

Supplementary Online Materials for
**Germanium distribution in Mississippi Valley-Type systems from sulfide deposition to
oxidative weathering: A perspective from Fule Pb-Zn(-Ge) deposit, South China**

CHEN WEI^{1,2} [†], MAX FRENZEL², LIN YE¹ ^{*}, ZHILONG HUANG¹, AND LEONID
DANYUSHEVSKY³

¹ State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of
Sciences, Guiyang 550081, China

² Helmholtz-Zentrum Dresden-Rossendorf, Helmholtz Institute Freiberg for Resource Technology,
Freiberg 09599, Germany

³ Centre for Ore Deposit and Earth Sciences, University of Tasmania, TAS 7001, Australia

[†]Current address: Helmholtz-Zentrum Dresden-Rossendorf, Helmholtz Institute Freiberg for
Resource Technology, Freiberg 09599, Germany

^{*} Corresponding author mail: yelin@vip.gyig.ac.cn (L, Ye)

Table of contents

1. PDF File:

Figs. A1 to A3

Tables A1 to A4

2. Excel File:

Data S1 to S3 (additional individual spreadsheets)

Figs. A1 to A3

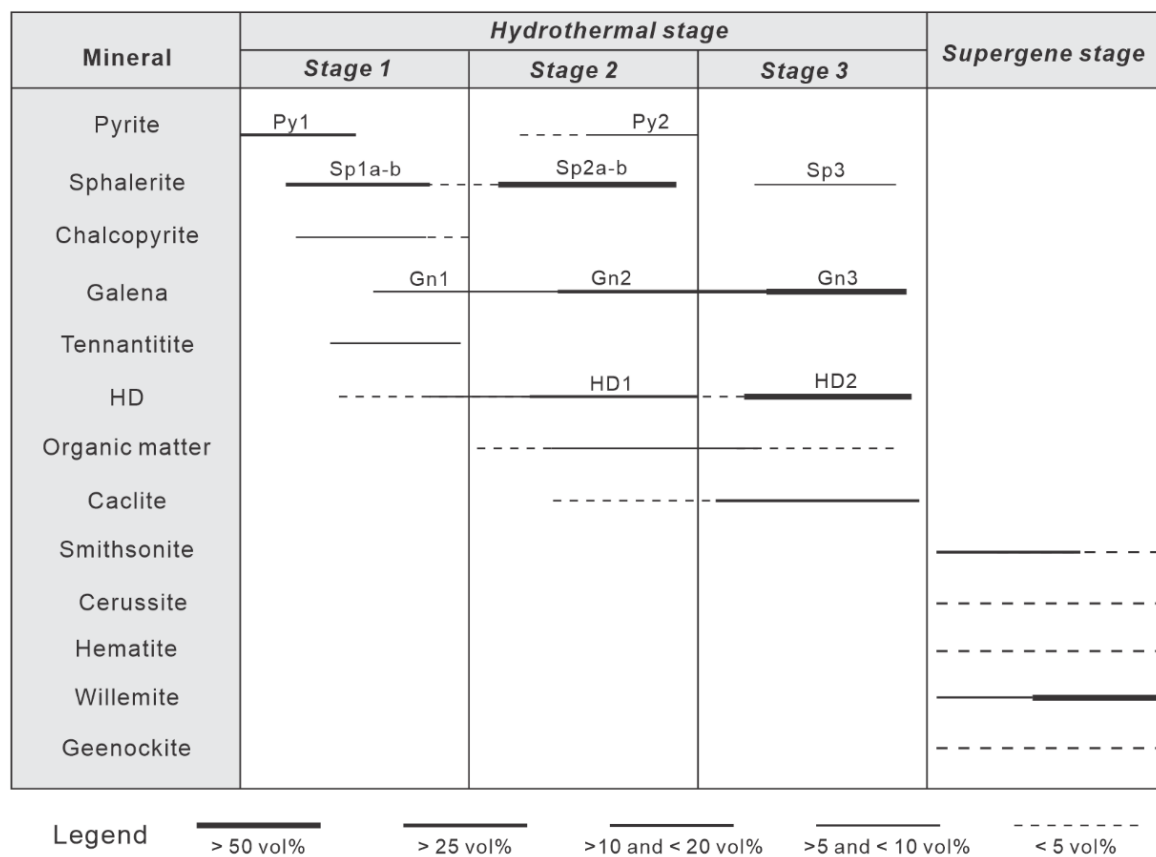


Figure A1 Mineral paragenetic sequence for the Fule deposit. Abbreviations: HD—hydrothermal dolomite

