<10	10	10	10	<10	10	<100	<100	<100	30	10	<100
Be	<0.05	<0.05	0.06	<0.05	<0.05	<0.05	<0.5	<0.5	<0.5	<0.05	<0.05	<0.5
Bi	11.05	1.55	1.89	2.14	1.02	4.17	2.0	4.5	7.3	1.42	1.43	2.3
Ca	0.02	0.08	0.13	0.37	0.04	0.07	0.2	<0.1	<0.1	0.05	0.08	<0.1
Cd	3.11	0.60	0.03	0.11	<0.02	0.03	<0.2	1.3	32.5	0.19	0.02	12.8
Ce	31.5	5.31	1.16	10.35	1.06	1.68	0.2	0.1	0.5	1.53	4.15	14.7
Co	404	242	515	1300	629	89.0	580	2	370	141.5	182.5	4
Cr	3	7	20	2	1	18	<10	<10	<10	7	4	<10
Cs	<0.05	0.06	0.19	0.12	0.05	0.10	<0.5	<0.5	<0.5	0.07	0.07	<0.5

Dy	0.25	0.27	0.10	0.44	0.13	0.19	<0.5	<0.5	<0.5	0.09	0.18	<0.5
Er	0.08	0.12	0.05	0.24	0.07	0.10	<0.3	<0.3	<0.3	0.04	0.08	<0.3
Eu	0.08	0.09	0.04	0.16	0.05	0.05	<0.3	<0.3	<0.3	0.04	0.07	<0.3
Ga	0.55	0.32	0.42	0.76	0.13	0.55	<0.5	0.7	0.6	0.33	0.32	0.8
Gd	0.69	0.39	0.13	0.54	0.12	0.22	<0.5	<0.5	<0.5	0.12	0.26	<0.5
Ge	0.16	0.14	0.13	0.21	0.12	0.12	1.6	1.8	1.8	0.14	0.15	1.9
Hf	<0.1	0.1	0.1	<0.1	<0.1	<0.1	<1	<1	<1	<0.1	<0.1	<1
Ho	0.04	0.04	0.02	0.08	0.02	0.04	<0.1	<0.1	<0.1	0.02	0.03	<0.1
In	0.458	0.013	0.007	0.029	<0.005	0.018	0.28	5.77	3.64	0.058	0.007	11.95
K	0.01	0.02	0.09	0.02	0.01	0.05	<0.1	<0.1	<0.1	0.07	0.03	<0.1
La	17.1	2.7	0.6	6.0	0.6	0.7	<5	<5	<5	0.8	1.9	9
Li	<0.2	1.4	1.6	2.8	0.2	0.9	<2	<2	<2	1.5	2.0	<2
Lu	0.01	0.01	0.01	0.03	0.01	0.01	<0.1	<0.1	<0.1	0.01	0.01	<0.1
Mg	<0.01	0.01	0.04	0.01	<0.01	0.01	<0.1	<0.1	<0.1	0.03	0.04	<0.1
Mn	<5	<5	<5	<5	<5	<5	<50	<50	<50	<5	<5	<50
Mo	14.95	23.3	5.44	1.76	5.13	6.66	12.3	0.7	4.2	9.25	1.52	9.4
Na	0.02	0.01	0.02	0.01	0.03	0.01	<0.1	<0.1	<0.1	0.02	0.01	<0.1
Nb	0.1	0.4	0.2	0.5	0.1	0.2	<1	<1	<1	0.6	0.1	<1
Nd	12.0	2.9	0.7	4.3	0.5	1.1	<1	<1	1	0.8	2.2	5
Ni	401	80.3	44.4	77.5	42.1	63.2	31	<2	230	71.8	21.0	<2
P	30	90	90	160	30	30	100	200	<100	40	40	<100
Pb	14.9	394	3.0	4.2	1.7	28.4	<5	<5	47	12.7	7.6	<5
Pr	3.20	0.67	0.15	1.13	0.13	0.24	<0.3	<0.3	<0.3	0.19	0.55	1.4
Rb	0.2	1.2	5.0	1.4	0.5	2.4	<1	1	2	2.8	1.9	<1
Re	0.005	0.002	<0.002	0.003	0.018	0.002	0.02	<0.02	<0.02	<0.002	<0.002	<0.02
S	0.04	0.12	0.22	0.14	0.07	0.08	>10.0	>10.0	>10.0	0.12	0.12	>10.0

