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## **Distribution of Se in the Wolverine Zn-Pb-Cu-Ag-Au Volcanic-Hosted Massive Sulfide Deposit, Finlayson Lake District, Yukon, Canada**

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Beamline(s): X26A

**Introduction:** Selenium in our environment generally occurs as a trace element, but under certain geological conditions, it can be concentrated into potentially noxious levels. The origin, distribution and concentration mechanisms for selenium in our environment are poorly understood and only have been the subject of study when selenium has been anthropogenically introduced. Natural selenium enrichment occurs in the Wolverine polymetallic volcanic-hosted massive sulfide (VHMS) deposit in the Finlayson Lake district of the Yukon Territory, Canada. This deposit contains a substantial resource of 6,237,000 tonnes grading 12.66% zinc, 1.33% copper, 1.55% lead, 370.9 g/t silver and 1.76 g/t gold but remains unexploited partly due to elevated selenium concentrations (>5000 ppm) of the massive sulfides. Investigation of test metallurgical concentrates found Se to be present in all of the major sulfide minerals: 0.36 wt% Se in chalcopyrite, 0.12 wt% in sphalerite, 0.047 wt% in pyrite and up to 11.2 wt% in galena. The distribution of Se in concentrates suggests a correlation of Se with Pb sulfides; however, such a correlation is in marked contrast to high Se zones of other VHMS deposits (e.g., Bornite zone at Kidd Creek), where Se correlates positively with Cu (Barrie et al., 1999). The aim of this study was to determine the distribution of Se in bulk massive sulfides (i.e., not in concentrates) of the Wolverine deposit and to assess the analysis of Se in sulfide minerals by SRXRF.

**Methods and Materials:** Pyrite ( $\text{FeS}_2$ ) is a ubiquitous mineral in the sulfide assemblage and provides a baseline to examine selenium distribution within the Wolverine deposit. Eleven standard thin section mounts corresponding to three stratigraphic sections were analyzed for selenium in pyrite. Analyses included spot, line and raster analyses of host minerals, pyrite grains and grain mount (epoxy & Si glass). For line and raster scans, scan increments varied from 1 to 20 microns and live times varied from 5 to 300 seconds. A focused monochromatic beam with a beam size of ~10 microns was used for analyses. Seventy-two analyses were completed over a 40-hour period.

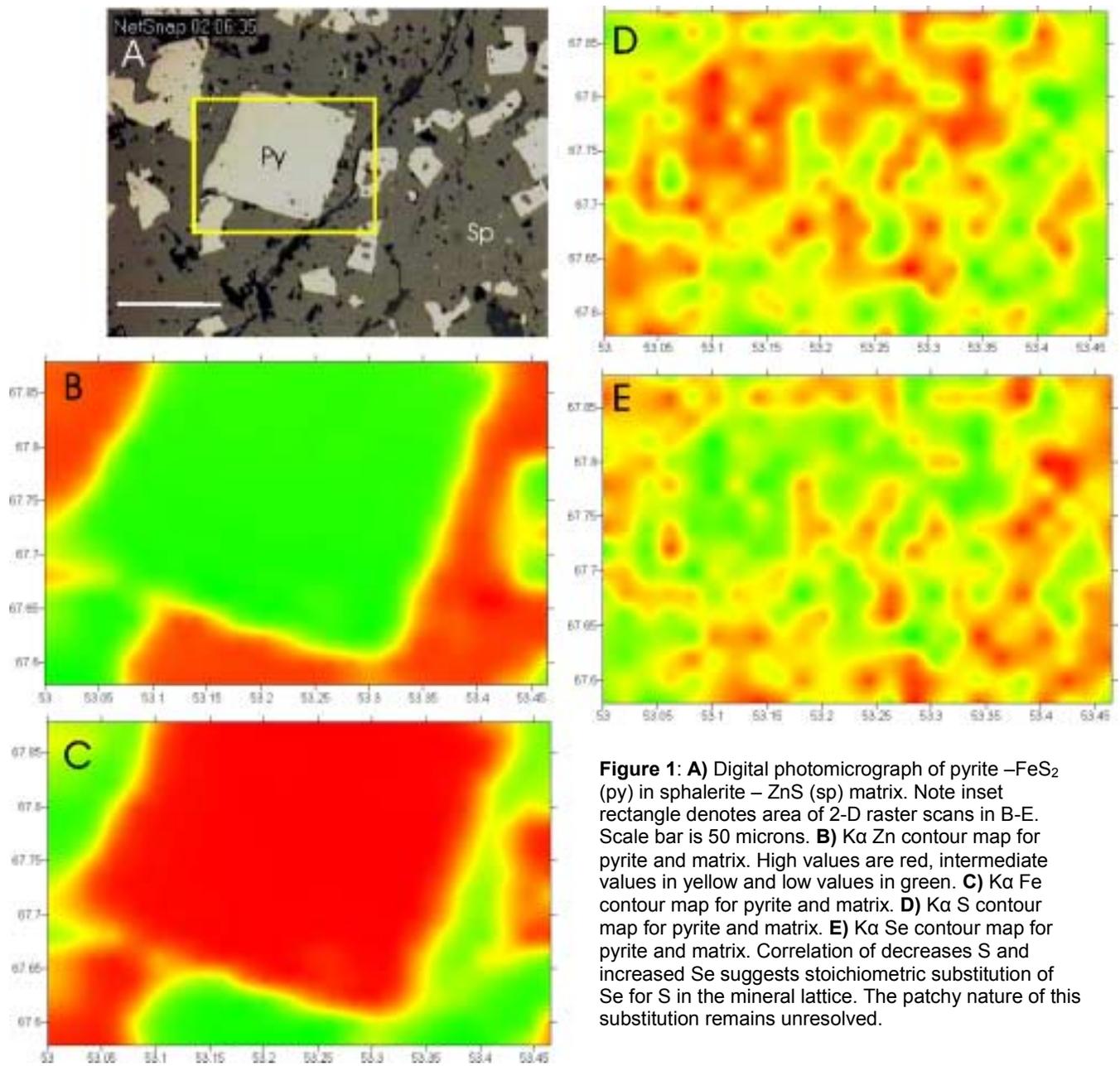
**Results:** The mounting medium (epoxy & Si-glass) contained elevated As and Pb, but negligible Se (<1 ppm), allowing quantification of Se in mounted samples. Selenium concentrations in pyrite varied from 2-340 ppm and reflect the stratigraphic height at which the sample was taken. Generally, as stratigraphic height increases selenium content decreases, which correlates with the distribution of Cu in the deposit. Comparison of the sulfur and selenium distributions within pyrite grains demonstrates a stoichiometric substitution of selenium for sulfur in the pyrite lattice along the pyrite ( $\text{FeS}_2$ ) – ferroselite ( $\text{FeSe}_2$ ) solid solution (Figure 1).