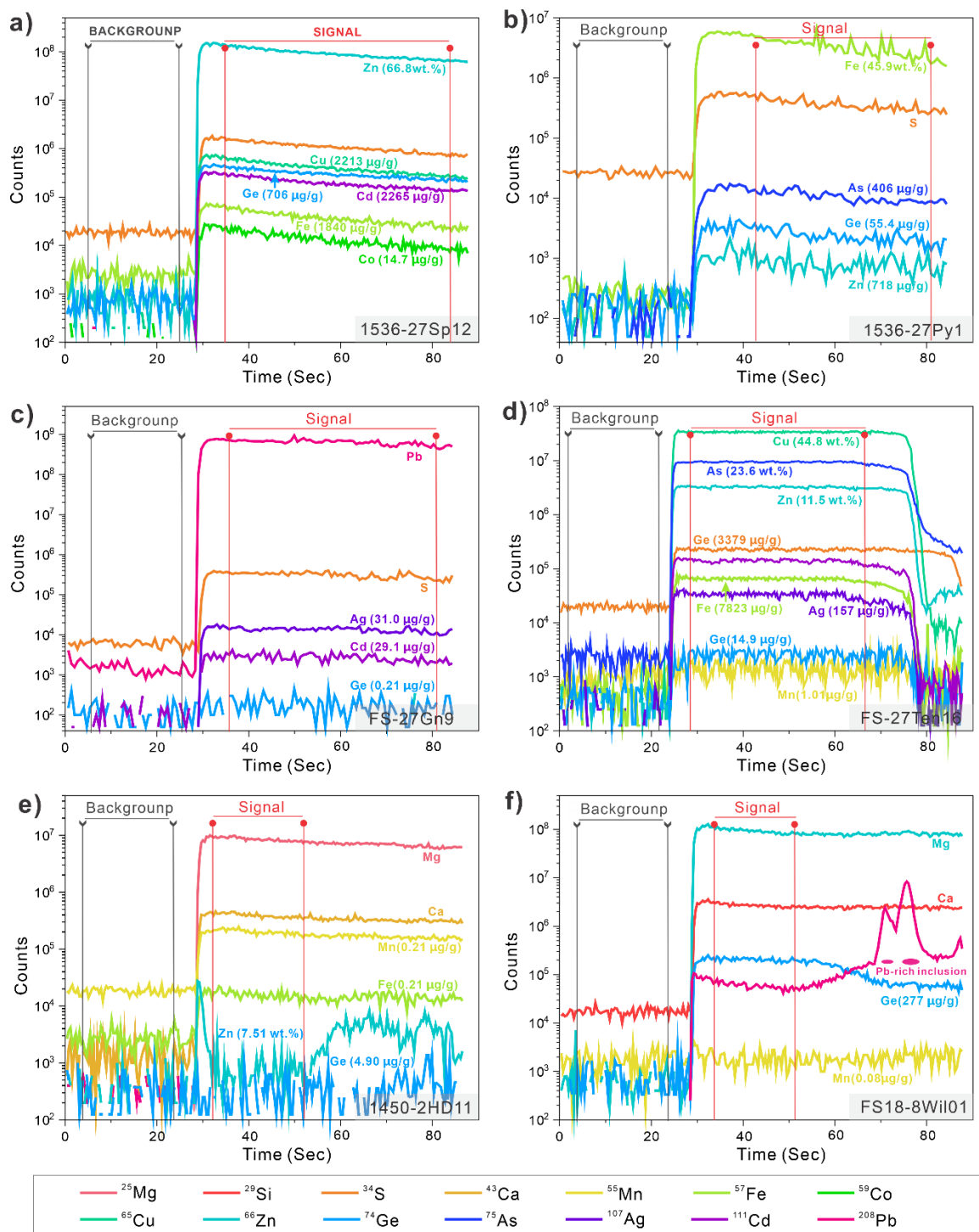


Figure A2 Time-integrated representative LA-ICP-MS spectra of sulfides, carbonate, and silicate. **(a)** Spectra in early sphalerite 1a show a smooth profile for Ge (706 µg/g) and other elements. **(b)** Spectra in the pyrite 1 highlight flat signals for the elements of interest, with a notably smooth and lower signal for Ge (55.4 µg/g). **(c)** Spectra in the galena 2 coexisting with sphalerite 2 show an extremely low Ge concentration (0.21 µg/g) and relatively smooth signals for other elements. **(d)** Spectra in the tennantite with a low Ge concentration (14.9 µg/g). **(e)** Spectra in carbonate highlighting the elements of Ge and Zn have similar peaks. **(f)** Spectra in willemite shows smooth Ge signals.