Sb	0.08	0.40	0.31	0.17	0.10	0.29	<0.5	<0.5	<0.5	0.15	0.28	<0.5
Sc	0.1	0.4	0.4	0.7	<0.1	0.4	<1	<1	<1	0.7	0.1	<1
Se	8	5	4	3	3	4	50	180	180	7	3	340
Sm	1.65	0.65	0.17	0.77	0.16	0.29	<0.3	<0.3	<0.3	0.17	0.44	0.6
Sn	23.7	0.4	0.7	1.2	0.4	0.3	<2	25	<2	0.4	0.3	32
Sr	3.8	16.7	5.5	79.0	2.6	27.7	14	2	33	5.3	10.3	3
Ta	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.5	<0.5	<0.5	0.05	<0.05	<0.5
Tb	0.06	0.05	0.02	0.08	0.02	0.03	<0.1	<0.1	<0.1	0.02	0.04	<0.1
Te	10.30	0.97	0.47	0.56	0.60	1.57	0.8	3.1	2.5	0.34	0.47	1.5
Th	0.65	0.59	0.36	0.90	0.29	0.35	0.1	0.1	0.8	0.85	0.14	0.2
Ti	<0.005	0.016	0.006	0.013	<0.005	0.010	<0.05	<0.05	<0.05	0.019	<0.005	<0.05
Tl	0.14	0.02	0.18	0.20	0.05	0.16	<0.2	<0.2	<0.2	0.06	0.13	<0.2
Tm	0.01	0.01	0.01	0.03	0.01	0.01	<0.1	<0.1	<0.1	0.01	0.01	<0.1
U	0.1	0.2	0.3	2.3	4.7	0.2	<1	<1	<1	0.1	0.1	<1
V	2	3	5	6	1	6	<10	<10	<10	4	1	<10
W	0.6	6.8	6.2	254	246	103.5	148	<1	1	0.7	2.2	1
Y	1.4	1.3	0.5	2.2	0.5	1.0	<1	<1	<1	0.5	0.8	1
Yb	0.04	0.08	0.04	0.20	0.07	0.09	<0.3	<0.3	<0.3	0.04	0.05	<0.3
Zn	505	21	<2	3	<2	<2	<20	170	2760	<2	<2	1730
Zr	0.5	1.4	1.5	1.4	1.1	1.6	<5	<5	<5	1.1	<0.5	<5

Mineralization stage	Chlorite-illite					Quartz-illite						
	0102-173	E601-93	E601-96	E902-67	0111-144	17PLT-1	17PLT-4	17PLT-4	18PL-55	0416-146	0416-165	0416-93
Sample	Ccp	Po	Po	Po	Py	Py	Py	Ccp	Ccp	Po	Po	Po
Major mineral	Qz-Chl-Ilt-Ccp	Qz-Chl-Ilt-Ccp-Po	Qz-Chl-Ilt-Py-Ccp-Po	Qz-Chl-Ilt-Py-Ccp-Po	Qz-Ilt-Py-Ccp	Qz-Ilt-Py-Ccp	Qz-Ilt-Py-Ccp	Qz-Cal-Ilt-Py-Ccp-Mol	Qz-Ilt-Py-Ccp	Qz-Ilt-Po	Qz-Ilt-Po	Qz-Ilt-Po
Trace element (ppm)												
Mo	0.17	0.35	0.67	0.36	2.25	4.64	0.63	1.03	0.37	0.18	0.62	0.82
Cu	>50000	4570	>10000	>10000	957	2450	7610	>50000	>50000	443	442	275
Fe	26.9	>50	>50	>50	42.6	43.7	42.7	37.2	28.7	>50	>50	48.3
Ag	21.5	2.82	0.53	15.25	1.00	7.00	4.32	12.1	32.2	0.23	0.55	0.58
Al	0.1	0.02	0.04	0.27	0.05	0.01	0.01	<0.1	<0.1	0.22	0.21	0.86
As	<2	5.6	5.5	1.3	3.5	244	144.0	92	30	1.3	2.2	1.1
Ba	<100	20	30	50	10	10	10	<100	<100	10	20	50
Be	<0.5	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.5	<0.5	0.08	<0.05	0.48
Bi	4.3	12.30	81.8	131.0	2.78	2.70	1.38	2.2	15.8	1.90	4.44	53.8
Ca	<0.1	0.08	0.04	0.09	0.20	0.03	0.04	0.1	<0.1	0.17	0.10	0.29
Cd	3.9	0.08	0.12	14.05	0.05	5.65	0.88	14.4	3.1	0.04	0.18	0.02
Ce	0.1	0.68	0.13	4.17	1.16	0.17	2.44	78.6	0.2	2.86	7.00	5.10
Co	5	251	270	655	41.7	2020	377	390	4	415	340	178.0
Cr	<10	4	6	7	5	8	10	<10	<10	9	8	7
Cs	<0.5	0.07	0.10	0.40	<0.05	<0.05	<0.05	<0.5	<0.5	0.17	0.17	0.77

