Critical elements in nonsulphide Zn deposits:

A reanalysis of the Kabwe Zn-Pb ores

(central Zambia)

APPENDIX 1

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Materials and Methods

Sample selection and preparation

For this study, 16 specimens of Kabwe area ore bodies, housed in the Natural History Museum Ore collection (London) (Table A1) were firstly selected. To define the ore textural, mineralogical and geochemical characteristics, from the 16 samples-batch, only a limited number of macroscopically diverse samples were further chosen. One willemite specimen, belonging to the Natural History Museum Mineralogy Collection (Table A1), was also used for oxygen isotopic analyses.

Table A1. Specimens of the Kabwe ores used for this study (Natural History Museum Ore Collection).

Specimen (Collection) ID	Specimen ID as used in the text	Specimen description as on the collection label
BM.1907,987	BM1907-987	Lead-zinc-ore
BM.1985,MI29629 1/2	MI29629 1/2	Partly oxidised lead-zinc ore
BM.1985,MI29629 2/2	MI29629 2/2	Partly oxidised lead-zinc ore
BM.1985,MI29631	MI29631	Oxidised ore - No.1 Orebody
BM.1985,MI29633	MI29633	Dolomite
BM.1985,MI32046	MI32046	Sphalerite disseminated in dolomite
OR.5303	OR5303	Vanadium Ore (containing descloizite and limonite)
OR.5304	OR5304	Sulphide Ore (containing zinc blende, galena and pyrite)
OR.5305	OR5305	Zinc-silicate' Ore
OR.5307	OR5307	Zinc-lead Carbonate Ore
OR.5309	OR5309	Zinc-silicate' Ore
OR.5310	OR5310	Tarbuttite
OR.5312	OR5312	Pyromorphite
OR.5314	OR5314	Calamine (hemimorphite)
BM.1985,MI10900	MI10900	Hemimorphite
BM.1930,372	BM1930-372	Blende showing large veined cleavage areas with galena, cerussite + limonite after pyrite - Carmarnor mine, 2.5 km W of Broken Hill
BM.1920,238*	BM1920-238	Willemite associated with sphalerite

* this specimen is housed by the Natural History Museum Mineralogy Collection.

The samples were cut in two halves: the first half was used to prepare polished blocks for Optical Microscopy (OM), Scanning Electron Microscopy with Energy Dispersive X-ray Spectrometry (SEM-EDS) and Automated Mineralogy analyses, whereas the second half (~5 g) of the sample was ground to produce powder for whole-rock X-ray Powder Diffraction (XRPD) and chemical analyses. Polished resin blocks (2 cm diameter) were prepared, mounted in bi-component epoxy resin (SpeciFix20), polished with alumina Al_2O_3 (0.3 μm) and diamond suspension (1 μm). Blocks were carbon coated prior to analysis in the SEM and microprobe.

X-ray diffraction analysis

XRPD patterns have been obtained by using a Enraf Nonius PDS120 diffractometer (Natural History Museum, London, UK), characterised by an asymmetric reflection geometry, with fixed angle between the X-ray tube, the sample surface and the detector. The diffractometer mounts a cobalt tube, a primary Germanium 111 monochromator and slits (0.14 x 5 mm). Cobalt $K\alpha 1$ radiations were used at 40 kV and 40 mA. The sample holder was a sample spinner with flat-plate sapphire substrate (zero background). The angle of incident beam – to – sample was 4º. INEL position sensitive detector collects 120º 2θ simultaneously, with a channel width of ~0.03°. The XRPD patterns were analysed by using the Highscore Plus (Panalytical) software; the PDF4 (powder diffraction file from ICDD) database was used for the phase identification. The adopted instrumental configuration and the sample preparation did not allow carrying out quantitative phase analysis with the Rietveld method. Mineral abundances have been determined as “wt.% ranges”, on the basis of the peak intensity ratio between mineral phases, the modal mineralogy of polished blocks and the whole-rock chemical analyses.

