

APPENDIX (Deposit item)

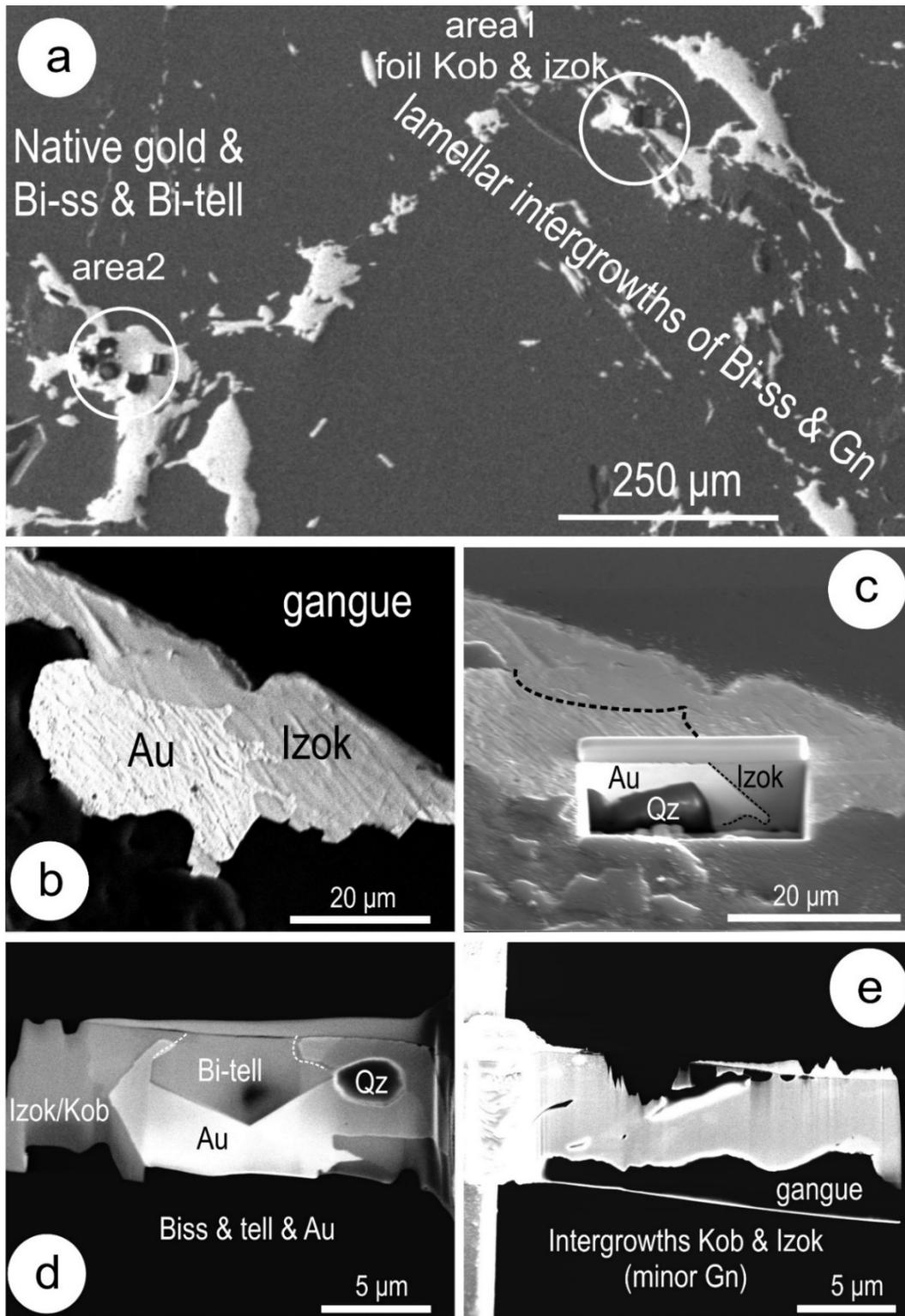


Figure A1. Secondary electron images showing the studied sulfosalt assemblage. (a) Sulfosalt (Bi-ss) + Au + Bi-telluride (Bi-tell) assemblages along stringer zones; minor galena (Gn) present. Note location of FIB-cuts as marked. Native gold-izoklakeite assemblage on the polished block surface (b) and in cross-section (c). (d) Foil showing Bi-tell, Au and izoklakeite (Izok) association. Gangue present as quartz (Qz). (e) Foil with kobellite (Kob) and Izok intergrowths studied by HAADF STEM imaging.