Dy	<0.5	<0.05	<0.05	0.19	0.08	<0.05	<0.05	<0.5	<0.5	0.27	0.39	0.58
Er	<0.3	<0.03	<0.03	0.09	0.04	<0.03	<0.03	<0.3	<0.3	0.14	0.18	0.31
Eu	<0.3	<0.03	<0.03	0.09	0.03	<0.03	<0.03	<0.3	<0.3	0.19	0.29	0.36
Ga	0.7	0.17	0.22	1.45	0.29	0.14	0.16	0.9	1.1	0.42	0.59	1.48
Gd	<0.5	<0.05	<0.05	0.28	0.11	<0.05	0.07	1.0	<0.5	0.38	0.58	0.79
Ge	2.1	0.13	0.13	0.15	0.12	0.12	0.12	1.4	2.1	0.17	0.15	0.15
Hf	<1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<1	<1	0.1	0.1	0.3
Ho	<0.1	<0.01	<0.01	0.04	0.01	<0.01	0.01	<0.1	<0.1	0.05	0.07	0.10
In	6.11	<0.005	<0.005	2.47	0.013	0.219	0.209	1.75	7.44	0.009	<0.005	<0.005
K	<0.1	0.02	0.03	0.11	0.01	0.01	0.01	<0.1	<0.1	0.06	0.07	0.40
La	<5	<0.5	<0.5	2.3	<0.5	<0.5	1.4	45	<5	1.0	1.4	1.1
Li	<2	0.5	0.7	1.5	7.7	1.2	1.1	<2	<2	0.3	0.4	1.0
Lu	<0.1	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.1	<0.1	0.02	0.02	0.04
Mg	<0.1	0.01	0.08	0.24	0.05	<0.01	<0.01	<0.1	<0.1	0.01	0.06	0.03
Mn	<50	<5	<5	11	<5	<5	<5	<50	<50	<5	<5	<5
Mo	3.7	0.82	1.11	0.85	2.80	5.41	1.30	1.4	1.3	0.62	0.67	1.34
Na	<0.1	0.01	0.01	0.02	0.02	0.01	0.01	<0.1	<0.1	0.09	0.06	0.25
Nb	<1	<0.1	<0.1	0.4	0.3	0.1	<0.1	<1	<1	1.0	1.7	1.1
Nd	<1	0.2	0.1	2.1	0.8	0.1	0.9	29	<1	2.3	5.4	4.5
Ni	<2	89.0	41.8	1970	34.6	117.5	162.0	130	<2	416	493	515
P	100	<10	10	50	30	10	<10	100	<100	100	40	430
Pb	<5	1.8	14.1	207	4.1	10.1	2.9	<5	<5	3.7	81.8	27.6
Pr	<0.3	0.07	<0.03	0.52	0.17	<0.03	0.26	7.6	<0.3	0.48	1.24	0.96
Rb	1	1.0	1.3	6.4	0.6	0.3	0.3	<1	1	4.7	6.6	39.0
Re	<0.02	<0.002	<0.002	0.003	0.003	0.003	0.002	<0.02	<0.02	0.007	0.002	<0.002
S	>10.0	0.12	0.18	0.25	0.21	0.09	0.08	>10.0	>10.0	0.17	0.13	0.20

