Appendix 2. Sample preparation and analytical methods

Sample preparation and basic textural investigation

Rock samples have been cut, included in epoxy-resin and polished for the systematic examination by reflected light microscopy in order to define the spatial distribution, petrographic association, and textural characteristics of sulfides. Selected colloform pyrite samples were etched for 30–120 s using 70% nitric acid (HNO$_3$), rinsed with distilled water, and air dried in a desiccator.

Scanning electron microscopy and energy dispersion X-ray spectroscopy analysis

Scanning electron microscopy (SEM) was used to examine the detailed mineralogical and textural characteristics of sulfides on polished and etched surface areas. Backscattered electron (BSE) and secondary electron (SE) imagery, as well as qualitative energy dispersive X-ray spectroscopy (EDS) analysis, was carried out on uncoated samples using a FEI XHR-Verios 460L field emission SEM (FESEM) at the Centre for Microscopy, Characterisation and Analysis, the University of Western Australia (CMCA-UWA). Electron imagery was performed at variable acceleration voltage (3-12 kV) and beam current (0.2–0.4 nA). Up to 15 kV and 0.8 nA was used for EDS analysis in order to ensure sufficiently high peak count rates for accurate determination of characteristic element-specific X-ray emission lines.

Wavelength-dispersive X-ray spectroscopy analysis

Quantitative wavelength dispersive X-ray spot analysis was performed using a JEOL 8530F field-emission gun electron probe micro-analyser at CMCA-UWA. Prior to analysis the samples were coated with a 20 nm carbon film. The operating conditions for spot analysis were 40 degrees take-off angle, and a beam energy of 20 keV. The beam was fully focused to give a spot size of about 1 μm with a 50 nA beam current. Three different sets of elements, listed in the table below along with the respective counting times (in seconds),
were used for analysing pyrite and arsenopyrite [1-py], sphalerite and chalcopyrite [2-sp], galena and Ag-Sb-Pb-Bi sulfosalts [3-ga].

| 1-py | S  | As | Sb | V  | Fe | Ti | Se | Au | Te | Cu | Pb | Ni | Zn | Co | Ag | Cd | Bi |
|------|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
|      | 20 | 100| 120| 80 | 20 | 80 | 80 | 200| 80 | 60 | 120| 60 | 60 | 120| 120| 120|
| 2-sp | S  | Sb | Fe | Se | Cu | Pb | Zn | Ag | Cd | Bi | Hg | Mn |
|      | 20 | 120| 60 | 120| 60 | 120| 40 | 120| 120| 120| 120| 120|
| 3-ga | S  | As | Sb | Fe | Se | Te | Cu | Pb | Ni | Zn | Ag | Cd | Bi | Hg | Mn |
|      | 20 | 60 | 40 | 60 | 100| 60 | 60 | 40 | 60 | 80 | 80 | 80 | 80 | 60 |

Elements were acquired using analysing crystals LiF for V kα, Fe kα, Ti kα, Au lα, Te lα, Cu kα, Ni kα, Zn kα, Co kα, Hg lα, Mn kα, PETJ for S kα, Ag lα, Cd lα, PETH for Sb lα, Pb mα, Bi mα and TAP for As lα, Se lα. The standards employed were an assortment of commercially available metals, oxides, sulfides and tellurides. Mean atomic number background corrections were employed throughout (Donovan and Tingle, 1996). Unknown and standard intensities were corrected for dead-time and the ZAF algorithm utilised for matrix absorption (Armstrong, 1988). Standard intensities were corrected for standard drift over time. On peak interference corrections were applied as appropriate (Donovan et al., 1993). Limits of detections (LODs) are included in Appendix-3.

Quantitative chemical maps were acquired using the calibration set up described above for S, As, Sb, Co, Fe, Ag, Pb, Zn, and Ni. Detection limit maps were acquired for these elements and applied as the minimum cut-off values for all maps. Map acquisition utilised an 80 nA beam current with a 1x1µm pixel dimension and 100 ms dwell time per pixel. Data were processed using the Calc-Image software package.

**Laser Ablation Inductively Coupled Mass Spectrometry**

Laser Ablation Inductively Coupled Mass Spectrometry (LA-ICP-MS) analyses were performed at the LabMaTer (Université du Québec à Chicoutimi, Canada), at the John de Laeter Centre (Curtin University, Australia), and at CODES (University of Tasmania).

