EA 5-1 LA-ICP-MS Methodology

1.1 Quantitative Elemental Mapping

 Element mapping of pyrite, sphalerite and arsenopyrite was carried out on selected areas of thick sections (~200 µm) by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) at the Geological Survey of Canada, using a Photon Machines/Teledyne Analyte G2 193 nm excimer laser ablation system, with a Helex two-volume ablation cell, coupled to an Agilent 7700x quadrupole ICP-MS. The mapping procedure closely follows the method of Lawley et al. (2015; 2020) and Paradis et al. (2020). Element maps were constructed by translating the sample stage under a focused laser beam, to form a series of raster line scans. Laser conditions during the analytical sessions include: a fluence of 4.2–5.0 J/cm2, a repetition rate of 30 Hz, a spot size of 4 to 20 µm, and a scan speed of 4 to 40 µm/s. The spot size and scan speed were selected such that the sample stage would advance one equivalent spot diameter every 0.5 seconds for the sphalerite map (20 µm @ 40 µm/s), or every 1 second for the pyrite (12 µm @ 12 µm/s, and 15 µm @ 15 µm/s) and arsenopyrite (4 µm @ 4 µm/s) maps. Prior to each ablation pass, the sample surface was cleaned by passing the laser across the sample at a rate of 2–3 pulses every equivalent spot diameter. The cleaning pass was followed by up to 60 s of washout, then each analysis began with 20 s of background measurement (gas blank). The ablation aerosol was transported out of the Helex cell using 1 L/min of helium gas and carried to the ICP-MS through ~1 m of 2 mm (inner diameter) Teflon tubing. Prior to entering the ICP-MS, the aerosol and helium gas were mixed ~ 1 L/min of argon gas. The ICP-MS was tuned on NIST-612 to achieve >9,000 cps/ppm on 175Lu (50 µm spot, ~ 7 J/cm2 at 10 Hz), while minimizing the production of oxides (< 0.2 % for ThO/Th) and maintaining a U/Th ratio of ~ 1.0. The total duty cycle time to measure all masses on the ICP-MS (in time-resolved analysis mode) was 250 ms. Utilizing these settings, the pyrite and arsenopyrite maps were constructed using a scan speed that matched the spot size, which allowed for four full scans of the mass spectrometer every 1.0 s (the equivalent of one spot diameter along the line scan). Whereas, settings for the sphalerite map provided two full sweeps of the analyzed masses (0.5s total) every 20 µm, or the equivalent of one spot diameter, and allowed for a larger region of interest to be analyzed. Dwell times were optimized based on expected count rates in the minerals of interest and the natural abundance of the specific isotope used in the acquisition method, such that major elements were measured for 1 – 3 ms (e.g., Fe, Al, Si), minor elements for 3 – 6 ms (e.g., Ni, Cu, Sb), and trace elements for 6 – 15 ms (e.g., Ag, Te, Au).

 The calibration procedures of Jackson (2008a) were followed during the mapping sessions. Standardization was achieved by calibrating the signals of unknowns against analyses of USGS doped synthetic basalt standard GSE-1G (for most major and trace elements) (Guillong et al., 2005), and internal reference materials pyrrhotite (sulphur calibration) and calcite (carbon calibration – where necessary), and normalizing total element (or element oxide) concentrations to 100%, on a pixel-to-pixel basis. Reference materials were analyzed every 20 unknowns (approximately every hour) to account for instrument drift during the mapping run. Line scans of secondary standards USGS GSD-2G or UQAC-Fe-S1 (doped pressed sulphide powder pellet prepared at LabMaTer, UQAC) were analyzed throughout the mapping sessions, and routinely yielded calculated concentrations within 5–10% of the accepted values for most elements. Reference values for GSE-1G were taken from the online geological and environmental reference materials database (GeoReM; Jochum et al., 2005), whereas information values were used for GSD-2G (supplied by the USGS Certificate). Internal working values for FeS-1 were provided by LabMaTer (UQAC – Dany Savard). The software programs LAMTRACE and PixeLAte (Jackson, 2008b) were used to calibrate the data and convert the line scans to quantitative elemental maps. Raw count rates for the individual Pb isotopes were summed prior to calibration, such that a Total Pb concentration could be calculated. The concentration for each of the three individual Pb isotopes was determined by comparing against the isotopic abundance of Pb in GSE-1G.

 Inspection of the time-resolved LA-ICP-MS spectra and conversion of the integrated signals to element concentrations was completed in the LADR data reduction software package by normalizing total element concentrations to 100%. The calculated major element concentrations for sphalerite include mean values of 65.3% Zn, 5.7 % Fe and 27.9% S – and compare well to a stoichiometric composition of ~ 64% Zn, 3% Fe and 33% S.

A1.2 Scanning Electron Microscopy and Energy-dispersive X-ray Spectroscopy

SEM imaging and EDS analyses were conducted on a Tescan Vega 3 SEM and Bruker Quantax 6 EDS system at the MERC Isotope Geochemistry Laboratory at Laurentian University. CL imaging was conducted at 10 kV accelerating voltage and beam current ~1 nA. EDS point analyses and area maps were conducted at 15 kV accelerating voltage and beam currents of ~1 nA and ~3 nA, respectively.

A1.3 References

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