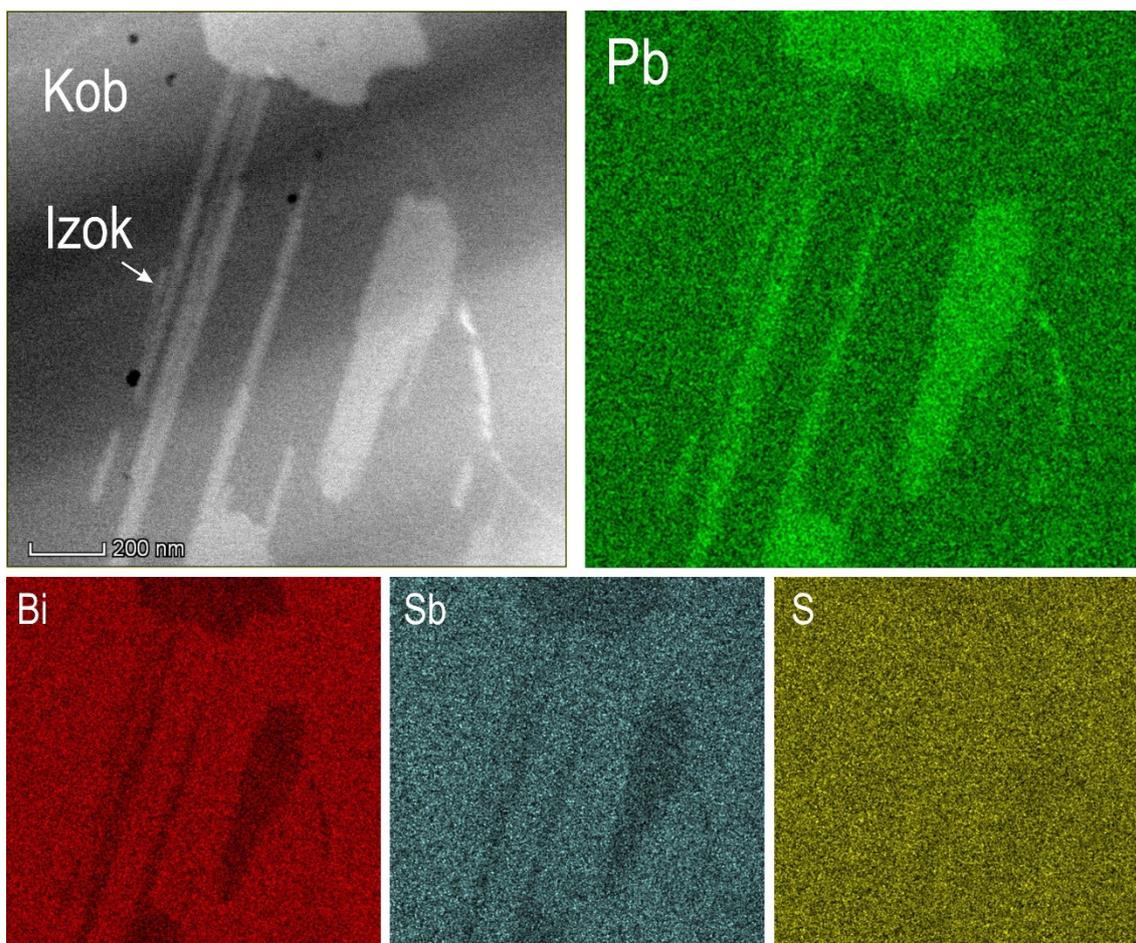


Figure A2. EDS-STEM maps and HAADF image (top left) showing an area with nanoscale intergrowths of kobellite (Kob) and izoklakeite (Izok). Note Izok is richer in Pb than Kob.

