

## Appendix DR1 – LA-ICP-MS Methodology

Analyses by laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) were performed at LabMaTer, Université du Québec à Chicoutimi (UQAC), using an Excimer 193 nm RESolution M-50 laser ablation system (Australian Scientific Instrument) equipped with a double volume cell S-155 (Laurin Technic) and coupled with an Agilent 7900 mass spectrometer. The LA-ICP-MS tuning parameters were a laser frequency of 10 Hz, a power of 3 to 5 mJ/pulse, a dwell time of 7.5 ms, a rastering speed of 5 to 10  $\mu\text{m/s}$ , and a fluence of 3  $\text{J/cm}^2$ . Line scans across the surface of sulfides grains were made with beam sizes of 44, 33, and 25  $\mu\text{m}$ , depending on grain size. The gas blank was measured for 30s before switching on the laser for at least 60s (Fig. A1a). The ablated material was then carried into the ICP-MS by an Ar–He gas mix at a rate of 0.8–1 L/min for Ar and 350 mL/min for He, and 2mL/min of nitrogen was also added to the mixture. Data reduction was carried out using the Iolite package for Igor Pro software (Paton et al., 2011).

Maps of element distribution were made on different sulfide minerals using a laser frequency of 15 Hz and a power of 5 mJ/pulse. The beam size (15 to 58  $\mu\text{m}$ ) and the stage movement speed (10 to 15  $\mu\text{m/s}$ ) were adapted to optimize spatial resolution and analysis time for grains of different sizes. The maps were generated using the Iolite software package on the basis of the time-resolved composition of each element. The maps indicate the relative concentration of the elements and are semi-quantitative.

The following isotopes were monitored:  $^{29}\text{Si}$ ,  $^{33}\text{S}$ ,  $^{34}\text{S}$ ,  $^{57}\text{Fe}$ ,  $^{59}\text{Co}$ ,  $^{61}\text{Ni}$ ,  $^{63}\text{Cu}$ ,  $^{65}\text{Cu}$ ,  $^{66}\text{Zn}$ ,  $^{75}\text{As}$ ,  $^{77}\text{Se}$ ,  $^{82}\text{Se}$ ,  $^{95}\text{Mo}$ ,  $^{99}\text{Ru}$ ,  $^{101}\text{Ru}$ ,  $^{103}\text{Rh}$ ,  $^{105}\text{Pd}$ ,  $^{108}\text{Pd}$ ,  $^{109}\text{Ag}$ ,  $^{111}\text{Cd}$ ,  $^{113}\text{In}$ ,  $^{115}\text{In}$ ,  $^{118}\text{Sn}$ ,  $^{121}\text{Sb}$ ,  $^{128}\text{Te}$ ,  $^{130}\text{Te}$ ,  $^{185}\text{Re}$ ,  $^{189}\text{Os}$ ,  $^{193}\text{Ir}$ ,  $^{194}\text{Pt}$ ,  $^{195}\text{Pt}$ ,  $^{197}\text{Au}$ ,  $^{203}\text{Tl}$ ,  $^{205}\text{Tl}$ ,  $^{208}\text{Pb}$  and  $^{209}\text{Bi}$ . Inclusions of accessory minerals such as platinum-group minerals (Fig. 1B) were commonly encountered during analysis and they were excluded from the signal to obtain the true sulfide composition. Analyses of pentlandite grains showing zonation of trace elements were performed in a perpendicular line from pyrrhotite to chalcopyrite (Fig. 1C; see manuscript for further explanation on the origin of zonation), and the signal was completely integrated to obtain the average composition (Fig. 1D and 1E).

Polyatomic interference of  $^{61}\text{Ni}^{40}\text{Ar}$  on  $^{101}\text{Ru}$  was corrected using  $^{101}\text{Ru}$  measured in a NiS blank which does not contain Ru. Polyatomic interference of  $^{63}\text{Cu}^{40}\text{Ar}$  on  $^{103}\text{Rh}$  was corrected using  $^{103}\text{Rh}$  measured in MASS-1, which contains 13.4%  $^{63}\text{Cu}$  but no  $^{103}\text{Rh}$ . The  $^{103}\text{Rh}$  values in chalcopyrite are not reported as the interference is too important to be corrected. Direct interferences of  $^{108}\text{Cd}$  on  $^{108}\text{Pd}$  and  $^{115}\text{Sn}$  on  $^{115}\text{In}$  were corrected manually by monitoring  $^{111}\text{Cd}$  and  $^{118}\text{Sn}$ , respectively.

Internal standardization was based on  $^{57}\text{Fe}$  using stoichiometric iron values of pentlandite (i.e. 32.56 %). Three certified reference materials were used for external calibration: Laflamme Po727, which is a synthetic FeS doped with ~40 ppm PGE and Au supplied by Memorial University of Newfoundland, was used to calibrate for PGE and Au; MASS-1 (Wilson et al., 2002), which is a ZnCuFeS pressed powder pellet doped with 50–70 ppm of most chalcophile elements, supplied by the United States Geological Survey (USGS), was used to calibrate for Cu, Se, Te, Tl and Zn; GSE-1g, which is a natural basaltic glass fused and doped with most elements at 300-500 ppm, supplied by the USGS, was used to calibrate for Ag, As, Bi, Cd, Co, In, Mo, Ni, Pb, Re, Sb and Sn using preferred values from the GeoReM database (Jochum et al., 2005). MASS-1, GSE-1g and JB-MSS5 (an FeS sulfide containing 50-70 ppm of most chalcophile elements, supplied by James Brennan) were also used for intra-standard quality control. The results obtained for this study were generally in good agreement with the working values (Appendix 2).