**Conclusions:** The positive correlation of Cu with Se in the deposit suggests that Se may have precipitated from a hydrothermal fluid at elevated temperatures (~350°C). In the absence of native selenium, the Se content of pyrite (and other sulfides) precipitating from a hydrothermal fluid is inversely correlated with increasing temperature (Huston et al., 1995). This, however, is contrary to what is observed at Wolverine. This suggests that the hydrothermal fluid that precipitated the selenium-rich pyrite at Wolverine must have been high temperature, but also must have had elevated Se concentrations. The stoichiometric substitution of Se for S in pyrite indicates reducing conditions during pyrite precipitation, which is consistent with precipitation at or near the seafloor in a mound structure.

The analysis of Se in sulfide minerals by SRXRF has significant advantages over other conventional microbeam techniques, and these can be directly attributed to the synchrotron excitation source. The very low angular divergence of the synchrotron X-ray beam, coupled with the high-brilliance of the linearly polarized beam, provide an efficient means of *in-situ* non-destructive (c.f. secondary induced mass spectrometry) microanalysis, facilitating the study of minute sample areas within pyrite grains and mapping the distribution of selenium (and other elements) in two dimensions.

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**References:** T.C. Barrie, M.D. Hannington, and W. Bleeker, 'The giant Kidd Creek volcanic-associated massive sulfide deposit, Abitibi Subprovince, Canada,' *Reviews in Economic Geology*, 8, 247-269, 1999.  
D. Huston, S.H., Soey, G.F. Sutter, D.R. Cooke, and R.A. Both, "Trace Elements in Sulfide Minerals from Eastern Australian Volcanic-Hosted Massive Sulphide Deposits: Part II. Selenium Levels in Pyrite: Comparison with  $\delta^{34}\text{S}$  Values and Implications for the Source of Sulfur in Volcanogenic Hydrothermal Systems," *Economic Geology*, 90, 1167-1196, 1995.



**Figure 1:** **A)** Digital photomicrograph of pyrite –FeS<sub>2</sub> (py) in sphalerite – ZnS (sp) matrix. Note inset rectangle denotes area of 2-D raster scans in B-E. Scale bar is 50 microns. **B)** Kα Zn contour map for pyrite and matrix. High values are red, intermediate values in yellow and low values in green. **C)** Kα Fe contour map for pyrite and matrix. **D)** Kα S contour map for pyrite and matrix. **E)** Kα Se contour map for pyrite and matrix. Correlation of decreases S and increased Se suggests stoichiometric substitution of Se for S in the mineral lattice. The patchy nature of this substitution remains unresolved.