Sb	<0.5	1.48	170.5	0.48	0.12	0.10	0.17	<0.5	1.0	0.19	0.14	0.20
Sc	<1	<0.1	<0.1	0.7	0.2	<0.1	0.1	1	<1	0.5	0.7	0.9
Se	290	1	2	3	3	5	5	100	340	5	4	4
Sm	<0.3	<0.03	<0.03	0.42	0.18	<0.03	0.13	2.9	<0.3	0.55	0.90	1.10
Sn	35	<0.2	<0.2	4.1	0.4	0.4	0.6	<2	30	1.4	1.8	1.6
Sr	4	282	6.1	8.3	11.9	1.1	1.3	3	3	21.1	12.8	88.1
Ta	<0.5	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.5	<0.5	0.07	0.09	0.08
Tb	<0.1	<0.01	<0.01	0.04	0.01	<0.01	0.01	0.1	<0.1	0.04	0.07	0.10
Te	1.4	7.02	48.4	77.9	1.25	1.32	1.17	1.6	6.1	0.72	1.86	32.3
Th	0.2	0.03	0.02	0.76	0.13	0.11	0.02	0.5	0.2	6.40	2.23	1.80
Ti	<0.05	<0.005	<0.005	0.017	0.009	<0.005	<0.005	<0.05	<0.05	0.039	0.062	0.042
Tl	<0.2	0.15	1.11	0.40	0.23	0.11	0.12	<0.2	<0.2	0.15	0.15	0.31
Tm	<0.1	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.1	<0.1	0.02	0.02	0.04
U	<1	0.4	0.1	0.6	0.1	<0.1	<0.1	<1	<1	1.0	0.5	1.7
V	<10	1	1	11	3	<1	1	<10	<10	6	13	10
W	<1	0.2	34.2	7.8	0.9	0.7	4.2	<1	<1	0.7	0.5	0.7
Y	<1	0.1	0.1	0.9	0.4	<0.1	0.2	1	<1	1.2	1.8	2.7
Yb	<0.3	<0.03	<0.03	0.08	0.03	<0.03	<0.03	<0.3	<0.3	0.11	0.15	0.26
Zn	120	<2	4	711	5	344	73	1490	210	<2	17	<2
Zr	<5	0.5	<0.5	0.8	0.7	<0.5	<0.5	<5	<5	2.5	2.5	5.6

Sample	19PL-39	19PL-12	19PL-1	19PL-2	19PL-3	0713-640	0713-692.5	0713-727	E203-34	E601-34	E004-61
	Surrounding rock					Quartz monzonite			Quartz diorite		
Major mineral	Whole rock										
Trace element (ppm)											
Mo	2.38	1.44	1.80	9.76	6.96	11.3	8.48	8.68	10.9	10.4	7.52
Cu	35.4	24.4	29.3	18.5	18.2	117.0	124.0	84.9	16.0	34.8	1.9
Fe	4.52	4.20	4.12	2.85	2.67	3.01	3.10	2.95	2.72	2.86	2.84
Ag	0.09	0.08	0.06	0.05	0.04	0.07	0.08	0.04	0.01	<0.01	<0.01
Al	7.90	9.15	9.04	4.65	4.46	7.40	7.70	7.49	7.82	8.26	7.66
As	18.0	16.5	16.9	12.7	13.2	8.2	10.2	10.2	8.2	8.6	8.4
Ba	880	360	382	183.5	175.5	1565	1185	1285	1400	1330	1835
Be	2.54	2.62	3.16	0.97	0.88	3.85	4.47	4.16	2.79	2.68	3.06
Bi	0.35	0.31	0.26	0.11	0.09	0.04	0.37	0.07	0.14	0.12	0.03
Ca	2.42	4.22	2.61	2.69	2.75	2.66	2.63	2.69	2.54	2.77	2.80
Cd	0.08	0.17	0.13	0.07	0.07	0.02	0.03	0.07	<0.02	<0.02	<0.02
Ce	78.8	82.8	79.3	42.8	41.7	63.8	61.2	61.0	55.7	68.2	134.0
Co	10.7	16.0	16.3	11.0	11.5	10.8	10.7	10.8	8.3	9.3	9.4
Cr	110	120	170	230	170	200	160	150	180	160	170
Cs	9.87	17.15	17.70	3.87	3.53	2.32	3.11	4.70	5.74	4.36	7.84
Dy	4.97	5.38	4.50	3.57	3.90	3.01	2.89	2.73	2.58	2.53	2.85
Er	2.71	3.01	2.75	2.16	2.37	1.46	1.53	1.48	1.44	1.39	1.36
Eu	1.03	1.31	1.08	0.82	0.78	1.25	1.14	1.20	1.11	1.19	1.82
Ga	21.3	25.1	25.8	11.8	10.7	17.7	18.5	16.8	19.1	18.6	19.0
Gd	5.52	5.73	4.86	3.58	3.44	4.05	3.85	3.86	3.63	3.25	5.00

