The mechanism of charge compensation in Cu-Fe-PGE thiospinels from the Penikat layered intrusion, Finland

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ABSTRACT

Thiospinels of Cu-(Fe) and platinum-group elements (PGE) are relatively abundant in the Kirakkajuppura PGE deposit of the Penikat layered complex, Finland. In actinolite-clinochlore rock that is nearly base-metal sulfide-free and relatively poor in chromite, the thiospinels occur as subhedral or anhedral grains (up to 0.4 mm). They are members of the cuprorhodsite-ferrorhodsite and cuprorhodsite-malanite series, relatively poor in cuproiridsite, and display considerable grain-to-grain variations in Cu, Fe, Pt, and Rh. Strong negative Fe-Cu, Pt(+Ir)-Fe, Rh-Cu, and Rh-Pt and strong positive Pt(+Ir)-Cu and Rh-Fe correlations in these thiospinels are indicative of a coupled substitution: Fe-for-Cu substitution in the tetrahedral (A) sites causes an excess in formal positive charge, which is compensated by Rh-for-(Pt+Ir) substitution in the octahedral (B) sites. Probable valence states in the Fe-free and Fe-rich end-members of the solid-solution series at Penikat are $Cu^{+}[Rh^{3+}(Pt,Ir)^{4+}]S_{4}^{2-}$ and $(Fe_{0.5}^{3+}Cu_{0.5}^{+})Rh^{3+}S_{4}^{2-}$, and these suggest the heterovalent substitution scheme ^AFe³⁺ + 2 ^BRh³⁺ \rightarrow ^ACu⁺ + 2 ^BPt⁴⁺(+2 Ir⁴⁺) to incorporate Fe in the ferrorhodsite-rich end member.