Goldschmidt 2021 Abstract
https://doi.org/10.7185/gold2021.5307

Trace element and coupled Cu - Fe isotope compositions of Cu-sulfides from Phalaborwa, South Africa: implications for metallogenesis

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The Loolekop intrusion of the Phalaborwa Igneous Complex in Limpopo, South Africa, represents the only known carbonatite–phoscorite intrusion-hosted Cu-sulfide ore deposit of economic relevance. Despite extensive research efforts, some aspects of the copper metallogenesis have remained elusive. This study aims to constrain ore material source(s) and the relative timing and processes involved in the sulfide mineralization, using combined textural analysis, PGE geochemistry, and Cu - Fe isotope systematics.

Petrographic observations and Mineral Liberation Analysis (MLA) reveal three distinct sulfide types: (i) disseminated bornite with chalcopyrite exsolution within the carbonatite – phoscorite intrusion, (ii) chalcopyrite veins with local cubanite exsolution, and (iii) valleriite $[(Fe^{2+},Cu)_4(Mg,Al)_3S_4(OH,O)_6]$ along boundaries and within cracks of pre-existing Cu-sulfides.

Whole-rock PGE analyses (Ru up to 4 ppb; Pd up to 8 ppb; Pt up to 9 ppb) point towards low-degree partial melting of a mantle source. *In-situ* LA-ICP-MS trace element analysis reveals an enrichment of PPGE (Pt, Pd; ~100 ppb) over IPGE (Os, Ir, Ru; <4 ppb) in sulfides of the Loolekop Pipe, which advocates the involvement of a monosulfide solid solution (mss) – intermediate solid solution (iss) system and the ascent of a Cu- and PPGE-rich sulfide liquid that precipitated assemblages of chalcopyrite and bornite during the magmatic stage of the intrusive process.

Iron isotope composition of disseminated sulfide separates (δ^{56}Fe = 0.02 to 0.38 ‰) suggest a magmatic origin, while vein-hosted sulfide compositions (δ^{56}Fe = -0.66 to -0.26 ‰) indicate magmatic – hydrothermal formation. The hydrothermal sulfide Fe isotope composition is consistent with leaching and break-down of deep-seated magnetite involving magmatic fluids that triggered the remobilization of light Fe isotopes and subsequent precipitation as chalcopyrite along fractures. The variable Fe isotope composition of valleriite points to the involvement of an isotopically heterogeneous, Fe-bearing fluid during late-stage sulfide alteration. The large Cu isotope composition variations among magmatic (δ^{65}Cu = -0.73 to 0.76‰) and magmatic – hydrothermal sulfide grains (δ^{65}Cu = -0.73 to 0.55‰) are consistent with a precipitation of sulfide droplets into complex bornite and chalcopyrite assemblages.