Ge	0.11	0.18	0.10	0.06	0.07	0.14	0.12	0.13	0.11	0.09	0.16
Hf	4.8	4.4	4.7	5.2	5.4	4.9	4.9	5.8	5.5	4.9	6.1
Ho	1.00	1.11	0.93	0.78	0.85	0.57	0.59	0.53	0.53	0.51	0.53
In	0.067	0.102	0.086	0.037	0.032	0.019	0.011	0.025	0.021	0.033	0.022
K	2.13	2.57	2.67	1.01	0.96	3.92	3.88	4.22	3.29	3.53	3.51
La	40.5	41.1	39.3	22.3	21.1	32.9	32.2	34.1	28.5	38.6	69.5
Li	73.2	77.7	78.2	22.1	20.6	7.5	9.5	8.1	10.7	8.7	14.9
Lu	0.42	0.45	0.41	0.32	0.37	0.23	0.22	0.21	0.22	0.20	0.19
Mg	1.55	1.24	1.21	0.82	0.79	1.38	1.42	1.37	1.04	1.05	1.69
Mn	695	770	528	453	443	440	354	391	264	297	292
Mo	2.36	1.87	1.44	10.30	6.84	13.75	8.52	8.67	10.85	10.60	7.03
Na	1.30	0.67	0.69	1.33	1.29	2.44	2.59	2.54	2.70	2.64	2.68
Nb	15.9	16.2	16.9	7.7	7.4	12.9	14.1	12.6	11.5	10.5	10.8
Nd	32.2	33.5	31.4	19.8	18.4	27.2	23.9	24.9	23.5	22.1	50.8
Ni	40.2	48.9	51.5	29.4	27.9	17.4	16.7	16.5	11.9	11.3	41.0
P	620	750	400	360	360	1520	1500	1560	990	970	1340
Pb	29.5	20.3	22.3	10.6	9.7	16.1	13.1	17.0	10.3	11.4	9.2
Pr	8.57	8.98	8.51	5.04	4.82	7.27	6.78	6.75	6.24	7.22	14.85
Rb	128.5	188.0	196.5	55.4	51.8	147.0	146.5	155.0	134.5	127.0	125.5
Re	<0.002	0.003	0.002	<0.002	<0.002	0.003	0.002	0.002	<0.002	<0.002	0.002
S	0.01	0.01	0.02	0.03	0.02	0.03	0.02	0.14	0.32	0.40	0.01
Sb	0.49	1.18	1.04	0.93	0.70	0.08	0.17	0.24	0.29	0.21	0.67
Sc	15.0	15.2	16.3	11.6	10.5	12.7	13.1	12.1	8.9	9.0	9.4
Se	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Sm	5.99	6.35	5.71	4.00	3.76	5.21	4.88	4.92	4.23	4.31	8.15
Sn	3.2	4.5	4.5	1.9	1.4	2.3	1.5	2.1	2.2	2.8	1.7

Sr	331	291	247	130.5	128.5	890	845	751	1010	1033	1560
Ta	1.00	1.16	1.16	0.40	0.39	0.89	1.07	0.98	0.77	0.75	0.76
Tb	0.87	0.90	0.77	0.58	0.59	0.55	0.52	0.51	0.48	0.47	0.58
Te	0.06	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Th	14.90	17.05	17.15	7.15	6.65	15.20	19.45	19.00	13.75	13.55	20.0
Ti	0.410	0.429	0.399	0.272	0.265	0.321	0.313	0.327	0.292	0.295	0.319
Tl	0.67	0.86	0.96	0.29	0.26	0.50	0.52	0.56	0.66	0.67	0.71
Tm	0.40	0.45	0.41	0.32	0.35	0.22	0.22	0.22	0.21	0.20	0.19
U	3.09	3.26	3.26	1.60	1.69	4.39	2.98	5.17	3.87	3.09	3.67
V	181	191	190	113	100	121	119	107	100	94	91
W	2.1	3.0	2.9	1.2	1.1	2.5	1.5	2.1	5.4	2.8	1.5
Y	26.9	30.0	25.5	21.6	23.4	16.0	16.2	14.8	15.0	13.8	14.6
Yb	2.55	2.85	2.61	2.12	2.32	1.43	1.41	1.42	1.39	1.31	1.19
Zn	83	105	99	50	52	28	24	28	22	24	24
Zr	183	160	164	203	215	182	177	205	206	189	235

Abbreviation: Py, Pyrite; Ccp, chalcopyrite; Mol, molybdenite; Po, pyrrhotite; Qz, quartz; Chl, chlorite; Ep, epidote; Ill, illite.