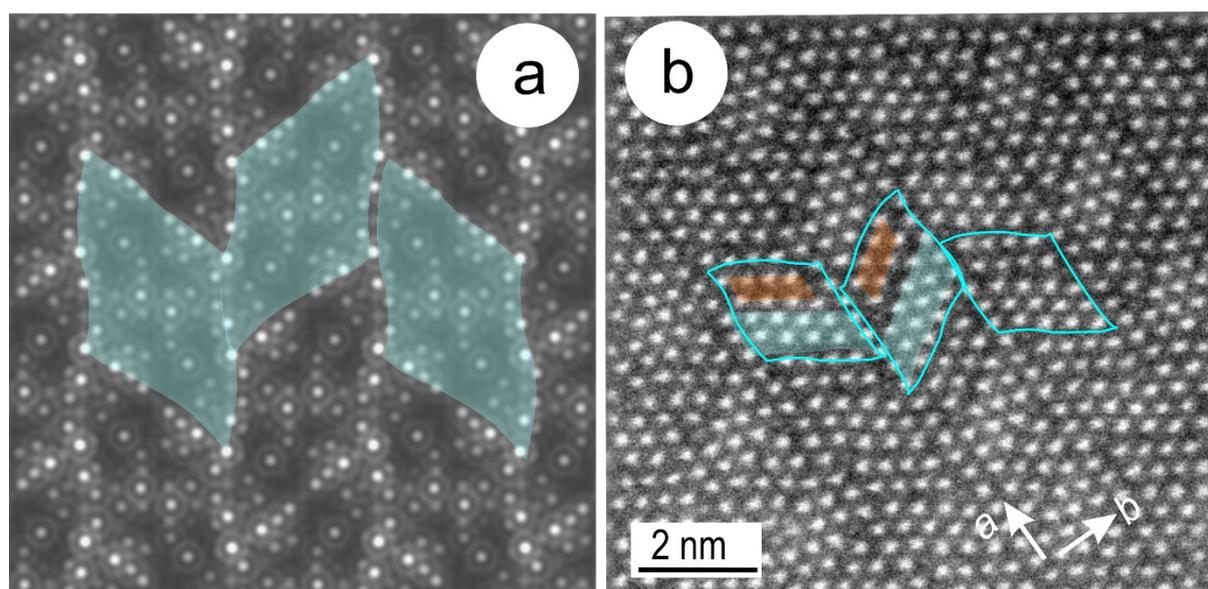


Figure A3. (a) STEM simulation of kobellite on [001] zone axis using crystal structures from Mische (1971). The motif combining e group of PbS + SnS motifs is shaded in blue. (b) HAADF STEM image of kobellite with the same motif outlined in blue. The PbS and SnS motifs shaded in blue and orange, respectively.