At the John de Laeter Centre trace elements analyses on pyrite were performed using a RESOlution M-50A-LR incorporating a Compex 102 excimer laser, coupled to an Agilent 7700s quadrupole ICP-MS. Following a 20 s period of background analysis, samples were spot ablated for 60s at a 7Hz repetition rate, using a 75µm beam and laser energy of 2.5 J*cm⁻². Oxide polyatomic interferences were minimized by tuning flow rates for a ThO/Th to < 0.5%. The sample cell was flushed with ultra-high purity He (350 mL min⁻¹) and N₂.
(3.8 mL min\(^{-1}\)) and high purity Ar was employed as the plasma carrier gas. The chalcogenide glass IMER-1 (Ding et al., 2011) was used as the primary reference material (RM), to calculate elemental concentrations (using \(^{34}\)S determined by WDS analyses as internal standard element) and to correct for instrument drift on all elements except Au. Certified RM Laflamme Po726 (synthetic pyrrhotite doped with platinum group elements and Au) was used as primary standard for Au calculation. A combination of 6 other RMs were used for quality control: GSD-1G, NIST610, NIST612, BHVO-2G, BCR-2G, BONN. The mass spectra were reduced using Iolite (Paton et al., 2011 and references therein). Data were collected on a total of 22 elements: \(^{34}\)S, \(^{55}\)Mn, \(^{57}\)Fe, \(^{59}\)Co, \(^{60}\)Ni, \(^{65}\)Cu, \(^{66}\)Zn, \(^{69}\)Ga, \(^{75}\)As, \(^{77}\)Se, \(^{95}\)Mo, \(^{107}\)Ag, \(^{111}\)Cd, \(^{118}\)Sn, \(^{121}\)Sb, \(^{125}\)Te, \(^{182}\)W, \(^{197}\)Au, \(^{202}\)Hg, \(^{205}\)Tl, \(^{208}\)Pb, \(^{209}\)Bi with a dwell time of 0.01ms.

At the LabMaTer trace elements analyses on pyrite and sphalerite were performed using an excimer 193nm laser system (RESOlation – Australian Scientific Instruments Pty. Ltd.) equipped with a dual-volumes cell (S-155 Laurin Technic, Australia) coupled to a 7900 Agilent mass spectrometer. Helium flow in the ablation cell was 350 mL/min and mixed to the ICP-MS argon carrier gas (~1.0 mL/min), and 2 mL/min nitrogen was added to the line. A tiny flow of helium (1 mL/min) was injected in the collision cell of the ICP-MS to reduce the formation poly-atomic interferences without affecting the sensitivity and stability of mid- and high-range masses. Instrument was tuned daily to maximise sensitivity and ensure oxide formation level being <1% based on 248/232 mass ratio. Typical short term stability shows <5% RSD. Spot analyses were performed on the samples using varying beam size (25 - 55 µm) with a pulsing rate of 20 Hz and a fluence of 2.0 J/cm\(^2\). Data reduction was performed using IOLITE software (Paton et al., 2011) using as internal standard (IS) \(^{57}\)Fe for pyrite and \(^{66}\)Zn for sphalerite determined by WDS analyses. Isotopes studied to generate a fully quantitative dataset are: \(^{55}\)Mn, \(^{57}\)Fe\(^*\), \(^{59}\)Co, \(^{60}\)Ni, \(^{65}\)Cu, \(^{66}\)Zn\(^**\), \(^{69}\)Ga, \(^{72}\)Ge, \(^{75}\)As, \(^{77}\)Se, \(^{95}\)Mo, \(^{107}\)Ag, \(^{111}\)Cd, \(^{118}\)Sn, \(^{121}\)Sb, \(^{125}\)Te, \(^{182}\)W, \(^{197}\)Au, \(^{202}\)Hg, \(^{205}\)Tl, \(^{208}\)Pb, \(^{209}\)Bi (* for sphalerite only, ** for pyrite only). A combination of 2 RM was necessary to cover the elements ranges: GSE-1g (USGS) and MASS-1 (USGS) and 2 more RM were used for quality control: AI-3 (UQAC house RM), Gprob6 and G- Probe-6 (USGS). All working values and LODs are reported in Appendix-5.

At the Centre for Ore Deposit and Exploration Studies (CODES), University of Tasmania, trace element imaging of pyrite was accomplished using a Coherent ArF gas-charged 193 nm excimer laser, coupled to a LaurinTechnic S-155 dual-volume ablation cell. The ablation cell was mated to an Agilent 7900 quadrupole mass spectrometer. Helium gas was continuously flushed through the ablation cell during image analysis, with a flow rate of approximately 350 mL/min. This was then mixed with argon carrier gas (flowing at 1-1.1 L/min) prior to the aerosol’s introduction into the torch of the mass spectrometer. Image parameters varied
depending on the characteristics of each sample. However, beam size was generally between 15-35 µm, and scan speed was between 1-2 times the beam size. Pulse rate was 10 Hz for all images. A method containing 42 elements was employed during imaging; the internal standard element was iron (57Fe). Elements measured in this method were as follows: 23Na, 24Mg, 27Al, 28Si, 34S, 38K, 43Ca, 49Ti, 51V, 53Cr, 55Mn, 57Fe, 59Co, 60Ni, 66Cu, 66Zn, 75As, 77Se, 91Zr, 93Nb, 95Mo, 107Ag, 109Ag, 111Cd, 118Sn, 123Sb, 125Te, 137Ba, 157Gd, 178Hf, 181Ta, 181W, 197Au, 205Hg, 205Ti, 206Pb, 207Pb, 209Bi, 232Th, and 238U. Standard reference materials used for this study were STDGL2b2 (Danyushevsky et al., 2011), GSD-1G (Jochum et al., 2005), and an internal natural pyrite standard (Gilbert et al., 2014). Data reduction was performed according to the procedures detailed in Steadman et al. (2013).

