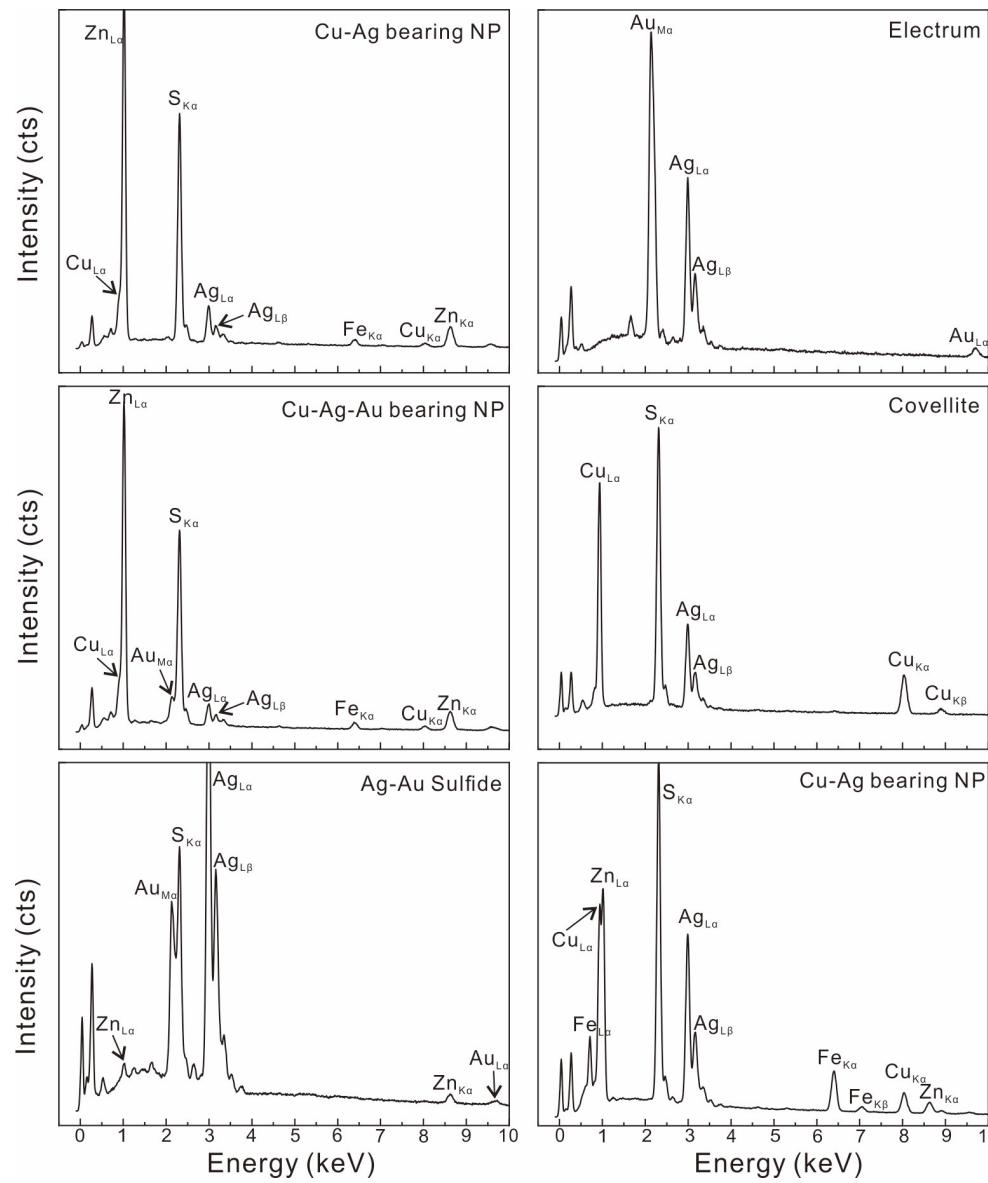
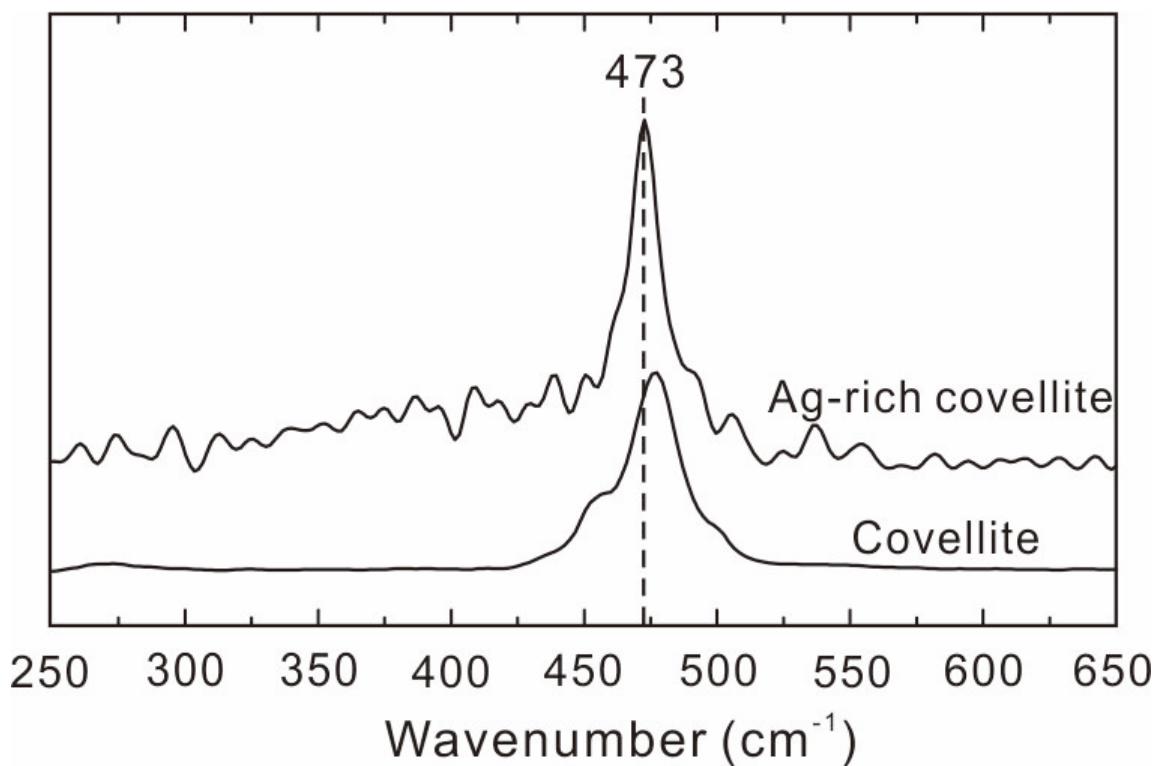


