

Supplemental¹. Additional information on analytical methodology

Electron Probe Microanalysis (EPMA)

TABLE S1. Elements analyzed, peak/background positions, count times, standards used and average minimum limits of detection for EPMA analysis of sulfosalts and BMS

Element/line	Diffracting Crystal/Sp#	Peak count time (sec)	Background type/fit	Background points (Lo/Hi)	Background count time (Lo/Hi) (sec)	Standard	Average minimum limits of detection (wt%)
S K α	LPET/1	15	Multipoint	2/2	10/10	Chalcopyrite	0.057
Pb M α	LPET/1	15	Multipoint	4/3	10/10	Galena	0.053
As L α	TAP/2	15	Multipoint	2/2	10/10	Gallium arsenide	0.047
Se L α	TAP/2	15	Multipoint	2/3	10/10	Bi ₂ Se ₃	0.037
Fe K α	LLIF/3	15	Multipoint	2/2	10/10	Chalcopyrite	0.024
Cu K α	LLIF/3	15	Linear	-	10/10	Chalcopyrite	0.030
Sb L α	LPET/4	15	Multipoint	2/2	10/10	Stibnite	0.037
Ag L α	LPET/4	15	Multipoint	1/2	10/10	Silver telluride	0.070
Zn K α	LLIF/5	15	Multipoint	2/2	10/10	Sphalerite	0.032
Te L α	LLIF/4	15	Multipoint	2/2	10/10	AgTe	0.041
Bi M α	LPET/1	15	Multipoint	2/2	10/10	Bi ₂ Se ₃	0.119
Cd L α	LPET/1	15	Multipoint	2/2	10/10	Greenockite	0.061
Hg L α	LLIF/5	15	Multipoint	3/3	10/10	Cinnabar	0.112

TABLE S2. Elemental overlap corrections used in sulfide package (EPMA)

Element/line	Diffracting crystal	Overlapping line/order	Overlap standard
S K α	LPET/1	Co III, Sb II, Hg I	Astimex Co metal, Astimex Stibnite, Astimex Cinnabar
Pb M α	LPET/1	Fe III, As V	P&H block Chalcopyrite, Astimex GaAs
Cd L α	LPET/1	PbIV, Ag I, Se IV	Astimex Galena, P&H block AgTe, AstimexBi ₂ Se ₃
As L α	TAP/2	Sb III, Fe V, Co VI	Astimex Stibnite, P&H Chalcopyrite, Astimex Co metal
Se L α	TAP/2	As I, Te III, Co V, Ni IV	Astimex GaAs, P&H AgTe, Astimex Co metal, Astimex Ni metal
Fe K α	LLIF/3	Pb II	P&H Galena
Ag L α	LPET/4	Hg IV, Cu III, Mn II	P&H Cinnabar, P&H Chalcopyrite, P&H Rhodonite
Sb L α	LPET/4	Bi III	P&H Bi ₂ Se ₃
Te L α	LPET/4	Sn I, Se III, Ni II	P&H Cassiterite, P&H Bi ₂ Se ₃ , Astimex Pentlandite
Bi M α	LPET/1	Pb I	P&H Galena
Cu	-	-	-
Zn	-	-	/
Ni	-	-	-
Hg	-	-	-

Note: "-"represents no overlapping corrections during calculation.

Laser-ablation inductively coupled plasma mass spectrometry (LA-ICP-MS)

LA-ICP-MS analyses were performed in spot mode using a laser beam of 20 to 40 μm , a repetition rate of 5 Hz, and laser energy of 4.0 to 5.5 J/cm². Total acquisition time for each analysis was 70 s, with 30 s background measurement followed by 40 s of sample ablation. Calibration for LA-ICP-MS spot analysis was performed using USGS sulfide standard MASS-1 (Wilson et al. 2002). Monitored isotopes included ³⁴S, ⁵⁵Mn, ⁵⁷Fe, ⁵⁹Co, ⁶⁰Ni, ⁶³Cu, ⁶⁶Zn, ⁶⁹Ga, ⁷⁵As, ⁷⁷Se, ⁹⁵Mo, ¹⁰⁷Ag, ¹¹¹Cd, ¹¹⁵In, ¹¹⁸Sn, ¹²¹Sb, ¹²⁵Te, ¹⁹⁷Au, ²⁰¹Hg, ²⁰⁵Tl, ²⁰⁸Pb, and ²⁰⁹Bi. Internal calibration used measured wt % EPMA data: Fe served for chalcopyrite; Cu for tetrahedrite and

bournonite; ^{208}Pb for giessenite-izoklakeite, jamesonite, robinsonite, boulangerite and galena; and Zn for sphalerite. Detection limits depend on spot size, which governs ablated mineral volume. Average minimum detection limits and dwell time for all elements are listed in Table S3. Data reduction were compiled and processed using Iolite v2.5, a software package for processing LA-ICP-MS data (Paton et al. 2011), as an add-in for the data analysis program Igor (WaveMetrics).

LA-ICP-MS mapping was conducted by ablating sets of parallel lines rastered across an area of the sample using beam sizes ranging from 7 to 10 μm dependent on grain size, at a laser frequency of 10 Hz. Dwell times for all elements are listed in Table S3. Re-deposition during mapping was minimized by pre-ablating each line prior to data collection. Identical raster lines were done on standard MASS-1 at the start and end of each mapping run to correct for instrument drift. Element maps were compiled and processed using Iolite data analysis program Igor.

TABLE S3. Average minimum detection limits and dwell times for LA-ICP-MS spot analysis and mapping

Isotope	dwell time/spot (sec.)	average minimum detection limit/spot/ for sulfosalts (ppm)	average minimum detection limit/spot/ for BMS (ppm)	dwell time/mapping (sec.)
^{34}S	0.005	-	-	0.005
^{55}Mn	0.01	0.47	0.48	-
^{57}Fe	0.005	-	-	0.005
^{59}Co	0.01	0.20	0.98	0.005
^{60}Ni	0.01	0.26	0.06	0.005
^{63}Cu	0.01	-	-	0.01
^{66}Zn	0.01	-	-	0.01
^{69}Ga	0.02	0.04	0.12	-
^{75}As	0.01	-	0.77	0.01
^{77}Se	0.03	2.14	0.26	0.02
^{95}Mo	0.02	0.03	0.01	-
^{107}Ag	0.03	0.44	0.24	0.04
^{111}Cd	0.02	0.16	-	0.01
^{115}In	0.02	0.05	3.63	0.01
^{118}Sn	0.02	0.23	0.04	0.01
^{121}Sb	0.02	-	1.53	0.01
^{125}Te	0.03	0.21	0.07	0.02
^{197}Au	0.03	0.13	0.03	0.04
^{201}Hg	0.005	1.26	3.60	0.005
^{205}Tl	0.02	0.02	0.004	-
^{209}Bi	0.02	-	0.06	0.01

References cited

- Paton, C., Hellstrom, J., Paul, B., Woodhead, J. and Hergt, J. (2011) Iolite: Freeware for the visualisation and processing of mass spectrometric data. *Journal of Analytical Atomic Spectrometry*. doi:10.1039/c1ja10172b
- Wilson, S., Ridley, W., and Koenig, A. (2002) Development of sulphide calibration standards for the laser ablation inductively-coupled plasma mass spectrometry technique. *Journal of Analytical Atomic Spectrometry*, 17, 406–409.