Secondary Ion Mass Spectrometer

Methods utilised to obtain, reduce, standardise and process the SIMS data collected from the CAMECA IMS1280 large-geometry ion probe at CMCA-UWA are detailed in LaFlamme et al. (2016), and specific analytical conditions are described below. Prior to analysis the samples were coated with a 30 nm gold film. Quadruple sulfur isotope (32S, 33S, and 34S) analysis was performed with the ion microprobe operating in multi-collection mode using a 10 keV Cs+ primary beam (~2.5 - 3 nA; Gaussian mode) and a normal incidence electron flood gun for charge compensation during all analyses. Following a 30 s pre-sputter, secondary sulfur ions from the target sample were extracted at -10 kV and admitted to the mass spectrometer with a field magnification of 133×, with automated centering of the secondary beam in the field aperture (both x and y; aperture size 4000µm) and entrance slit (x direction only; slit width 60 µm). The NMR magnetic field controller locked the axial mass at the beginning of each session, and the mass spectrometer operated at a mass resolution (M/ΔM) of about 2500 (exit slit width of 500 µm on the multi-collector). 33S was simultaneously detected by three Faraday Cups using amplifiers with 10\(^{11}\) Ω (L’2) and 10\(^{10}\) Ω resistors (L1 and H1). 36S was measured using a low-noise ion counting electron multiplier (EM). A primary beam current of 5nA, raster size of 25 µm for pre-sputter and 20 µm for analysis and an acquisition time of 279 s in 45 integration cycles were necessary to achieve good precision on 36S. The EM high voltage was optimised using a Pulse Height Amplitude (PHA) distribution curve at the start of each session, and the grain drift was measured more than three times during each analysis (at the beginning, middle and end). Measurements of unknowns were interspersed with matrix-matched reference materials, listed below, to calibrate isotope ratios and monitor external precision.
<table>
<thead>
<tr>
<th>PHASE</th>
<th>REFERENCE MATERIAL</th>
<th>$\delta^{33}$S (%)</th>
<th>$\delta^{34}$S (%)</th>
<th>$\delta^{36}$S (%)</th>
<th>REFERENCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>pyrite</td>
<td>Sierra</td>
<td>1.09</td>
<td>2.17</td>
<td>3.96</td>
<td>LaFlamme et al., 2016</td>
</tr>
<tr>
<td>chalcopyrite</td>
<td>Nifty-b</td>
<td>-1.78</td>
<td>-3.58</td>
<td>-7.15</td>
<td>LaFlamme et al., 2016</td>
</tr>
<tr>
<td>pyrrhotite</td>
<td>Alexo</td>
<td>1.73</td>
<td>5.23</td>
<td>10.98</td>
<td>LaFlamme et al., 2016</td>
</tr>
</tbody>
</table>

Uncertainties on each $\delta^{33}$S spot are included in Appendix-7 and were calculated by propagating (i) the errors on instrumental mass fractionation determination, including the standard deviation on the matrix-matched standard measurements and the uncertainty associated with the bulk characterisation of the matrix-matched standard, and (ii) internal error on each sample data point (LaFlamme et al., 2016; Whitehouse, 2013).

**Multiple Sulfur Isotope Notation**

Results are described using standard delta notation

$$\delta^{3i}S = 1000 \times \left( \frac{\delta^{3i}S_{sample}}{\delta^{3i}S_{standard}} \right) - 1$$

where $3i$ superscript refers to 33, 34, or 36 and standard concentrations refers to the Vienna-Cañon Diablo Troilite (V-CDT; Ding et al., 2001).

Deviations of $\delta^{33}$S and $\delta^{36}$S from the mass-dependent fractionation array, are described using capital delta notation

$$\Delta^{33}S = \delta^{33}S - 1000 \times \left( 1 + \frac{\delta^{34}S}{1000} \right)^{0.515} - 1$$

$$\Delta^{36}S = \delta^{36}S - 1000 \times \left( 1 + \frac{\delta^{34}S}{1000} \right)^{1.9} - 1$$

0.515 and 1.9 correspond to $\lambda$, the slope of the mass dependent fractionation line for $\delta^{33}$S and $\delta^{36}$S respectively (Ono et al., 2006).