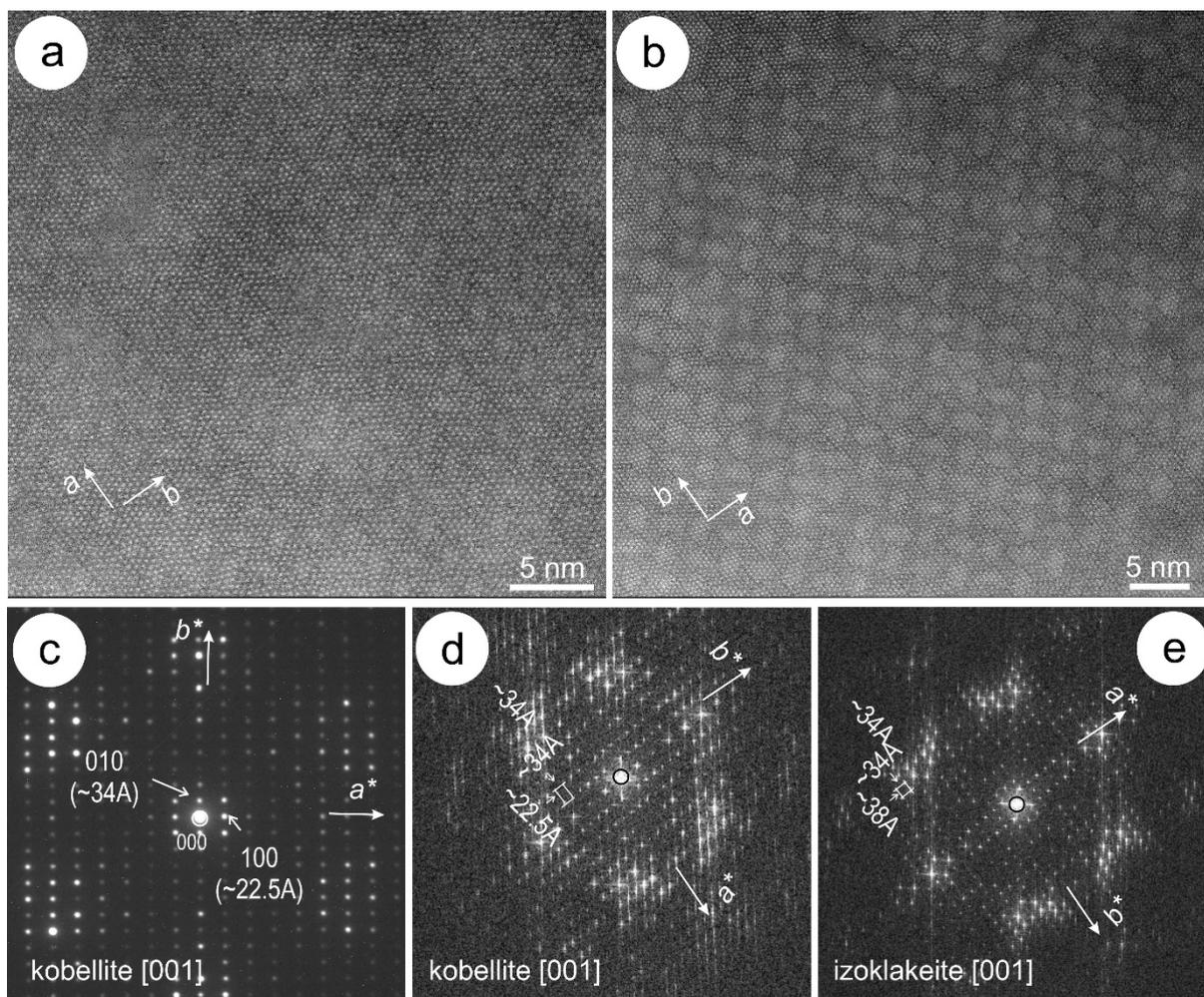


Figure A4. HAADF STEM images of kobellite (a) and izoklakeite (b) on [001] zone axis. Selected area of electron diffraction (SAED) in (c) showing kobellite on [001] zone axis. (d, e) Fast Fourier Transforms (FFT) of kobellite and izoklakeite on [001] zone axis obtained from images in (a) and (b), respectively. Note marked d measurements corresponding to odd reflections of the type $h00 \neq 2n$ and $0k0 \neq 2n$ which are incompatible with symmetry in $Pnmm$ space group. See text for additional explanation.

