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Nanoscale partitioning of Ru, Ir, and Pt in base-metal sulfides from the Caridad chromite deposit, Cuba

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Abstract

We report new results of a combined focused ion beam and high-resolution transmission electron microscopy (FIB/HRTEM) investigation of platinum-group elements (PGE)-rich base-metal sulfides. The Ni-Fe-Cu base-metal sulfides (BMS) studied are millerite (NiS), pentlandite $[(Ni,Fe)_9S_8]$, pyrite (FeS_2), and chalcopyrite $(CuFeS_2)$. These BMS were found forming composite inclusions (<60 μm across) within larger unaltered chromite from the Caridad chromite deposit, which is hosted in the mantle section of the Mayarí-Baracoa Ophiolite in eastern Cuba. Electron probe microanalysis of BMS revealed PGE values of up to 1.3 wt%, except for pentlandite grains where PGE concentrations can reach up to 12.8 wt%. Based on the amount of Ru, two types of pentlandite are defined: (1) Ru-rich pentlandite with up to 8.7 wt% of Ru and <3.5 wt% of Os, and (2) Ru-poor pentlandite with Ru <0.4 wt% and Os <0.2 wt%. Ru-rich pentlandite contains Ir-Pt nanoparticles, whereas the other sulfides do not host nanometer-sized platinum-group minerals (PGM). The Ir-Pt inclusions are found as: (1) idiomorphic, needle-shape (acicular) nanoparticles up to 500 nm occurring along the grain boundaries between Ru-rich pentlandite and millerite, and (2) nanospherical inclusions (<250 nm) dispersed through the matrix of Ru-rich pentlandite. HRTEM observations and analysis of the selected-area electron diffraction patterns revealed that nanoparticles of Ir-Pt form domains within Ru-rich pentlandite. Fast Fourier transform analyses of the HRTEM images showed epitaxy between Ir-Pt domain and PGE-poor millerite, which argues for oriented growth of the latter phase. These observations point to sub-solidus exsolution of the Ir-Pt alloy, although the presence of nanospherical Ir-Pt inclusions in some other grains suggest the possibility that Ir-Pt nanoparticles formed in the silicate melt before sulfide liquid immiscibility. These Ir-Pt nanocrystals were later collected by the sulfide melt, preceding the formation of Ru-rich pentlandite. Early crystallization of the Ru-rich pentlandite and Ir-Pt nanoparticles led to the efficient scavenging of PGE from the melt, leaving a PGE-poor sulfide residue composed of millerite, pyrite, chalcopyrite, and a second generation of PGE-poor pentlandite.

Keywords: Nanoparticles, platinum-group elements (PGE), focused-ion beam (FIB), transmission electron microscopy (TEM), chromite, Cuba; Applications of Fluid, Mineral, and Melt Inclusions