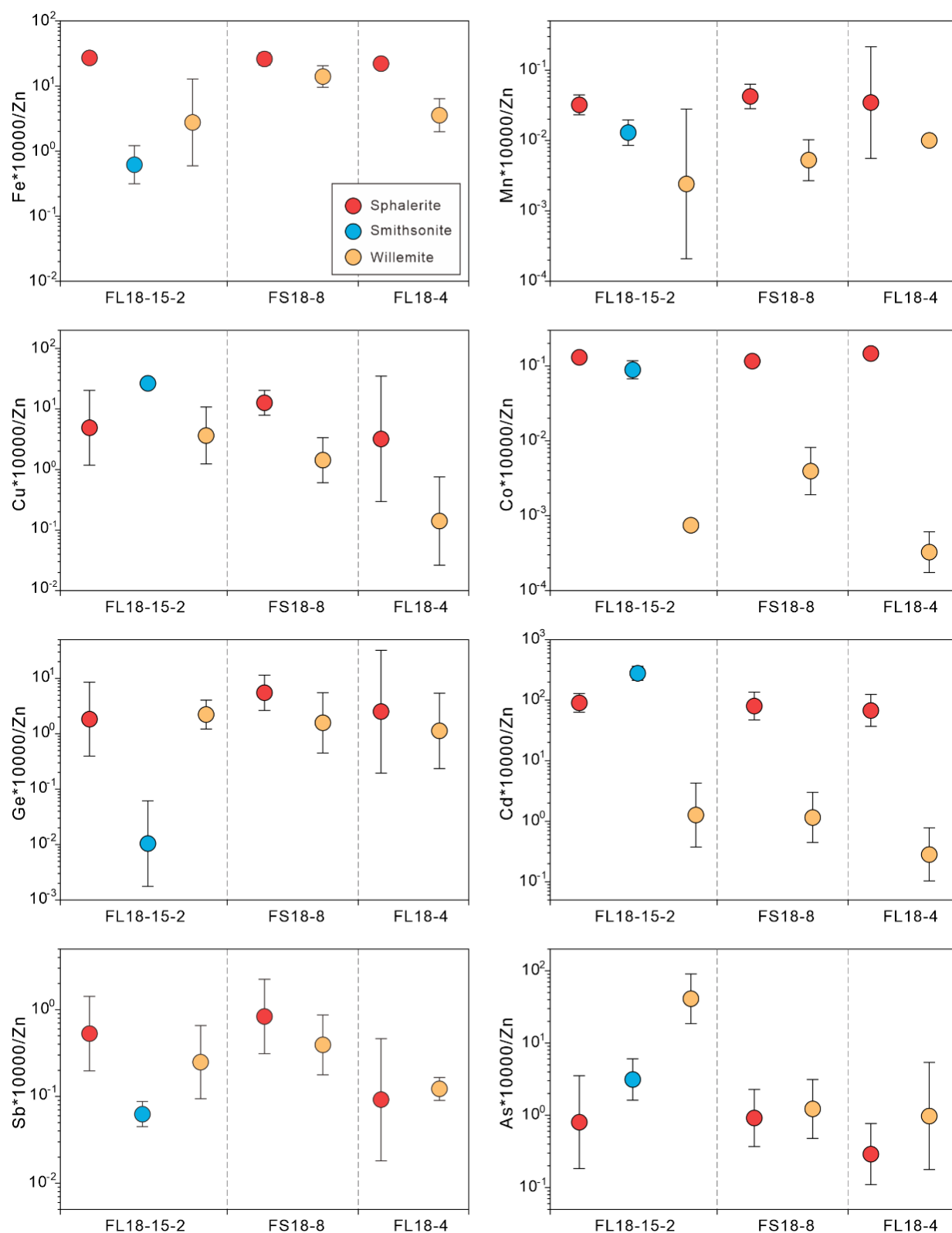


Figure A3 Mass ratios of minor/trace elements between Zn for willemite and smithsonite compared to the original sphalerite. Symbols represent the geometric mean, and the lower/upper error bars represent the 95% confidence interval of the mean.

Tables A1 to A4

TABLE A1 Mineral abundances of the different samples estimated by optical microscopy

No	Sample ID	Mining area	Elevation (m)	Sulfides					Accessory minerals	Carbonates			Silicates Wil	Hem	Others
				Py	Sp	Gn	Cpy	Ten		HD	Smi	Cer			
27	1536-27	Fusheng	1536	xxx	xxxx	xxx	x	xx	—	xxxx	—	—	—		—
26	FS-27	Fusheng		xx	xxxxx	xxx	x	xx	—	xx	—	—	—		—
3	FL-3	Fule	1410	xx	xxxxx	xxx	x	x	—	xx	—	—	—		—
16	FL-16	Fule	1440	x	xxxx	xxx	x	x	—	xxx	—	—	—		—
2	1450-2	Fule	1450	x	xxxx	xx	x	x	OM	xxx	—	—	—		—
15	FL18-15-2	Fule		—	xxxx	xx	—	—	—	xxx	xx	xx	xxx	xx	Gck
4	FL18-4	Fule		—	x	xxx	—	—	—	x	x	x	xxxxx	x	Ap
8	FS18-8	Fusheng		—	xx	xx	—	—	—	xxxx	x	x	xxxx	x	—

Abbreviations: Cpy = chalcopyrite, Sp = sphalerite, Gn = galena, Py = pyrite, Ten = tennantite, OM = organic matter, HD = hydrothermal dolomite, Smi = smithsonite, Wil = willemite, Gck = greenockite, Hem = hematite, Ap = apatite. — not detected, x: trace (<1%), xx: minor (1–5%), xxx: common (5–30 %), xxxx: abundant (30–60 %), xxxxx (>60 %).