Table S2. Calculated Mo isotope compositions of metal sulfides for Raleigh fractionation modeling.

$\delta^{65}\text{Mo}_{\text{initial}}$ (‰)	-0.16				0.21							
metal sulfides	Molybdenite				Pyrite-chalcopyrite							
$\text{Mo}_{\text{initial}}$ (ppm)									10	50	100	150
$\alpha_{\text{liquid-sulfide}}$	0.9987	0.9985	0.9990	0.9992	0.9993	0.9995	0.9996	0.9998				
温度	332°C	300°C	400°C	500°C								
f	$\delta^{65}\text{Mo}_{\text{fluid}}$ (‰)				Mo_{fluid} (ppm)							
1.00	-0.160	-0.160	-0.160	-0.160	0.210	0.210	0.210	0.210	10	50	100	150
0.95	-0.093	-0.083	-0.109	-0.119	0.246	0.236	0.231	0.220	10	48	95	143
0.90	-0.023	-0.002	-0.055	-0.076	0.284	0.263	0.252	0.231	9	45	90	135
0.85	0.051	0.084	0.003	-0.030	0.324	0.291	0.275	0.243	9	43	85	128
0.80	0.130	0.175	0.063	0.019	0.366	0.322	0.299	0.255	8	40	80	120
0.75	0.214	0.272	0.128	0.070	0.411	0.354	0.325	0.268	8	38	75	113
0.70	0.304	0.375	0.197	0.125	0.460	0.388	0.353	0.281	7	35	70	105
0.65	0.400	0.486	0.271	0.185	0.512	0.425	0.382	0.296	7	33	65	98
0.60	0.504	0.606	0.351	0.249	0.568	0.465	0.414	0.312	6	30	60	90
0.55	0.617	0.737	0.438	0.318	0.629	0.509	0.449	0.330	6	28	55	83
0.50	0.741	0.880	0.533	0.395	0.695	0.557	0.487	0.349	5	25	50	75
0.45	0.878	1.038	0.639	0.479	0.769	0.609	0.530	0.370	5	23	45	68
0.40	1.032	1.215	0.757	0.573	0.852	0.668	0.577	0.393	4	20	40	60
0.35	1.205	1.416	0.890	0.680	0.945	0.735	0.630	0.420	4	18	35	53
0.30	1.406	1.647	1.045	0.803	1.053	0.812	0.692	0.451	3	15	30	45
0.25	1.644	1.921	1.227	0.949	1.181	0.904	0.765	0.487	3	13	25	38
0.20	1.934	2.257	1.450	1.128	1.337	1.015	0.854	0.532	2	10	20	30
0.15	2.309	2.689	1.739	1.359	1.539	1.159	0.969	0.590	2	8	15	23
0.10	2.837	3.299	2.145	1.683	1.823	1.362	1.132	0.671	1	5	10	15

Table S3. Parameters used for the calculation of isotopic fractionation in different Mo species at varied oxidation state.

	Phase	Cation charge	Coordination	Average bond valence		Bond length	Force constant	Reference
				\bar{Z}_{Mo}	$C_{N_{\text{Mo}}}$			
$\text{Mo}^{6+}\text{O}_4^{2-}$	Melt, fluid	6	4	1.5	0.5	1.76	349.5	Farges et al. (2006)
Mo^{4+}S_2	Molybdenite	4	6	0.67	0.67	2.387	83.86	Bart and Ragaini (1980)
Mo^{6+}O_3	Mineral	6	6	1	0.67	1.98	219.3	Kihlborg (1963)
Metal- Mo^{6+}O	Oxide	6	4	1.5	0.5	1.8	326.7	Hardcastle and Wachs (1990)
Mo^{4+}O_2	Mineral, melt	4	6	0.67	0.67	2.01	140.4	Brandt et al. (1967)

Table S4. Comparison of Mo isotope compositions of the reference materials analyzed in this study to the literature values.