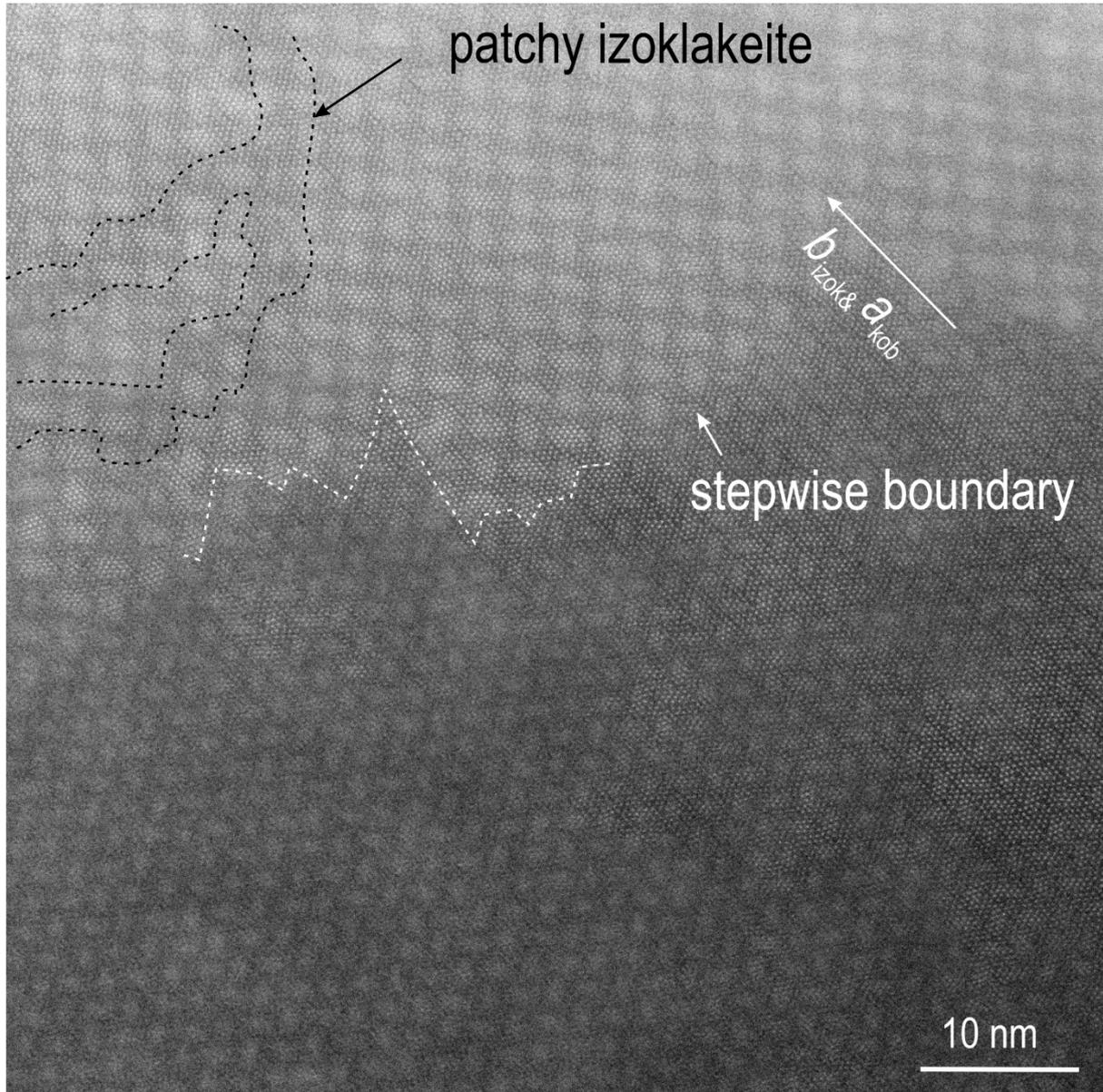


Figure A5. HAADF STEM image showing secondary replacement of izoklakeite observed as irregular slabs of kobellite ‘intruding’ into izoklakeite in associations which display step-wise contacts between the two species as marked.

EPMA Methodology

EPMA data was obtained on a Cameca SX-Five Electron Probe Microanalyser (EPMA) running Probe Software (Donovan et al. 2016). Microprobe operating conditions were 20 keV accelerating voltage, 20 nA beam current, 40° takeoff angle, and a beam size of 1 μm . The following elements were measured: Cu ($K\alpha$), Ag ($L\alpha$), Pb ($M\alpha$), Cd ($L\alpha$), Bi ($M\alpha$), Sb ($L\alpha$), S ($K\alpha$), Te ($L\alpha$), and Se ($L\alpha$). Iron ($K\alpha$) and As ($L\alpha$) were also measured but were below minimum detection limits (0.03 and 0.04 wt%, respectively) in all analyses. Count times were 20 s for both standards and unknowns. Standards used were chalcopyrite (Cu, Fe), Ag_2Te (Ag, Te), galena (Pb), Bi_2Se_3 (Bi, Se), stibnite (Sb), Bi_2Se_3 (Se), CdS (Cd, S), and GaAs (As). Average minimum limits of detection (wt%) were 0.03 (Cu), 0.07 (Ag), 0.05 (Pb), 0.07 (Cd), 0.05 (Bi), 0.03 (Sb), 0.01 (S), 0.04 (Te), and 0.03 (Se). Detection limits were calculated at 99% confidence levels (3σ) taking peak and background count times, beam current, and the concentration and X-ray intensity of the element in the standard into account.

Donovan, J.J., Singer, J.W., and Armstrong, J.T. (2016) A new EPMA method for fast trace element analysis in simple matrices. *American Mineralogist*, 101, 1839–1853.