TABLE A2 Summary of LA-ICP-MS trace element results for different types of sphalerite

Sample	Generation	n		Mn (μg/g)	Fe (wt.%)	Co (μg/g)	Ni (μg/g)	Cu (μg/g)	Ge (μg/g)	As (μg/g)	Ag (μg/g)	Cd (wt.%)	Sb (μg/g)	Tl (μg/g)
1450-2	Sp1a	3	<i>Mean</i>	1.71	0.21	12.4	1.69	1715	538	22.7	1.89	0.29	3.24	0.45
			<i>C.I. Min</i>	1.05	0.13	7.47	0.84	628	314	1.71	1.69	0.11	0.22	0.03
			<i>C.I. Max</i>	2.79	0.36	20.6	3.41	4687	924	301	2.12	0.75	46.7	7.36
	Sp1b	3	<i>Mean</i>	2.00	0.24	11.9	1.78	1133	314	85.7	4.33	1.20	114	-
			<i>C.I. Min</i>	0.92	0.21	8.29	1.21	604	207	10.3	1.70	1.02	40.2	-
			<i>C.I. Max</i>	4.34	0.28	17.1	2.63	2124	476	714	11.0	1.42	323	<0.02
	Sp2a	3	<i>Mean</i>	1.64	0.21	14.9	1.90	1089	185	227	10.1	1.50	439	0.11
			<i>C.I. Min</i>	0.63	0.14	9.58	1.25	930	81.8	155	3.40	0.88	243	0.02
			<i>C.I. Max</i>	4.30	0.33	23.1	2.87	1275	418	331	30.3	2.57	794	0.76
	Sp2b	5	<i>Mean</i>	2.58	0.28	13.0	2.02	369	34.3	18.7	3.97	1.81	138	0.03
			<i>C.I. Min</i>	1.61	0.21	10.0	1.52	144	12.2	4.92	1.83	1.20	49.7	-
			<i>C.I. Max</i>	4.15	0.37	16.9	2.69	947	96.4	71.1	8.6	2.73	383	-
	Sp3	7	<i>Mean</i>	3.19	0.27	12.3	1.90	29.3	1.53	3.19	1.95	2.30	1.90	0.08
			<i>C.I. Min</i>	2.23	0.24	9.84	1.24	5.62	0.87	1.90	1.63	1.69	0.17	0.01
			<i>C.I. Max</i>	4.58	0.31	15.4	2.91	153	2.71	5.35	2.33	3.13	21.4	0.47
1536-27	Sp1a	4	<i>Mean</i>	1.64	0.21	13.2	1.78	2081	671	41.5	2.49	0.35	11.4	0.09
			<i>C.I. Min</i>	1.44	0.17	10.2	1.25	1577	529	10.0	1.81	0.14	2.35	0.06
			<i>C.I. Max</i>	1.88	0.25	17.0	2.52	2745	851	171	3.41	0.84	55.6	0.15
	Sp1b	2	<i>Mean</i>	2.13	0.21	14.1	1.76	1307	422	86.4	3.35	0.38	20.9	0.07
			<i>C.I. Min</i>	1.07	0.13	3.07	0.60	685	303	29.0	2.70	0.09	8.30	0.01
			<i>C.I. Max</i>	3.14	0.33	65.1	5.19	2494	588	257.7	4.17	1.54	52.4	0.49
	Sp2a	4	<i>Mean</i>	2.93	0.24	9.41	2.29	825	123	236	4.33	0.95	51.4	0.19
			<i>C.I. Min</i>	2.37	0.18	8.12	1.99	679	92.9	170	3.58	0.63	37.9	0.11
			<i>C.I. Max</i>	3.63	0.33	10.9	2.64	1004	162	327	5.22	1.44	69.5	0.32
	Sp2b	5	<i>Mean</i>	1.56	0.26	14.7	2.08	689	56.0	131	15.0	1.54	324	0.22
			<i>C.I. Min</i>	1.15	0.19	12.5	1.09	480	38.5	100	8.72	0.97	193	0.13
			<i>C.I. Max</i>	2.12	0.35	17.4	3.96	988	81.3	171	25.7	2.43	543	0.40
	Sp3	7	<i>Mean</i>	2.66	0.30	14.7	1.90	15.8	2.10	2.34	1.75	1.80	1.99	0.07
			<i>C.I. Min</i>	1.75	0.23	12.7	1.32	6.23	0.96	0.43	1.45	0.99	0.24	0.04
			<i>C.I. Max</i>	4.06	0.39	17.0	2.72	40.3	4.61	12.7	2.12	3.26	16.9	0.13
FS-27	Sp1a	3	<i>Mean</i>	1.74	0.18	13.2	1.52	1847	573	86.3	2.98	0.43	13.7	0.12
			<i>C.I. Min</i>	1.18	0.11	11.8	0.86	1256	313	56.3	1.51	0.18	10.3	0.002
			<i>C.I. Max</i>	2.55	0.28	14.8	2.67	2716	1049	132	5.88	1.03	18.1	8.86
	Sp1b	2	<i>Mean</i>	2.24	0.29	13.5	2.07	1171	324	221	4.70	1.00	36.6	0.05
			<i>C.I. Min</i>	0.78	0.18	12.9	1.72	659	266	167	2.64	0.73	14.3	-
			<i>C.I. Max</i>	7.09	0.46	14.2	2.49	2081	394	292	8.35	1.37	93.9	-

