## The origin of pyrite-sphalerite banding in metamorphosed volcanogenic massive sulphide deposits: Using EBSD, EPMA and LA-ICP-MS

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Volcanogenic massive sulphide (VMS) deposits are commonly metamorphosed to greenschist or amphibolite facies conditions after their formation and can exhibit mm to cm thick pyrite-sphalerite banding within the (semi-)massive sulphide lens. The origin of this banding is commonly assumed to be epigenetic, forming as a result of metamorphic remobilization and recrystallization. However, detailed investigations constraining the chemical and physical processes forming this banding have not been investigated yet. Here we present detailed textural (ore microscopy, scanned electron microscopy), microstructural (electron back-scattered diffraction) and compositional (electron microprobe, laser inductively coupled plasma mass spectrometry) results from pyrite-sphalerite bands in massive sulphide lenses from six VMS deposits metamorphosed to greenschist to lower amphibolite facies. The investigated deposits are from oldest to youngest: Kidd Creek, Canada, Flin Flon, Canada, Kristineberg, Sweden, LaRonde-Penna, Canada, Ming, Canada, and Mount Morgan, Australia. All of these deposits are or have been economic relevant producers of Cu, Zn, and/or Au.

Textural observations show that pyrite occurs in two main textures in these massive sulphide lenses including: (1) as disseminated, subhedral, recrystallized grains with concave grain boundaries within massive sphalerite (i.e., caries texture), and (2) as annealed aggregates of several mm to cm thickness forming triple junctions with neighboring pyrite grains. The microstructure of pyrite in these textures was analyzed using electron-back scattered diffraction. Results show that the deformation textures observed in pyrite are both a function of grain size and neighboring phases (i.e., surrounded by sphalerite or pyrite). Abundant intra-grain misorientation angles of  $<5^{\circ}$  show subgrain development between pyrite grains in annealed aggregates (texture 2) in particular with pyrite grains of  $35\mu$ m size. In pyrite aggregates with  $>100\mu$ m grain size, intra-grain misorientation angles are less abundant indicating that subgrain development and hence dynamic crystallization via dislocation creep is a minor process compared to smaller grains at similar P-T conditions. In contrast, larger pyrite grains in annealed aggregates in the brittle-ductile transition and show both pressure solution and ductile flow deformation.

Chemical remobilization in pyrite-sphalerite bands was tested using both EPMA and LA-ICP-MS analyses. Electron microprobe analyses on pyrite and sphalerite from textures (1) and (2) show a wide range of FeS content in sphalerite (LaRonde and Ming: < 5mol% FeS; Flin Flon and La Ronde: 5.50 – 7.5 mol% FeS; Kid Creek: > 10 mol% FeS) displaying original redox fluid compositions. Rim-core analyses of neighboring pyrite and sphalerite grains in both textures show, however, increasing concentrations of Zn and Fe towards the rim of pyrite and sphalerite, respectively. This cannot be explained by syngenetic dissolution-precipitation since no concentric zoning is observed under SEM. Trace element behavior shows that Co and Ni enriches in low-strain domains within recrystallized pyrite of both textures, whereas low melting chalcophile elements (LCMEs) Bi and Sb and precious element Ag will enrich in cataclastic cracks in pyrite formed under brittle deformation textures. Element behavior in recrystallized sphalerite is more complex.

Microtextural, microstructural and compositional results indicate that pyrite-sphalerite bands formed as result of greenschist to amphibolite facies metamorphism in which pyrite recrystallized and aligned within a preferred direction in anhedral sphalerite. Dynamic recrystallization resulted in subgrain development especially with small grains in annealed pyrite. Chemical remobilization resulted in the enrichment of Fe on pyrite-sphalerite rims and concentration of Co and Ni in low strain domains in recrystallized pyrite. Later brittle deformation formed cataclastic cracks in which LCMEs and Ag enriched.