Whole-rock chemical analyses

Whole-rock chemical analyses of major (Zn, Fe, Ca, Mg, Al, K, S) and minor (V, Co, Ni, Cu, Sr, Y, Zr, Nb, Ba, Pb, P, As, Cd, Tl, Na, Sb, Mo, Rb, Li, Sn, Cr, La, Ce, Th, U, Ge, Ga) elements were carried out at Natural History Museum, London, UK. Approximately 50 mg of powdered rock sample was dissolved in Savillex 60 ml fluoropolymer vessels. 2-4.5 ml HCl and 0.05-0.25 ml HNO_3 were added to all samples and the mixture was shortly heated up to 70°C and the temperature rose to 100°C once the reaction had subsided. After samples were cooled down, 1 ml HNO_3, 1 ml

$HClO_4$ and 2 ml HF was added to each, the vessels were capped and heated overnight at 100°C. The solutions were evaporated down at 150°C and reconstructed in 50 ml of ca. 0.6 M HNO_3 with traces of H_2O_2. The solutions were analysed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) using an Agilent 7700x mass spectrometer. To minimise polyatomic interferences, the instrument was run with 5 ml min -1 He (99.9995% purity) in the collision-reaction octopole cell (CRC) as well as with no collision gas entering the CRC. Ga (^{71}Ga) was determined in the 'no gas' mode while all other elements were determined in the 'He mode'. To minimise the contamination of the instrument with high lead concentrations the solutions were further diluted 100-fold with ca. 0.7M HNO_3. The instrument was calibrated using multi-elements standards (Inorganic Ventures) typically with a 4-point calibration with a correlation coefficient of > 0.9999. Accuracy was monitored by analysing certified reference materials JLk-1 (Lake sediment, GSJ) and SdAR-1 (Modified river sediment, IAG) at the beginning and at the end of the run. All values were found to be within the uncertainty of the published data. The limits of quantification were calculated as 10 times the standard deviation of HNO_3 blank solution analysed at least 10 times during the run.

Scanning electron microscopy

SEM-EDS analyses were carried out by using a ZEISS EVO LS 15 scanning electron microscope (Natural History Museum, London, UK) at 20 kV, with 8.5 mm working distance and 3 nA current mounting with X-Max detectors. A Co standard was used for the instrument calibration. Quantitative data sets of selected samples were obtained by wavelength dispersion spectrometry (WDS), using a Cameca SX100 electron microprobe operating at 20 kV, 20 nA, and 10 μm spot size (Natural History Museum, London, UK).

The modal mineralogy of the samples was investigated on polished blocks using the Mineralogic system, which is an automated ZEISS EVO•50 SEM, equipped with two Bruker xFlash 5010 EDS detectors. The analyses were carried out with an acceleration voltage of 20 kV with 13 mm working distance, 0.050 s dwell time corresponding to ~3000 EDS counts per spectra. The calibration of the EDS detectors was carried out every 60 minutes using a Cu standard (Cu Kα peak). The analyses were carried out adopting the "full map" analytical mode, in order to obtain high resolution distribution maps of the mineral phases occurring, correlated with a database containing statistical information of the samples. Not recognised phases have been reported as "unclassified" in the mineral list.

Laser ablation ICP-MS analysis

Laser ablation (LA)-ICP-MS analyses were carried out on an ESI NWR193 UV 193 nm short pulse width (<4 ns) laser fitted with a TwoVol2 ablation cell and coupled to an Agilent 7700x quadrupole ICP-MS configured with dual external rotary pumps for enhanced sensitivity, located in the LODE laboratory - Natural History Museum (London). Ablated spots were 35-50 μm in diameter, with a fluence of 3.5 Jcm^{-2}, fired at a frequency of 10 Hz. The transport gas used was He at a flow rate of 0.5 $l\ min^{-1}$ mixed with Ar at a flow rate of 1.1 $l\ min^{-1}$, in a signal smoothing device.

The element menus and ICP-MS dwell time settings that were employed to obtain the compositions of the various minerals are listed in Appendix 2. Element ratios to an internal standard element (^{29}Si for willemite and hemimorphite, ^{57}Fe for goethite and hematite, and ^{66}Zn for smithsonite, descloizite and sphalerite) were determined by referencing background-corrected integrated intensities from mineral signals to the external calibration standard. This was GSD-1g glass (USGS) for goethite and hematite, and NIST 610 for descloizite. Following the procedure in Choulet *et al.* (2016), the external calibration standard for willemite and hemimorphite was NIST 612. External calibration with GSD-1g glass gave element concentrations for hemimorphite and willemite that were within <5 % (±) of the concentrations calculated with NIST 612. Without a matrix-matched carbonate mineral standard (appropriate for this study) being commercially available, we used NIST 610 for smithsonite. GSD-1g, NIST 612, or NIST 610 were used as secondary standards; NIST

2782 and BC_28 (the in-house magnetite standard of Dare *et al*., 2014) were also monitored during Fe oxide or oxy-hydroxide analysis.

More complicated was the analytical approach to the sphalerite analysis and the choice of the appropriate external standard. The polymetallic sulphide material MASS-1 is commonly adopted for external calibration of sphalerite (Belissont *et al*., 2014), because the nature itself of MASS-1 makes this material more matrix-matching to the mineral than a glass. Main limitations of the MASS-1 as a standard for this work were that Ge is not certified or even included as a reference value, and that the material can be heterogeneous (Fig. A1).