FL18-3	Sp2a	8	Mean	3.22	0.37	14.6	2.54	980	175	307	7.93	1.30	93.0	0.30
			C.I. Min	2.56	0.32	12.6	2.12	781	139	237	6.45	0.96	71.4	0.17
			C.I. Max	4.04	0.41	17.0	3.05	1231	221	397	9.73	1.76	121	0.54
	Sp2b	4	Mean	3.62	0.34	11.4	2.63	439	70.4	136	4.37	1.58	45.1	0.08
			C.I. Min	1.45	0.25	9.35	1.78	305	41.4	71.8	2.07	1.11	23.6	0.04
			C.I. Max	9.07	0.45	14.0	3.88	631	120	259	9.25	2.26	85.9	0.18
	Sp3	3	Mean	4.35	0.41	11.0	2.90	34.0	6.09	7.56	2.82	2.37	9.73	0.38
			C.I. Min	2.53	0.33	8.44	1.11	5.86	0.65	0.29	1.80	1.54	2.34	-
			C.I. Max	7.46	0.50	14.3	7.56	198	56.8	197	4.42	3.63	40.5	-
	Sp1a	4	Mean	1.35	0.19	12.5	1.51	1887	632	20.2	2.65	0.34	13.5	0.17
			C.I. Min	1.12	0.16	9.17	0.98	1510	519	7.27	1.10	0.17	2.45	0.03
			C.I. Max	1.61	0.22	16.9	2.33	2359	768	55.9	6.39	0.68	74.1	0.96
	Sp1b	3	Mean	2.37	0.28	11.5	2.51	1190	260	168	4.12	0.59	16.3	0.06
			C.I. Min	1.01	0.12	8.5	0.92	1016	172	35.2	2.00	0.19	3.12	0.02
			C.I. Max	5.56	0.65	15.5	6.87	1395	393	802	8.51	1.82	84.8	0.18
	Sp2a	6	Mean	2.90	0.33	11.3	2.45	1004	133	295	8.77	0.88	79.8	0.26
			C.I. Min	2.40	0.26	10.3	1.89	760	113	142	3.38	0.71	23.8	0.11
			C.I. Max	3.50	0.41	12.4	3.17	1326	156	613	22.8	1.09	267	0.62
	Sp2b	3	Mean	2.60	0.33	10.5	2.26	339	74.8	187	8.11	1.33	123	0.22
			C.I. Min	1.24	0.13	9.43	1.00	76.8	27.3	107	3.34	0.84	42.1	0.09
			C.I. Max	5.42	0.84	11.6	5.06	1493	205	327	19.7	2.11	361	0.53
	Sn3	4	Mean	2.93	0.34	11.6	2.81	7.96	5.71	1.62	1.19	2.11	13.7	0.05
			C.I. Min	1.27	0.21	7.7	0.83	0.59	0.56	0.08	0.94	1.15	3.67	-
			C.I. Max	6.77	0.55	17.4	9.57	107	58.2	31.4	1.50	3.87	51.1	-
FL-16	Sp1a	4	Mean	2.22	0.24	8.73	1.79	2383	680	5.56	1.66	0.29	21.9	0.06
			C.I. Min	1.93	0.21	7.85	1.52	1928	545	0.92	1.33	0.25	4.78	0.04
			C.I. Max	2.57	0.27	9.70	2.10	2946	848	33.7	2.08	0.33	99.9	0.09
	Sp1b	3	Mean	2.03	0.23	8.21	1.73	1561	440	13.7	2.55	0.31	25.4	0.04
			C.I. Min	1.87	0.21	7.76	1.40	1063	289	2.15	1.94	0.25	5.51	0.01
			C.I. Max	2.20	0.25	8.67	2.13	2292	668	87.2	3.36	0.38	117.2	0.10
	Sp2a	4	Mean	1.93	0.22	4.94	1.02	784	112	60.6	3.63	1.13	43.9	<0.03
			C.I. Min	0.87	0.17	0.20	0.40	388	84.3	5.8	2.90	0.70	6.04	-
			C.I. Max	4.28	0.28	123	2.60	1584	148	629	4.54	1.81	319	-
	Sp2b	7	Mean	1.82	0.25	4.63	1.69	429	70.9	0.91	1.14	0.94	10.4	0.06
			C.I. Min	1.18	0.19	2.19	0.88	180	51.5	0.26	1.05	0.46	3.95	0.02
			C.I. Max	2.82	0.32	9.77	3.23	1022	97.6	3.15	1.25	1.93	27.2	0.25
	Sp3	2	Mean	2.91	0.40	8.67	1.54	117	6.33	<0.13	1.02	3.45	2.20	<0.03
			C.I. Min	1.64	0.27	-	-	26.9	0.32	-	0.64	2.54	1.02	-
			C.I. Max	5.16	0.58	-	-	506	125	-	1.61	4.69	4.75	-

Mean, geometric mean; ***C.I. Min.***, lower bound of the 95% confidence interval of the mean; ***C.I. Max.***, upper bound of the 95% confidence interval of the mean. All statistics were calculated from measurements unaffected by mineral inclusions (smooth ablation traces). The entire LA-ICP-MS dataset for sphalerite is in the table listed in the “sphalerite” subfolder of supplementary data S2.