Sample	Rock type	$\delta^{98}\text{Mo}$ (‰)	2SD	n	Reference
Seawater	Atlantic seawater	2.06	0.04	8 ^a	This study
		2.04	0.05		Zhao et al. (2016)
		2.04	0.07		Pearce et al. (2009)
		2.09	0.05		Greber et al. (2012)
		2.00	0.03		Li et al. (2014)
AGV-2 (USGS ^b)	Andesite	-0.23	0.04	8 ^a	This study
		-0.14	0.05		Zhao et al. (2016)

^a Number of analyses

^b USGS: United States Geological Survey

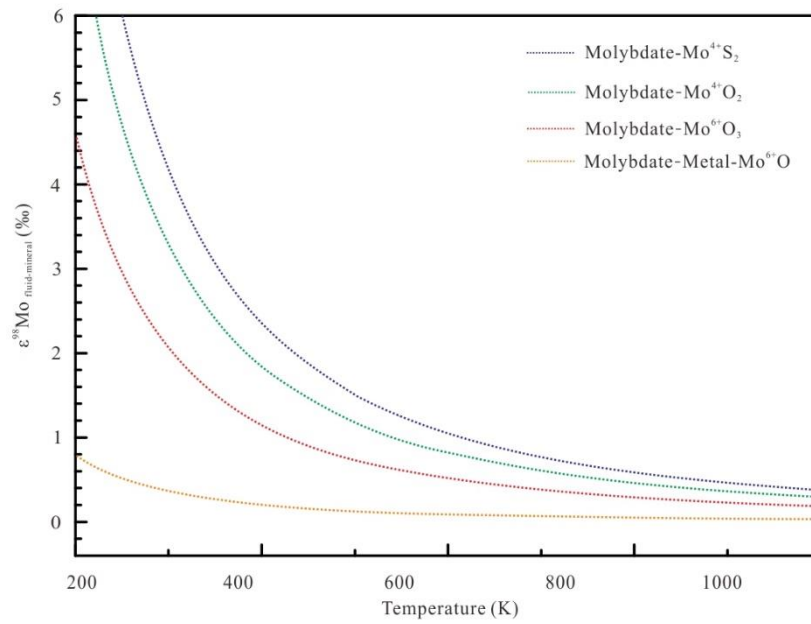


Fig. S1. Modelled isotopic fractionation $\epsilon^{98}\text{Mo}$ fluid-mineral between oxidized molybdate and different magmatic-hydrothermal phases as a function of temperature were calculated according to Young et al. (2015). These curves depict the combined effect of valence, coordination, and anion (O vs. S) changes.

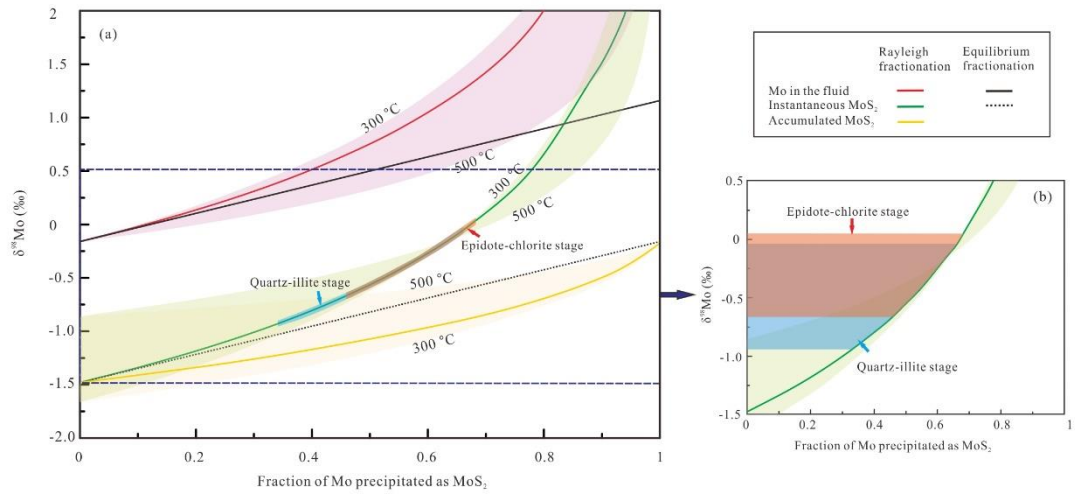


Fig. S2. Quantitative model of Rayleigh fractionation between ore-forming fluids and molybdenite at 332°C. The light bands illustrate the variation of the fractionation curve in the temperature range of 350–550°C.