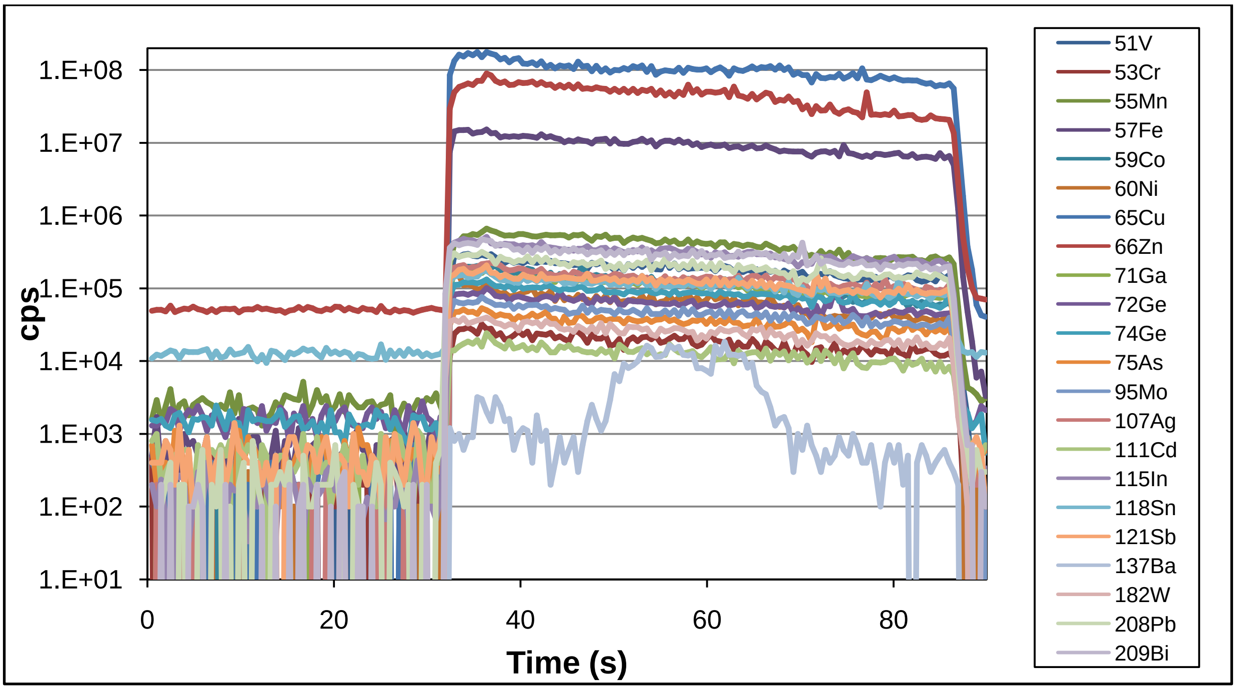

Fig. A1 - Examples of time resolved LA-ICP-MS spectra of the polymetallic sulphide material MASS-1.

These limitations usually do not affect glass standards (e.g. NIST glass), which on the other hand are less counts/sensitivity-matching to the mineral (sphalerite) than MASS-1, when using Zn as internal standard: in fact, MASS-1 contains 21 wt.% Zn, whereas NIST 610 and NIST 2782 contain only 460 ppm and 1254 ppm Zn, respectively. By using external calibration by NIST 610 for calculating compositions of MASS-1 as secondary standard, we obtained element concentrations of the reference material very variable among different spots and far from the reference values (Table A2).

Table A2. Compositions (ppm) of polymetallic sulphide material MASS-1 from external calibration through NIST 610 (int. Standard = Zn).