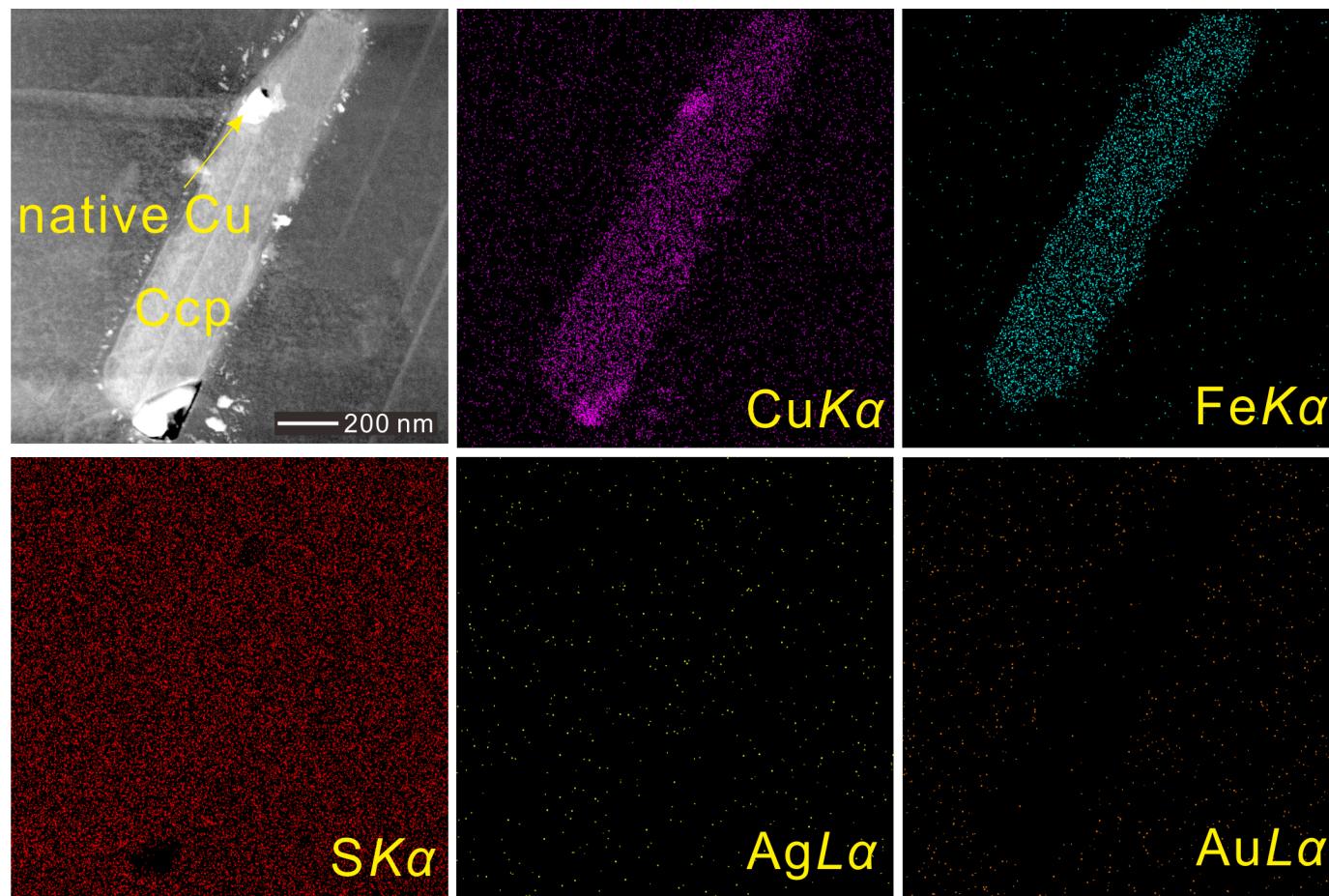
**FIGURE S1.** Representative reflected light photomicrograph of Maluntou sulfides. Abbreviations: Sp = sphalerite, Ccp = chalcopyrite, Gn = galena.



