**APPENDIX 1**

*Supplementary Electron Microprobe Methods*

A total of 22 thin section samples were analyzed for 17 elements (Ag, As, Au, Ba, Bi, Ca, Cd, Cu, Fe, Ge, Hg, Mn, Ni, Pb, S, Sb, Sn, Sr, Te, V, Zn) in 15 phases (excluding unknowns; barite, sphalerite, pyrite, galena, chalcopyrite, tetrahedrite, bornite, colusite, sulvanite, reinerite, electrum, stromeyerite, bournonite, pearceite and miargyrite). LIF, PET and TAP diffracting crystals detected element wavelengths for each mineral phase. Large area and high intensity LIF and PET crystals are indicated with an H and L, respectively. Measured elements using the LIF crystal included: Ba Lα (brt); Fe Kα (brt,); Zn Kα (sp); Cu Kα (py, gn, ccp et al., col); Ni Kα (ccp et al.). Measured elements using the LIFH crystal included: Cu Kα (sp, elec); Mn Kα (sp). Measured elements using the LIFL crystal included: Fe Kα (brt, sp, py, gn, ccp et al., col, elec); Mn Kα (sp); Cu Kα (sp, py, gn, elec); Zn Kα (py, gn, ccp et al., col); Hg Lα (py, gn, ccp et al., elec); Bi Lα (ccp et al.); V Kα (col). Measured elements using the PET crystal included: S Kα (brt, sp, py, gn, ccp et al., col, elec); Ca Kα (brt); Sb Lα (py, gn, ccp et al., col); Pb Mα (pb, gn, elec); Ag Lα (elec); Au Mα (elec). Measured elements using the PETH crystal included: Ag Lα (brt, sp, py, gn, ccp et al., col, elec); Au Mα (brt, py, gn, col, elec); Sr Lα (brt); Pb Mα (brt, ccp et al.); Cd Lα (sp); Sb Lα (py, gn, elec); Te Lα (ccp et al.); Sn Lα (col). Measured elements using the PETL crystal included: Sr Lα (brt); Ca Kα (brt); Pb Mα (brt); Te Lα (brt); Ba Lα (brt); Cd Lα (sp). Measured elements using the TAP crystal included: Ge Lα (brt, sp, col); As Lα (py, gn, ccp et al., col, elec). The data were processed using the CITZAF V3.5 online software program for JEOL™ written by J. T. Armstrong (California Institute of Technology). Interference corrections were made for Au Mα interference with Pb Mα in galena.

The lower limit of detection (LLD) was calculated using the formula below for each spot analyzed by electron microprobe (Equation D.1.1). Abreviations are as follows: ZAF = total matrix correction factor; std = standard; unk = unknown; bkg = background; C = concentration (wt%); I = intensity ((s\*nA)-1); t = count time (s); curr = current (nA) (pers comm B. Joy, 2013).

*Lower Limit of Detection (LLD) calculation for EMPA analyses.*

|  |
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| (i)LLD (3σ) = 3\*ZAF\*(C\_std/I\_std,net)\*√2\*√(I\_unk,bkg/(t\_unk,bkg\*curr\_unk)) |
| (ii) ZAF =C\_unk/(I\_unk,net/I\_std,net)\*C\_std |

*Supplementary Laser Ablation ICPMS Methods*

Of the 33 total elements detected in this study, 14 elements (Ba, Cu, Fe, Hg, Ir, Nb, Pt, Rb, Sc, Sr, Te, W, Zn, Zr) were not considered due to: (i) lack of standard data; (ii) inconsistencies with preferred values for the calibration curve; (iii) inconsistencies with preferred values for the external standard; (iv) below lower limit of detection in unknowns; or (v) above upper limit of detection in unknowns. Published and preferred data for the standards used (GSC-1G, GSD-1G, GSE-1G and BHVO-2G) were found on the Geological and Environmental Reference Materials database (<http://georem.mpch-mainz.gwdg.de/sample_query_pref.asp>) and are included in Table E.1.1. A total of 185 analyses were conducted on 6 phases (sphalerite, pyrite, galena, chalcopyrite, tetrahedrite and bornite). Analyses were mostly conducted using the spot technique for laser ablation of in-situ minerals; however, some line analyses were conducted for the sake of comparison. The lower limit of detection (LLD) was calculated for each set of unknown analyses using the gas blank, and applied to corrected laser data (Equation E.1.1). Abbreviations are as follows: xblank = element mass in He-ArF carrier gas; σblank = standard deviation of element mass in carrier gas.

*Lower Limit of Detection (LLD) calculation for LAICPMS analyses.*

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| LLD = xblank + 3 σblank |

*List of Standard Reference Materials*

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Element mass  (ppm) | USGS Standard | | | | |
| **GSC-1G** | **GSD-1G** | **GSE-1G** | **BHVO-2G** | **MASS-1** |
| **Ag** | 4.1 | 23 | 200 |  | 67 |
| **As** | 3.2 | 27 | 260 |  | 65 |
| **Au** | 6 | 4 | 7 |  | 47.72 |
| **Ba** | 34.8 | 67 | 427 | 131 |  |
| **Bi** | 3.4 | 35 | 320 | 0.01 | 7 |
| **Cd** | 1.9 | 18 | 160 | 0.1 | 70 |
| **Co** | 5.9 | 40 | 380 | 44 | 67.45 |
| **Cr** | 10.3 | 42 | 400 | 293 | 37 |
| **Cu** | 16 | 42 | 380 | 127 | 129500 |
| **Fe** | 106531.9 | 103421.5 | 98755.8 | 87869.4 | 156000 |
| **Ge** | 4 | 32 | 320 | 1.6 | 50 |
| **Hg** |  |  |  |  | 57 |
| **In** | 4.5 | 38 | 370 | 0.1 | 50 |
| **Ir** | 2 | 12 | 120 |  | 63.51 |
| **Mn** |  |  |  | 1316.8 | 260 |
| **Mo** | 4.6 | 39 | 390 | 3.8 | 61 |
| **Nb** | 4.5 | 42 | 420 | 18.3 |  |
| **Ni** | 21 | 58 | 440 | 116 | 91.49 |
| **Pb** | 14 | 50 | 378 | 1.7 |  |
| **Pt** | 2 | 6 | 30 | 0.46 | 61.78 |
| **Rb** | 4.92 | 37.3 | 356 | 9.2 |  |
| **Sb** | 5.3 | 43 | 450 | 0.3 | 55 |
| **Sc** | 5.4 | 52 | 530 | 33 |  |
| **Se** | 0.2 | 2 | 20 |  | 53 |
| **Sn** | 5.3 | 29 | 280 | 2.6 | 55 |
| **Sr** | 32.3 | 69.4 | 447 | 396 |  |
| **Te** |  |  |  |  |  |
| **Ti** | 8213.4 | 7434.1 | 449.6 | 16726.6 |  |
| **Tl** | 0.27 | 0.9 | 2 |  |  |
| **V** | 5.4 | 44 | 440 | 308 | 63 |
| **W** | 4.5 | 43 | 430 | 0.23 |  |
| **Zn** | 12.7 | 54 | 460 | 102 | 210000 |
| **Zr** | 6.8 | 42 | 410 | 170 |  |