

The phase system Pd-Ni-Fe-S between high and solidification temperatures and its implications for the ore associations of palladium

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The condensed phase system Pd-Ni-Fe-S was studied at 900, 725, 550 and 400°C by synthesis in evacuated silica glass tubes and a combination of textural and electron microprobe studies.

The monosulfide solid solution $\text{Fe}_{1-x}\text{S} - \text{Ni}_{1-x}\text{S}$ persists at all temperatures. Maximum solubility of Pd, exhibited at elevated x values, drops from 5.5 at.% at 900°C through 2.0 at.%, and 0.7 at.%, to 0.1 at.% at 400°C. For pyrrhotite-rich mineral associations, the decreasing solubility supports a model of mss being a principal concentrator of Pd at high temperatures, with its gradual release on cooling, making it available for subsequent reactions with intergranular solutions containing As,Sb,Bi,Te and Sn. At low sulfur fugacities, however, palladium concentrates in its Fe-Ni alloys.

The field of sulfide melt covers most of the Ni-Fe-Pd area (except for the FeS corner) at 900°C; it is reduced to Ni-Pd rich two thirds of this area at 725°C, and to a narrow Ni-Pd stripe at 550°C. At 900°C, sulfur contents in the melt range from 30-40 at.% to 45-50 at.% S in the Pd-poor melt portions relevant for Pd deposits. These melts are limited to the interval 30-40 at.%S at 550°C, i.e. they are consistently metal-rich. Retreat of the melt field results in a plethora of phase associations in its place. On the sulfur-poor side, several associations contain alloys with only low nickel contents, close in composition to Pd₃Fe. Both at 725°C and 550°C, composition fields of alloys associated with melt and those associated with $\sim(\text{Ni, Fe})_{3\pm x}\text{S}_2$ extend to surprisingly high palladium contents. Shrinkage of the $\sim(\text{Ni, Fe})_{3\pm x}\text{S}_2$ phase field (the β_1 - β_2 pair of Kitakaze et al.) and appearance of pentlandite represent the most important developments in the phase system between 725° and 400°C. The former dissolves up to 2 at.% Pd at 725°C and similar amounts at 550°C. Pentlandite dissolves up to 4 at.% Pd in association with palladium-rich phases at 550°C, and 5.4 at.% Pd at 400°C, representing almost 92 % occupancy of the octahedral site by palladium. Significantly, at 550°C, palladium-rich pentlandite coexists with sulfide melt which has between 17 and 47 at. % Pd and 28-38 at. % S. Can the rare occurrences of such pentlandite in nature indicate palladium rich residual melts? Other cases of Pd-rich pentlandite associate with Pd-rich alloy or phases like PdS and Pd₂S. In the association with mss, Pd is concentrated in the sulfide melt at all temperatures; this trend becomes stronger with decreasing temperature. At low temperatures or high S fugacities, nickel prefers mss. Presence of pentlandite and $\sim(\text{Ni, Fe})_{3\pm x}\text{S}_2$ introduces further complications into this simple scheme.

Comparison of our results with natural occurrences will help to unravel their formation- and alteration history.