Supplementary Text: The Rayleigh fractionation modelling

Rayleigh fractionation was performed to model the Mo isotope compositions within mineralizing fluids as the metal sulfides were progressively precipitated. The $\delta^{98}\text{Mo}$ for the remaining ore-forming fluid is calculated using an approximate form of the Rayleigh distillation equation:

$$\delta^{98}\text{Mo}_{\text{fluid}} = (\delta^{98}\text{Mo}_0 + 1000) f^{(\alpha-1)} - 1000 \quad (1)$$

Where $\delta^{98}\text{Mo}_{\text{fluid}}$ and $\delta^{98}\text{Mo}_0$ are the Mo isotope composition for the residual fluid and initial fluid, respectively. f and α refers to the fraction of Mo remaining in fluid and the sulfide-fluid fractionation factor, respectively. We assume that the $\delta^{98}\text{Mo}$ for the initial hydrothermal fluid is approximated to the derived-magma prior to sulfide precipitation, that is, -0.16‰. The Mo isotope fractionation factor for molybdenite as a function of temperature was calculated to be 332 °C corresponding to 0.9987 (Fig. S1). While the Mo isotopic fractionation factor for Fe-Cu sulfides is derived from the equation: $\Delta^{98}\text{Mo}_{\text{fluid-sulfide (measured)}} = 1000 \ln\alpha_{\text{fluid-sulfide}}$, and we assume that $\Delta^{98}\text{Mo}_{\text{fluid-sulfide}}$ is -0.37‰, which corresponds to an α of 0.9996. The isotope composition of the Mo remaining in the ore-forming fluid can thus be calculated (Table S2).

3. References

- Bart, J. and Ragaini, V. (1980) Molybdenum-sulphur bond-strength bond-length relationships. Phosphorus Sulfur and Silicon and The Related Elements 8, 161-169.
- Brandt, B., Skapski, A., Thom, E., Stoll, E., Eriksson, G., Blinc, R., Paušak, S., Ehrenberg, L. and Dumanović, J. (1967) A Refinement of the Crystal Structure of Molybdenum Dioxide. Acta Chemica Scandinavica - ACTA CHEM SCAND 21, 661-672.
- Farges, F., Siewert, R., Ponader, C., Brown, G., Pichavant, M. and Behrens, H. (2006) Structural environments around molybdenum in silicate glasses and melts. II. Effect of temperature, pressure, H₂O, halogens and sulfur. Canadian Mineralogist 44, 755-773.
- Greber, N.D., Siebert, C., Nagler, T.F. and Pettke, T. (2012) $\delta^{98}/^{95}\text{Mo}$ values and Molybdenum Concentration Data for NIST SRM 610, 612 and 3134: Towards a Common Protocol for

Reporting Mo Data. *Geostandards and Geoanalytical Research* 36.

Hardcastle, F. and Wachs, I. (1990) Determination of Molybdenum–Oxygen Bond Distances and Bond Orders by Raman Spectroscopy. *Journal of Raman Spectroscopy* 21, 683-691.

Kihlborg, L. (1963) The Crystal Chemistry of Molybdenum Oxides. *The Crystal Chemistry of Molybdenum Oxides*.

Li, J., Liang, X.R., Zhong, L.F., Wang, X.C., Ren, Z.Y., Sun, S.L., Zhang, Z.F. and Xu, J.F. (2014) Measurement of the Isotopic Composition of Molybdenum in Geological Samples by MC-ICP-MS using a Novel Chromatographic Extraction Technique. *Geostandards & Geoanalytical Research* 38, 345-354.

Pearce, C., Cohen, A. and Parkinson, I. (2009) Quantitative Separation of Molybdenum and Rhenium from Geological Materials for Isotopic Determination by MC-ICP-MS. *Geostandards and Geoanalytical Research* 33.

Young, E.D., Manning, C.E., Schauble, E.A., Shahar, A., Macris, C.A., Lazar, C. and Jordan, M. (2015) High-temperature equilibrium isotope fractionation of non-traditional stable isotopes: Experiments, theory, and applications. *Chemical Geology* 395, 176-195.

Zhao, P.P., Zhang, L., Wang, Z.B., Kong, D.X., Ma, J.L., Wei, G.G. and Xu, J.F. (2016) Molybdenum Mass Fractions and Isotopic Compositions of International Geological Reference Materials. *Geostandards and Geoanalytical Research* 40.