Measured isotope	^{51}V	^{53}Cr	^{55}Mn	^{57}Fe	^{59}Co	60Ni	^{65}Cu	71Ga	^{72}Ge	^{75}As	^{95}Mo	^{107}Ag	^{111}Cd	^{115}In	^{118}Sn	^{121}Sb	^{137}Ba	^{182}W	^{208}Pb	^{209}Bi
USGS MASS-1 reference values (ppm)	63	65	280	156000	60	97	134000	64	-	65	59	50	60	50	59	60	14	20	68	60
Spot MY26B04	129	127	248	263729	92	225	333515	127	131	128	114	153	71	110	126	134	2	39	167	148
Spot MY26B05	136	134	257	275024	86	236	295227	137	140	143	127	145	74	118	133	145	3	40	172	148
Spot MY26B06	144	137	260	288784	88	236	317268	145	151	155	134	152	77	128	142	151	3	41	181	159
Spot MY26B27	120	117	234	253989	90	223	289896	119	121	119	109	133	65	103	116	119	3	35	147	134
Spot MY26B28	140	137	265	301083	86	227	312252	142	153	157	130	152	81	134	143	154	3	41	189	163
Spot MY26B29	145	137	267	300450	88	238	330911	145	153	159	132	155	79	131	143	152	6	44	183	164
Spot MY26C31	118	117	228	245950	86	215	271261	118	121	120	105	128	64	101	114	121	2	33	148	128
Spot MY26C32	117	116	235	249509	81	193	287351	119	124	123	113	132	69	106	116	123	2	34	149	128
Spot MY26C33	130	129	244	282481	83	234	323488	135	137	133	122	138	70	126	126	137	3	39	172	146
Mean value	131	128	249	273444	87	225	306796	132	137	137	121	143	72	117	129	138	3	38	168	146
Difference = Mean value – reference value	68	63	-31	117444	27	128	172796	68	-	72	62	93	12	67	70	78	-11	18	100	86
Relative error (%)	52	49	13	43	31	57	56	52	-	53	51	65	17	57	54	56	347	48	59	59

The overestimation of MASS-1 element concentrations externally calibrated by NIST 610 is probably related to the low concentration of the internal standard (Zn) in the NIST 610, compared to the MASS-1. For this reason, we considered MASS-1 more appropriate than NIST glass for external calibration of sphalerite. Given the absence of a certified value for Ge in the MASS-1, NIST 610 was used instead for evaluating the Ge concentration in sphalerite. This concentration is probably affected by sensitivity issues and would result probably higher than the real one. Belissont *et al*. (2014) report a Ge concentration of 57.8 ± 2.6 ppm in the polymetallic sulphide material MASS-1 (Dr. Stephen Wilson, personal communication, in Belissont *et al*. 2014). This value is ~1/2 the amount calculated with external calibration by NIST 610 (Table A2).

Absolute element concentrations were calculated from internal standard element concentrations (predetermined by SEM-EDS and SEM-WDS) in the program ExLAM (Zachariáš and Wilkinson, 2007). Limits of detection were set at the conventional 3σ of the background signal variation (Longerich *et al*. 1996).

Contamination of the phase of interest by inclusions (e.g. chalcopyrite in sphalerite; galena in willemite; Mn-oxy-hydroxides in goethite and hematite) or the crossing of grain boundaries was avoided by monitoring a number of non-formula elements associated with these contaminant phases. Zonation was registered only in willemite (Pb-zoning), and it was handled in the following way during data treatment: the signal was split into high and low regions and processed as two separate signals to give an expression of the range. The other analysed minerals were remarkably un-zoned.

Time-resolved raw cps signals were meticulously screened and the longest ‘clean’ integration intervals possible (up to 60secs of signal) were retained; analyses with significant contamination were discarded outright. Tuning was optimised for the whole mass range, and oxide formation (as represented by ^{248}ThO/^{232}Th) and doubly-charged species formation (observed via ^{22}Ca/^{44}Ca) were kept below 0.2%. No correlation was observed between calculated ^{57}Fe and ^{72}Ge, excluding any polyatomic interference of ^{56}Fe^{16}O on ^{72}Ge.

Stable isotope analysis

Carbon and oxygen isotope analyses were performed on smithsonite and cerussite. Hand-picked carbonate mineral specimens were analysed at SUERC (East Kilbride, Scotland) on an Analytical Precision AP2003 mass spectrometer equipped with a separate acid injector system, after reaction with 105% H_3PO_4 under He atmosphere at 70 °C. Isotopic results are reported using the conventional δ‰-notation. Mean analytical reproducibility based on replicates of the SUERC laboratory standard MAB-2 (Carrara Marble) was around ±0.2‰ for both carbon and oxygen. The δ^{13}C are reported relative to V-PDB, whereas the δ^{18}O of carbonates are quoted to V-SMOW.

Oxygen isotopic composition of willemite was analysed on hand-picked crystals, by using a laser fluorination procedure, involving total sample reaction with excess ClF_3 using a CO_2 laser as a heat source (in excess of 1500°C; following Sharp, 1990). All combustions resulted in 100% release of O_2 from the silica lattice. This O_2 was then converted to CO_2 by reaction with hot graphite, then analysed on-line by a VG Isotech SIRA II spectrometer. Reproducibility is better than ±0.3‰ (1σ), based on repeat analyses of international and internal lab standards run during these analyses. Results are reported in standard notation (δ^{18}O) as per mil (‰) deviations from the Standard Mean Ocean Water (V-SMOW) standard.

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