

Variation of trace elements in chalcopyrite from worldwide Ni-Cu sulfide deposits: implications for mineral exploration

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Summary

Chalcopyrite is one of the most common sulfides in mineral deposits and its composition in trace elements varies with deposit type. This variation is controlled principally by the geological environment, as well as by its crystal structure, making it a potential indicator mineral for mineral exploration (Duran et al., 2018; George et al., 2018). However, chalcopyrite composition can vary widely within a single deposit type (e.g., Ni-Cu-PGE sulfide deposits: Dare et al. 2014; Mansur et al. 2019) which must be considered when developing discrimination diagrams for mineral exploration.

Ni-Cu-PGE deposits form when an immiscible sulfide liquid collects chalcophile elements from a mafic or ultramafic magma (Barnes and Lightfoot, 2005). Crystallization of sulfides results in fractionation of the chalcophile elements. First, Fe-rich monosulfide solid solution (MSS) crystallizes (1190°C), concentrating, Co, Ni, and IPGE resulting in a fractionated Cu-rich sulfide liquid, enriched in Ag, As, Bi, Cd, In, Pb, Pd, Pt, Sb, Se, Te, Tl and Zn, from which Cu-rich intermediate solid solution (ISS) crystallizes (900-850°C) (Barnes and Lightfoot, 2005; Dare et al., 2014; Mansur et al., 2019; Naldrett, 2004). Below 650-500°C pyrrhotite and pentlandite exsolve from MSS and chalcopyrite (\pm cubanite and pentlandite) exsolve from ISS. Cu-rich residual melt and MSS cumulate separation by physical processes can lead to Cu-rich and Cu-poor zonation at the deposit scale (e.g., Voisey's Bay, Noril'sk and Sudbury) In unzoned deposits, the Cu-rich residual melt coexists with MSS). The aim of this project is to investigate the variation of a full suite (36) of trace elements in chalcopyrite as a function of sulfide texture (massive to disseminated) and crystallization stage (MSS, ISS and unzoned) from a wide range of magmatic sulfide deposits worldwide and evaluate its potential as an indicator mineral.

Methods

The samples (65) are from 12 representative Ni-Cu sulfide deposits, belonging to 6 deposit types according to classification based on related magmatism: 1) komatiite, 2) flood basaltic, 3) ferropicrite, 4) anorthosite-granite-troctolite, 5) picritic to tholeiitic and 6) impact melt. A mineralogical and textural analysis was carried out with an optical microscope and scanning electron microscope (SEM) with the aim to describe sulfide relations, identify inclusions and select inclusion-free areas in chalcopyrite for subsequent in situ chemical analysis. Minor and trace elements were analyzed, respectively, by electron probe micro-analysis (EPMA, ULaval) and laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS, UQAC). Additionally, cubanite, pyrrhotite and pentlandite were analyzed in order to determine partition coefficients between the sulfide minerals during solidus exsolution. Only elements containing <40% censored values were retained for statistical analysis and imputed applying Log-ratio EM estimation procedure from zComposition R-package (Makvandi et al., 2016). Closure effect on compositional data was overcome using centered log-ratios. Univariate and bivariate plots were investigated with the aim of learning about distribution, dispersion and possible trends of the variables. A partial least squares-discriminant analysis (PLS-DA) was made to classify the data in order to evaluate chalcopyrite as an indicator mineral and its ability to discriminate groups into Ni-Cu sulfide deposits.

Results and discussion

In zoned deposits (Voisey's Bay, Noril'sk Talnakh and Sudbury) chalcopyrite in ISS ores has high contents of Ag, Ge, In, Pb, Se, Sn, Te and Tl whereas Co, Ga and Zn are concentrated in chalcopyrite from MSS ores. This is mainly a result of sulfide fractionation. During subsolidus exsolution, Ge, Se, Ti and Zn are equally distributed between cubanite and chalcopyrite (D_{cb}^{ccp} 0.91 - 1.08). Silver, Co, Mn, Pb, Sb, Te and Tl are concentrated in cubanite (D_{cb}^{ccp} 0.23 - 0.70), whereas Bi, Cd, In, Ni and Sn are concentrated in chalcopyrite (D_{cb}^{ccp} 1.32 - 5.83). PLS-DA shows that variable composition in chalcopyrite can discriminate ore types, especially between ISS and MSS. ISS ores are characterized by an association of Cd, Ge, In, Se, Sn and Te, whereas elements associated with MSS ores are Co, Ga, Ni, Mn, Ti and Zn (Fig. 1). Chalcopyrite formed during MSS crystallization stage incorporates compatible (Co) and incompatible (Bi, Zn, Sb) elements available in residual liquid, whereas chalcopyrite formed from ISS incorporates incompatible elements. Unzoned ores have a composition similar to MSS. Our data shows that trace element composition in chalcopyrite is sensitive to the style and stage of crystallization and their variation could reflect physicochemical conditions as well as the availability of certain elements during MSS and ISS crystallization.

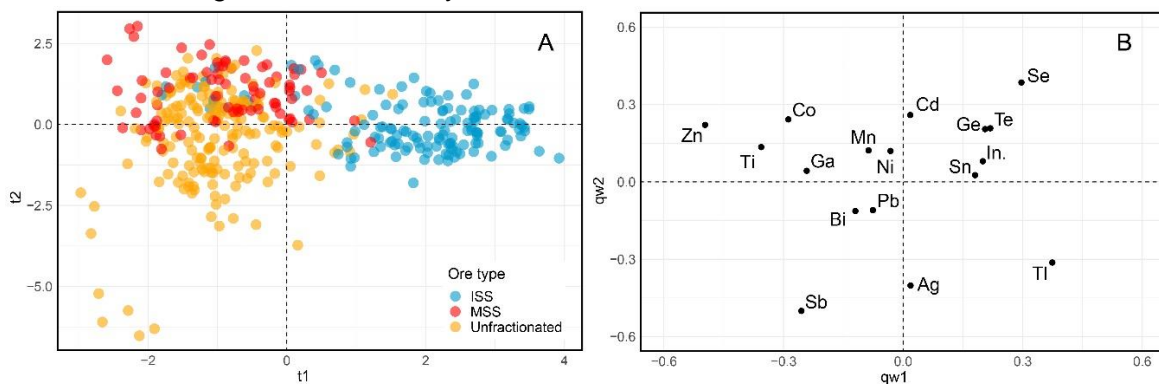


Figure 1. PLS-DA of chalcopyrite LA-ICP-MS data classified by ore type. (A) Samples projected on first and second latent variable (t1-t2). (B) Loading plot which shows element associations.

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