Table A1. Electron probe microanalytical data for izoklakeite																								
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	Mean (n=22)	
Cu	1.07	1.04	1.09	1.03	1.18	1.01	1.25	1.34	1.39	1.23	1.17	1.21	1.14	1.22	1.16	1.12	1.13	1.16	1.16	1.17	1.26	1.19	1.17	
Ag	0.12	0.17	0.26	0.42	0.54	0.17	0.22	0.48	0.44	0.42	0.17	0.32	0.25	0.23	0.34	0.32	0.17	0.13	0.13	0.30	0.20	0.22	0.27	
Fe	<mdl	0.12	0.08	<mdl	0.04	<mdl	<mdl	0.01																
Cd	0.11	<mdl	0.10	<mdl	<mdl	0.11	<mdl	0.07	0.11	0.08	<mdl	0.15	<mdl	0.03										
Pb	50.55	52.08	51.13	53.35	48.23	53.58	48.81	46.90	45.99	46.80	48.48	47.62	50.40	48.45	48.49	50.86	47.80	47.57	47.21	47.30	47.72	48.18	48.98	
As	<mdl	<mdl	<mdl	0.04	0.04	<mdl	0.12	<mdl	0.01															
Sb	7.99	7.37	7.10	7.35	8.55	7.20	8.53	7.26	7.70	8.48	7.77	7.56	7.10	7.68	7.24	7.01	8.11	8.65	7.62	8.52	8.16	8.03	7.77	
Bi	23.62	23.58	25.07	21.98	25.17	21.58	24.19	27.08	27.74	25.84	26.09	25.95	24.05	25.54	25.99	25.20	25.67	25.80	27.17	24.82	24.78	24.91	25.08	
S	16.35	16.62	16.65	16.81	17.33	16.43	16.93	17.16	17.48	16.70	16.93	16.92	16.56	16.68	16.97	16.89	16.63	16.64	16.63	16.82	16.79	16.87	16.81	
Te	0.10	0.09	0.08	0.05	0.09	0.11	0.04	<mdl	<mdl	0.09	<mdl	0.05	0.08	0.07	0.08	0.07	0.07	0.08	0.07	0.07	0.09	0.09	0.07	
Se	0.05	0.05	0.07	0.07	0.07	0.08	0.07	0.07	0.08	0.07	0.07	0.07	0.06	0.10	0.06	0.09	0.06	0.07	0.08	0.10	0.09	0.07	0.07	
Total	99.96	101.00	101.56	101.10	101.21	100.27	100.03	100.49	101.00	99.71	100.67	99.83	99.65	99.95	100.32	101.57	99.63	100.11	100.11	99.10	99.19	99.57	100.27	
<i>Calculated formulae (based on 96 metals and 210 apfu)</i>																								
Cu	3.72	3.56	3.73	3.50	3.95	3.49	4.24	4.53	4.62	4.22	3.98	4.14	3.96	4.18	3.95	3.82	3.88	3.99	3.99	4.00	4.31	4.06	3.99	
Ag	0.25	0.35	0.52	0.85	1.07	0.35	0.43	0.95	0.86	0.84	0.33	0.65	0.51	0.46	0.68	0.64	0.34	0.27	0.27	0.60	0.40	0.44	0.55	