TABLE A3 Summary of LA-ICP-MS trace element results for sulfides from different ore-stages

Sample	Ore-stage	Sulfides	n		Mn (μg/g)	Co (μg/g)	Ni (μg/g)	Cu (μg/g)	Ge (μg/g)	As (μg/g)	Se (μg/g)	Ag (μg/g)	Cd (μg/g)	Sb (μg/g)	Tl (μg/g)
1536-27	Stage 1	Py1	8	<i>Mean</i>	1.08	17.06	23.8	845	26	177	78.8	1.48	29.2	59.5	1.48
				<i>C.I. Min</i>	0.48	6.40	9.51	362	5.01	49.0	25.7	0.72	3.79	23.9	0.44
				<i>C.I. Max</i>	2.41	45.5	59.3	1166	138	636	242	3.04	225	148	4.94
		Sp1	6	<i>Mean</i>	1.70	13.5	1.77	1782	575	53.0	0.88	2.75	3580	14.0	0.08
				<i>C.I. Min</i>	1.55	11.5	1.47	1332	435	23.1	0.60	2.19	2267	5.83	0.06
				<i>C.I. Max</i>	1.87	15.8	2.14	2384	760	121	1.30	3.45	5653	33.4	0.11
		Ten	4	<i>Mean</i>	1.75	1.65	1.30	430841	1.91	229681	39.7	133	4197	3016	0.20
				<i>C.I. Min</i>	0.43	0.53	-	388893	0.77	217575	10.3	68.7	3190	477	0.15
				<i>C.I. Max</i>	7.21	5.18	-	477313	4.77	242459	153	256	5523	19082	0.28
		Gn1	3	<i>Mean</i>	<0.45	0.03	0.11	3.49	0.19	3.29	N/A	12.6	83.1	38.3	18.8
				<i>C.I. Min</i>	-	-	-	0.02	0.14	0.09	-	2.33	52.9	18.4	13.4
				<i>C.I. Max</i>	-	-	-	564	0.25	127	-	67.8	131	79.5	26.5
	Stage 2	Py2	6	<i>Mean</i>	0.94	2.10	234	823	6.27	1046	14.0	1.67	11.1	188	1.07
				<i>C.I. Min</i>	0.29	0.36	156	704	4.83	464	8.06	0.73	0.18	151	0.32
				<i>C.I. Max</i>	3.07	12.3	349	962	8.15	2355	24.3	3.81	690	234	3.57
		Sp2	1	<i>Mean</i>	2.14	11.8	2.18	754	82.8	176	0.98	8.04	12100	129	0.21
				<i>C.I. Min</i>	1.62	9.74	1.69	635	58.6	133	0.73	4.80	8995	62.1	0.15
				<i>C.I. Max</i>	2.83	14.2	2.82	895	117	231	1.31	13.5	16275	268	0.28
		Gn2	5	<i>Mean</i>	<0.46	0.01	0.17	2.83	0.17	2.37	N/A	82.3	111	259	30.8
				<i>C.I. Min</i>	-	0.003	-	1.26	0.04	0.40	-	41.7	91.6	132	25.5
				<i>C.I. Max</i>	-	0.02	-	6.35	0.75	14.0	-	162	134	508	37.2
	Stage 3	Sp3	7	<i>Mean</i>	2.66	14.7	1.90	15.8	2.10	2.34	0.96	1.75	17989	2.0	0.07
				<i>C.I. Min</i>	1.75	12.7	1.32	6.23	0.96	0.43	0.10	1.45	9927	0.24	0.04
				<i>C.I. Max</i>	4.1	17.0	2.72	40.3	4.61	12.7	9.43	2.12	32597	16.9	0.13
		Gn3	3	<i>Mean</i>	<0.47	0.04	0.11	7.07	0.15	2.76	-	91.1	74.5	187	12.4
				<i>C.I. Min</i>	-	-	-	0.39	-	0.87	-	54.9	24.3	60.1	0.82
				<i>C.I. Max</i>	-	-	-	128	-	8.77	-	151	228	580	188
FS-27	Stage 1	Py1	7	<i>Mean</i>	2.24	15.82	30.6	572	6.41	383	10.8	0.50	5.00	69.9	0.25
				<i>C.I. Min</i>	0.41	5.00	13.5	158	2.10	167	5.29	0.18	0.67	23.2	0.10
				<i>C.I. Max</i>	12.2	50.0	69.4	2069	19.59	878	22.2	1.40	37	211	0.63
		Sp1	5	<i>Mean</i>	1.96	13.3	1.72	1539	456	126	1.55	3.57	6004	20.3	0.09
				<i>C.I. Min</i>	1.51	12.8	1.29	1094	293	65.1	1.46	2.41	3109	10.3	0.02
				<i>C.I. Max</i>	2.54	13.9	2.30	2164	711	243	1.65	5.30	11595	40.1	0.43
		Ten	6	<i>Mean</i>	0.97	4.07	0.78	440765	3.72	236443	29.8	170	3503	3783	0.33
				<i>C.I. Min</i>	0.76	2.78	-	433357	1.36	230090	13.1	141	3225	999	0.06
				<i>C.I. Max</i>	1.23	5.95	-	448299	10.2	242971	67.9	206	3804	14322	1.73