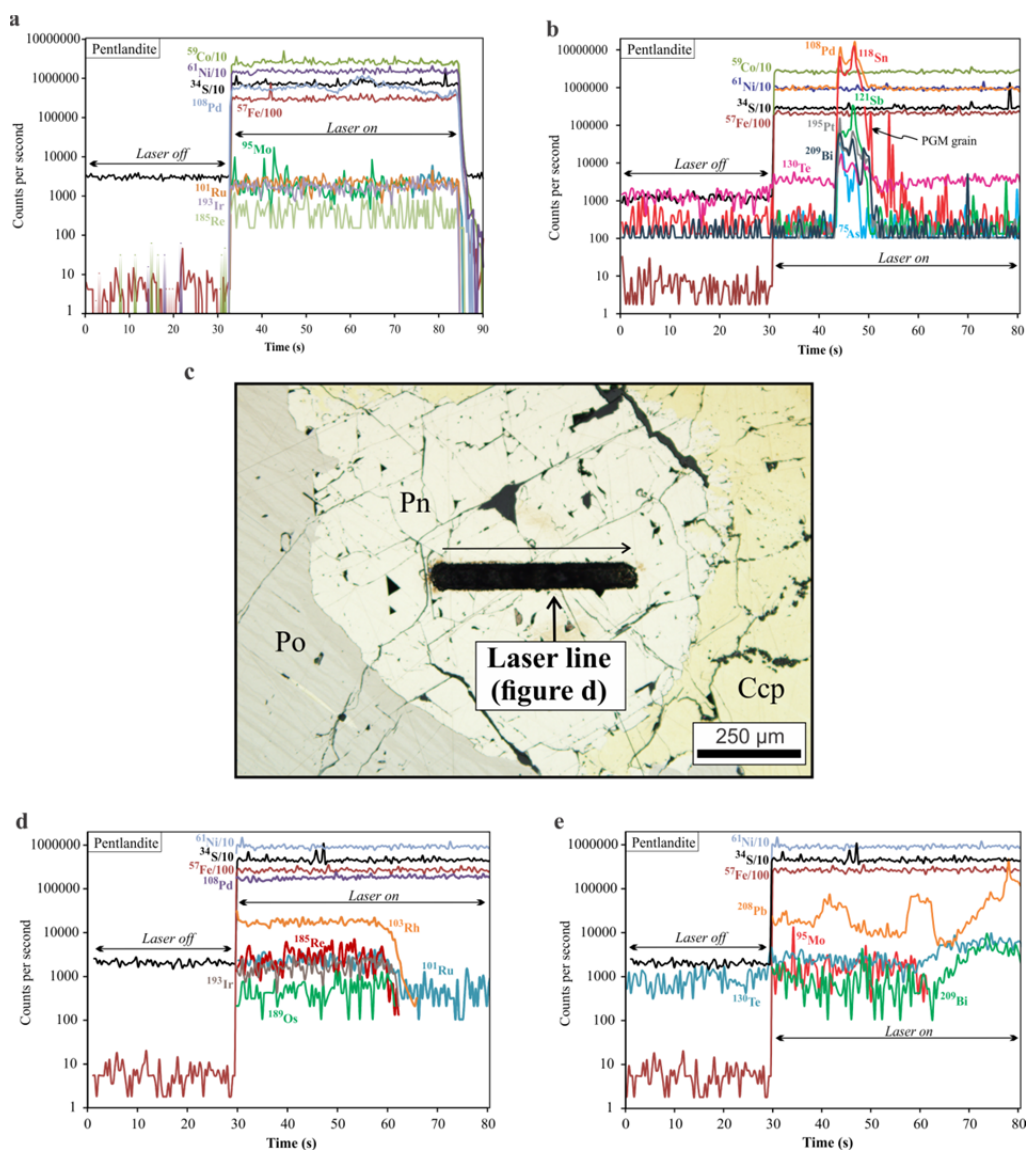


Figure D R 1 - Time (seconds) versus counts spectra for LA-ICP-MS analyses of pentlandite. A) Granular pentlandite containing Co, Mo, Re, Pd, Ru and Ir in solid solution. Note that the concentration of trace elements is constant through all the line scan. B) Granular pentlandite hosting an inclusion of PGM grain with Pd-Pt-As-Bi-Sb-Sn-Te, intersected by the laser at 45-50s. C) Reflected light photomicrography of contact pentlandite in between pyrrhotite and chalcopyrite showing the laser ablation line scan. Note that the laser line was positioned perpendicular from pyrrhotite towards chalcopyrite (arrow indicating the direction of the line scan). D)/E) Contact pentlandite obtained from laser line scan in figure “c”. Note the zonation of Re, Rh, Ru and Os, with higher counts near the contact with pyrrhotite, decreasing towards the contact with chalcopyrite, and increasing counts of Te, Bi and Pb towards the same contact. Ccp – chalcopyrite; Pn – pentlandite; Po – pyrrhotite.

## References:

Jochum, K. P., Nohl, U., Herwig, K., Lammel, E., Stoll, B., and Hofmann, A.W., 2005, GeoReM: a new geochemical database for reference materials and isotopic standards: *Geostandards and Geoanalytical Research*, v. 29, p. 333-338.

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Wilson, S. A., Ridley, W. I., and Koenig, A. E., 2002, Development of sulfide calibration standards for the laser ablation inductively-coupled plasma mass spectrometry technique: *Journal of Analytical Atomic Spectrometry*, v. 17, p. 406-409.

## **Appendix DR2: Complete data set of analyses of reference materials and pentlandite obtained in this study**

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