Fe	-	-	-	-	-	-	-	0.46	0.31	-	-	-	-	-	-	-	-	-	0.14	-	-	-	0.04	
Cu+Ag+Fe	3.97	3.90	4.25	4.35	5.02	3.84	4.68	5.95	5.79	5.06	4.31	4.79	4.47	4.64	4.63	4.45	4.23	4.26	4.41	4.60	4.71	4.50	4.58	
Pb	53.77	54.84	53.63	55.79	49.39	56.93	50.89	48.51	46.98	49.11	50.57	49.83	53.48	51.04	50.67	52.99	50.49	50.00	49.80	49.69	50.14	50.54	51.32	
Cd	0.20	-	0.18	-	-	0.21	-	0.14	0.20	0.16	-	0.28	-	-	-	-	-	-	-	-	-	-	0.06	
Pb+Cd	53.97	54.84	53.81	55.79	49.39	57.14	50.89	48.65	47.18	49.28	50.57	50.12	53.48	51.04	50.67	52.99	50.49	50.00	49.80	49.69	50.14	50.54	51.38	
As	-	-	-	0.11	0.11	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.33	0.03	
Sb	14.46	13.20	12.68	13.07	14.90	13.01	15.13	12.78	13.38	15.14	13.79	13.46	12.83	13.76	12.87	12.44	14.58	15.47	13.67	15.24	14.60	14.34	13.85	
Bi	24.91	24.63	26.07	22.79	25.55	22.73	25.00	27.77	28.10	26.89	26.99	26.92	25.30	26.67	26.92	26.03	26.89	26.89	28.41	25.85	25.81	25.91	26.05	
Bi+Sb+As	39.37	37.83	38.74	35.97	40.56	35.75	40.13	40.55	41.47	42.03	40.78	40.39	38.13	40.43	39.79	38.47	41.47	42.36	42.09	41.09	40.74	40.25	39.93	
Total M	97.31	96.58	96.81	96.11	94.97	96.73	95.70	95.15	94.44	96.37	95.66	95.29	96.08	96.10	95.09	95.92	96.19	96.62	96.29	95.39	95.60	95.29	95.89	
S	112.36	113.13	112.85	113.60	114.70	112.84	114.05	114.67	115.35	113.29	114.15	114.45	113.60	113.52	114.62	113.71	113.54	113.04	113.39	114.22	114.02	114.35	113.79	
Te	0.18	0.15	0.14	0.09	0.15	0.19	0.07	-	-	0.15	0.00	0.08	0.14	0.11	0.13	0.12	0.12	0.14	0.12	0.11	0.15	0.15	0.11	
Se	0.15	0.14	0.20	0.20	0.18	0.23	0.18	0.18	0.21	0.19	0.19	0.18	0.18	0.27	0.17	0.25	0.16	0.20	0.21	0.28	0.24	0.20	0.20	
S(+Te+Se)	112.69	113.42	113.19	113.89	115.03	113.27	114.30	114.85	115.56	113.63	114.34	114.71	113.92	113.90	114.91	114.08	113.81	113.38	113.71	114.61	114.40	114.71	114.11	
Sb/(Sb+Bi)	0.37	0.35	0.33	0.36	0.37	0.36	0.38	0.32	0.32	0.36	0.34	0.33	0.34	0.34	0.32	0.32	0.35	0.37	0.32	0.37	0.36	0.36	0.35	