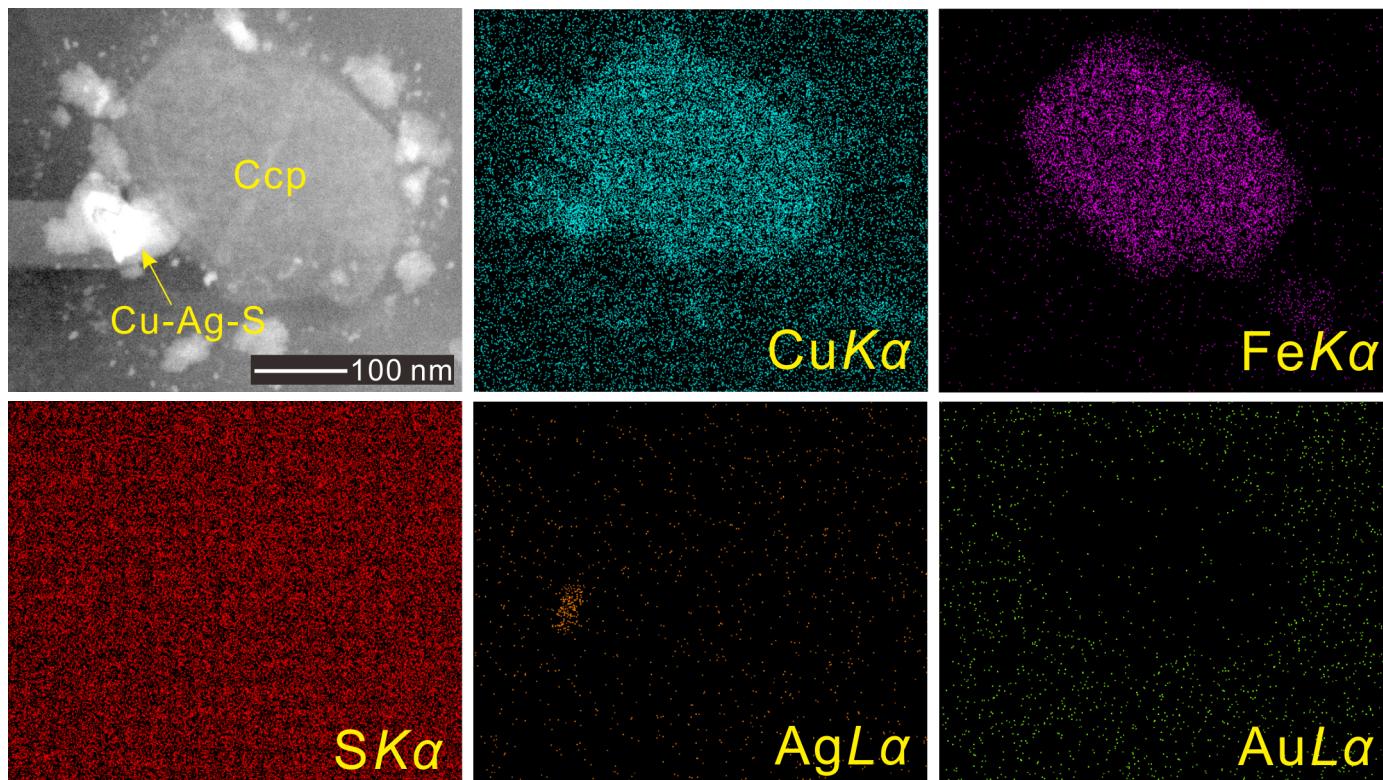
**FIGURE S2.** Representative EDS spectra for the Ag-(Au)-bearing phases shown in the BSE images.