FL-3	Stage 2	Gn1	4	<i>Mean</i>	<0.40	0.01	0.15	4.04	0.20	4.65		23.7	55.7	51.5	25.6
				<i>C.I. Min</i>	-	-	-	3.29	0.06	0.40	-	14.9	25.7	25.4	7.53
				<i>C.I. Max</i>	-	-	-	4.95	0.64	54.0	-	37.7	121	105	86.7
		Py2	7	<i>Mean</i>	2.65	2.40	239	695	4.32	1093	18.2	1.59	12.6	176	1.96
				<i>C.I. Min</i>	0.53	0.57	94.8	496	2.93	461	10.1	1.05	1.73	133	0.81
				<i>C.I. Max</i>	13.3	10.1	603	974	6.39	2590	32.7	2.40	91.3	232	4.78
		Sp2	1	<i>Mean</i>	3.35	13.5	2.57	750	129	234	1.42	6.50	13890	73.1	0.19
				<i>C.I. Min</i>	2.64	11.9	2.24	557	92.3	169	-	4.95	11303	53.7	0.11
				<i>C.I. Max</i>	4.25	15.3	2.95	1009	181	325	-	8.54	17070	99.5	0.34
	Stage 3	Gn2	3	<i>Mean</i>	<0.36	0.002	0.07	1.14	0.20	1.47	N/A	67.6	68.6	201	18.2
				<i>C.I. Min</i>		0.00	0.01	0.06	0.07	0.55	-	11.2	10.5	28.5	4.67
				<i>C.I. Max</i>		0.13	0.43	21.0	0.55	3.9	-	409	446	1414	70.6
		Sp3	3	<i>Mean</i>	4.35	11.0	2.90	34.0	6.09	7.56	4.04	2.82	23652	9.73	0.38
				<i>C.I. Min</i>	2.53	8.44	1.11	5.86	0.65	0.29	-	1.80	15408	2.34	-
				<i>C.I. Max</i>	7.46	14.3	7.56	198	56.8	197	-	4.42	36306	40.5	-
		Gn3	4	<i>Mean</i>	<0.40	0.01	0.07	1.16	0.19	1.30	N/A	59.1	102	108	12.1
				<i>C.I. Min</i>	-	-	-	0.68	0.15	0.75	-	33.2	79.4	60.3	8.16
				<i>C.I. Max</i>	-	-	-	1.97	0.23	2.23	-	105	131	193	18.0
	Stage 1	Py1	9	<i>Mean</i>	1.95	19.4	16.0	160	1.24	145	9.28	0.37	1.56	77.7	1.18
				<i>C.I. Min</i>	0.23	9.00	3.05	75.5	0.77	35.1	5.71	0.08	0.01	35.4	0.22
				<i>C.I. Max</i>	16.5	41.8	84.4	338	2.02	599	15.1	1.69	246	171	6.27
		Sp1	7	<i>Mean</i>	1.72	12.0	1.88	1549	432	50.0	1.56	3.21	4333	14.6	0.12
				<i>C.I. Min</i>	1.22	10.4	1.29	1209	274	15.4	0.85	2.05	2750	6.62	0.05
				<i>C.I. Max</i>	2.42	13.9	2.74	1985	680	163	2.86	5.03	6828	32.2	0.29
		Gn1	3	<i>Mean</i>	<0.44	<0.03	0.13	3.91	0.22	7.11	N/A	61.9	82.0	109	20.9
				<i>C.I. Min</i>	-	-	-	0.55	0.11	0.86	-	12.5	11.7	26.8	3.73
				<i>C.I. Max</i>	-	-	-	27.6	0.45	58.7	-	306	575	445	117
	Stage 2	Py2	5	<i>Mean</i>	2.06	3.52	361	327	0.80	724	7.92	1.82	11.4	338	7.28
				<i>C.I. Min</i>	0.51	0.23	109	228	-	148	0.75	0.91	-	157	4.74
				<i>C.I. Max</i>	8.40	53.3	1199	469	-	3552	83.91	3.66	-	731	11.2
		Sp2	9	<i>Mean</i>	2.79	11.0	2.38	699	110	254	0.96	8.55	10084	92.2	0.25
				<i>C.I. Min</i>	2.37	10.4	1.96	423	82.5	159	0.85	4.83	8154	44.1	0.16
				<i>C.I. Max</i>	3.29	11.7	2.90	1156	146	404	1.10	15.1	12471	193	0.37
		Gn2	4	<i>Mean</i>	<0.36	0.01	0.07	0.73	0.18	1.09	N/A	91.3	143	297	22.4
				<i>C.I. Min</i>	-	-	-	0.22	-	-	-	31.5	97.3	104	10.9
				<i>C.I. Max</i>	-	-	-	2.43	-	-	-	265	210	844	46.3
	Stage 3	Sp3	3	<i>Mean</i>	2.93	11.6	2.81	7.96	5.71	1.62	1.05	1.19	21138	13.7	0.05
				<i>C.I. Min</i>	1.27	7.74	0.83	0.59	0.56	0.08	0.04	0.94	11549	3.67	-
				<i>C.I. Max</i>	6.77	17.4	9.57	107	58.2	31.4	25.5	1.50	38687	51.1	-