Table A2. Electron probe microanalytical data for kobellite

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	Mean (n=22)
Cu	2.29	2.35	2.36	1.84	1.88	1.91	2.04	1.95	1.84	1.88	1.91	2.04	1.95	1.87	1.81	1.88	1.79	1.80	1.89	1.83	1.84	1.97	1.95
Ag	<mdl	0.09	<mdl	<mdl	<mdl	0.08	<mdl	<mdl	<mdl	<mdl	0.07	0.01											
Fe	0.04	0.04	<mdl	0.30	0.25	0.29	0.20	0.25	0.30	0.25	0.29	0.20	0.25	0.26	0.26	0.24	0.29	0.27	0.25	0.27	0.27	0.20	0.23
Cd	0.15	0.12	<mdl	0.07	0.17	<mdl	<mdl	0.10	0.07	0.17	<mdl	<mdl	0.10	0.10	0.10	0.09	<mdl	0.10	0.07	0.11	0.10	0.14	0.08
Pb	35.11	35.04	34.39	33.71	34.61	34.30	33.60	33.50	33.71	34.61	34.30	33.60	33.49	34.91	34.39	33.70	34.78	34.17	34.38	34.73	34.27	34.39	34.26
As	0.04	0.05	<mdl	<mdl	<mdl	<mdl	<mdl	<mdl	<mdl	<mdl	<mdl	0.00											
Sb	12.44	12.39	12.67	12.10	12.04	11.97	11.53	12.21	12.09	12.03	11.96	11.52	12.20	12.25	12.08	11.06	11.08	11.27	12.69	12.17	12.16	11.69	11.98
Bi	31.64	30.88	31.49	32.64	31.47	31.29	32.01	32.26	32.64	31.47	31.29	32.01	32.26	33.42	33.39	33.40	34.30	33.65	32.65	33.28	33.19	34.04	32.49
S	18.14	17.97	17.92	18.00	18.32	18.17	17.68	17.74	18.00	18.32	18.17	17.68	17.74	18.42	18.54	17.97	18.74	18.45	18.44	18.48	18.44	18.35	18.17
Te	<mdl	<mdl	<mdl	<mdl	<mdl	0.04	<mdl	<mdl	<mdl	0.00													
Se	<mdl	0.03	0.04	0.07	<mdl	0.06	0.05	0.04	0.07	<mdl	0.06	0.05	0.04	0.06	0.04	0.07	0.05	0.05	<mdl	0.06	0.05	0.06	0.04
Total	99.84	98.98	98.88	98.73	98.74	98.00	97.11	98.04	98.72	98.73	97.98	97.10	98.03	101.30	100.62	98.41	101.11	99.76	100.41	100.93	100.33	100.91	99.21
<i>Calculated formulae (based on 56 metals and 126 apfu)</i>																							
Cu	4.42	4.58	4.59	3.59	3.64	3.72	4.05	3.83	3.59	3.64	3.72	4.05	3.83	3.57	3.46	3.70	3.40	3.46	3.62	3.50	3.54	3.78	3.78
Ag	-	0.10	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.09	-	-	-	-	0.08	0.01
Fe	0.09	0.09	-	0.67	0.55	0.65	0.45	0.55	0.67	0.55	0.65	0.45	0.55	0.57	0.56	0.53	0.63	0.60	0.55	0.59	0.59	0.43	0.50
Cu+Ag+Fe	4.52	4.76	4.59	4.25	4.19	4.38	4.49	4.39	4.25	4.19	4.38	4.49	4.39	4.14	4.02	4.23	4.12	4.06	4.16	4.09	4.13	4.29	4.30
Pb	20.78	20.89	20.56	20.18	20.57	20.52	20.48	20.25	20.18	20.57	20.53	20.48	20.25	20.43	20.15	20.31	20.30	20.20	20.17	20.34	20.14	20.22	20.39
Cd	0.16	0.14	-	0.08	0.18	-	-	0.12	0.08	0.18	-	-	0.12	0.11	0.11	0.10	-	0.11	0.07	0.12	0.10	0.15	0.09
Pb+Cd	20.94	21.03	20.56	20.26	20.75	20.52	20.48	20.36	20.26	20.75	20.53	20.48	20.36	20.54	20.26	20.41	20.30	20.31	20.24	20.45	20.25	20.36	20.47
As	0.06	0.09	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.01
Sb	12.53	12.58	12.89	12.33	12.18	12.19	11.96	12.56	12.32	12.17	12.18	11.95	12.55	12.19	12.05	11.33	11.00	11.34	12.67	12.13	12.16	11.69	12.13
Bi	18.56	18.26	18.66	19.38	18.54	18.56	19.35	19.33	19.38	18.54	18.57	19.35	19.33	19.39	19.40	19.95	19.84	19.72	18.98	19.32	19.34	19.84	19.16
Bi+Sb+As	31.15	30.92	31.55	31.71	30.72	30.75	31.30	31.89	31.70	30.71	30.74	31.30	31.88	31.58	31.44	31.28	30.84	31.06	31.65	31.45	31.50	31.53	31.30
Total M	56.61	56.71	56.70	56.22	55.66	55.65	56.27	56.64	56.21	55.65	55.65	56.27	56.64	56.26	55.72	55.92	55.25	55.43	56.05	55.99	55.87	56.19	56.07
S	69.39	69.24	69.24	69.67	70.34	70.26	69.64	69.30	69.68	70.35	70.27	69.65	69.30	69.64	70.22	69.97	70.67	70.49	69.91	69.93	70.05	69.72	69.86
Te	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.04	-	-	-	0.00
Se	-	0.05	0.06	0.11	-	0.09	0.09	0.06	0.11	-	0.09	0.09	0.06	0.10	0.07	0.11	0.08	0.08	-	0.09	0.08	0.10	0.07
S(+Te+Se)	69.39	69.29	69.30	69.78	70.34	70.35	69.73	69.36	69.79	70.35	70.35	69.73	69.36	69.74	70.28	70.08	70.75	70.57	69.95	70.01	70.13	69.81	69.93
Sb/(Sb+Bi)	0.40	0.41	0.41	0.39	0.40	0.40	0.38	0.39	0.39	0.40	0.40	0.38	0.39	0.39	0.38	0.36	0.36	0.37	0.40	0.39	0.39	0.37	0.39