**FIGURE S3.** Representative room-temperature Raman spectrum of natural Ag-rich covellite from the Maluntou deposit. Standard covellite is collected from the RRUFF database (<http://rruff.info/>). Selected wavenumber range is from 250 and 650 cm<sup>-1</sup>.



**FIGURE S4.** STEM and EDS maps showing the distribution of native Cu. The Cu signal is partially from the TEM grid.



**FIGURE S5.** STEM and EDS maps showing the distribution of Cu-Ag-S nanoparticle. The Cu signal is partially from the TEM grid.

**Table S1.** Representative EMPA data (in wt%) of sphalerites from the Maluntou deposit.

No	Fe (0.03)	Cu (0.05)	Zn (0.06)	Pb (0.05)	S (0.01)	As (0.02)	Au (0.02)	Sb (0.01)	Ni (0.02)	Ag (0.006)	Mn (0.01)	Total
1	1.29	1.33	62.88	0	32.79	b.l.	b.l.	0.02	b.l.	b.l.	0.22	99.11
2	2.38	1.82	62.55	0.22	32.57	b.l.	b.l.	b.l.	0.02	b.l.	0.19	99.30
3	1.82	1.64	62.74	0.14	32.40	b.l.	0.02	b.l.	b.l.	b.l.	0.23	98.28
4	0.13	b.l.	65.81	b.l.	32.68	b.l.	b.l.	0.02	b.l.	b.l.	0.01	99.57
5	0.18	b.l.	66.13	0.09	32.47	b.l.	b.l.	b.l.	b.l.	b.l.	0.02	98.29
6	0.22	0.09	66.47	b.l.	32.20	b.l.	b.l.	b.l.	b.l.	b.l.	0.02	98.97
7	0.14	0.06	66.41	b.l.	32.03	b.l.	b.l.	b.l.	b.l.	b.l.	0.05	98.35
8	0.18	0.03	65.94	b.l.	32.29	0.03	b.l.	b.l.	b.l.	b.l.	0.03	99.15

Note: b.l. = below detection limit; Detection limits are presented below each element label.