Gn3	5	Mean	<0.37	0.01	0.04	3.58	0.20	1.41	N/A	82.4	110	223	11.3
		C.I. Min	-	-	-	1.33	0.17	0.57	-	34.7	38.9	66.6	2.95
		C.I. Max	-	-	-	9.65	0.23	3.48	-	196	312	749	43.3

Mean, geometric mean; **C.I. Min.**, lower bound of the 95% confidence interval of the mean; **C.I. Max.**, upper bound of the 95% confidence interval of the mean. All statistics were calculated from measurements unaffected by mineral inclusions (smooth ablation traces). The entire LA-ICP-MS dataset for sulfides is in the table listed in supplementary data S2.

TABLE A4 Summary of LA-ICP-MS trace element results for supergene minerals and corresponding sphalerite

Sample	minerals	n		Mn (µg/g)	Fe (µg/g)	Co (µg/g)	Ni (µg/g)	Cu (µg/g)	Ge (µg/g)	As (µg/g)	Se (µg/g)	Ag (µg/g)	Cd (µg/g)	Sb (µg/g)	Tl (µg/g)
FL18-	Sp	9	<i>Mean</i>	2.06	1791	8.85	1.22	323	123	51.2	4.78	2.18	6010	35.3	0.08
			<i>C.I. Min</i>	1.47	1530	8.03	0.94	76.9	26.6	10.8	-	1.25	4219	13.2	-
			<i>C.I. Max</i>	2.88	2096	9.76	1.58	1356	565	244	-	3.81	8561	94.2	-
	Smi	7	<i>Mean</i>	0.67	32.2	4.62	3.03	1376	0.15	163	N/A	1.67	14480	3.19	0.02
			<i>C.I. Min</i>	0.40	16.5	3.50	2.03	1144	0.05	84.4	-	0.89	11119	2.26	0.01
			<i>C.I. Max</i>	1.13	62.8	6.12	4.51	1655	0.46	314	-	3.14	18859	4.49	0.05
	Wil	6	<i>Mean</i>	0.16	161	0.04	0.14	213	130	2396	1.17	2.72	74.3	14.6	0.01
			<i>C.I. Min</i>	0.02	34.7	0.01	0.02	72.2	71.4	1083	0.32	1.06	22.1	5.63	0.01
			<i>C.I. Max</i>	1.42	749	0.21	1.01	629	236	5300	4.27	6.98	249	38.0	0.02
FS18-	Sp	1	<i>Mean</i>	2.66	1673	7.67	1.21	891	401	59.1	N/A	2.56	4938	49.8	0.08
			<i>C.I. Min</i>	1.67	1369	7.23	0.92	575	203	26.4	-	1.46	3011	20.2	0.03
			<i>C.I. Max</i>	4.25	2044	8.13	1.59	1379	791	132	-	4.47	8099	122	0.20
	Wil	8	<i>Mean</i>	0.32	818	0.24	3.46	83.6	92.3	71.7	11.7	2.79	67.7	23.0	0.02
			<i>C.I. Min</i>	0.17	558	0.13	2.10	35.5	26.3	28.2	1.23	1.20	26.2	10.3	0.01
			<i>C.I. Max</i>	0.61	1197	0.47	5.70	197	323	183	110	6.49	175	50.9	0.03
FL18-	Sp	7	<i>Mean</i>	2.26	1467	9.77	1.28	213	165	19.2	5.97	1.25	4498	5.94	0.04
			<i>C.I. Min</i>	0.23	1254	8.97	0.72	19.5	12.5	7.15	2.72	0.95	2455	1.09	0.02
			<i>C.I. Max</i>	22.3	1715	10.6	2.25	2317	2177	51.7	13.1	1.63	8239	32.5	0.05
	Wil	8	<i>Mean</i>	0.58	208	0.02	0.21	8.27	65.8	57.1	2.07	1.13	16.6	7.15	0.01
			<i>C.I. Min</i>	-	116	0.01	0.06	1.54	13.7	10.3	0.81	0.79	6.04	5.27	0.001
			<i>C.I. Max</i>	-	374	0.03	0.72	44.3	317	317	5.31	1.63	45.5	9.69	0.05

Mean, geometric mean; *C.I. Min.*, lower bound of the 95% confidence interval of the mean; *C.I. Max.*, upper bound of the 95% confidence interval of the mean. All statistics were calculated from measurements unaffected by mineral inclusions (smooth ablation traces). The entire LA-ICP-MS dataset for sphalerite and corresponding supergene minerals (smithsonite and willemite) is in the table listed in supplementary data S3.