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Thermodynamics of Ni-Fe-Co-Ag pentlandite solid solutions and implications for natural occurrences

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Pentlandite is an abundant mineral in magmatic sulfide deposits, but it also occurs in trace amounts in many hydrothermal mineralization settings [1]. It is an important global source for nickel and synthetic pentlandite compounds have important industrial applications [2,3]. Pentlandite group compounds exhibit a cubic crystal structure and have chemical formula of M_9S_8, where M is typically Fe, Ni, Co and to some degree Ag. There are no naturally occurring pure Fe- and Ni-endmembers, but solid solution between pentlandite ($[Ni,Fe]_9S_8$), cobaltopentlandite (Co_9S_8) and argentopentlandite ($Ag[Ni,Fe]_8S_8$) has been observed [4,5]. Natural pentlandite is relatively rare in most setting, but has a wide geographic distribution, and its compositional variability and its stability range make it ideal for understanding formation conditions and processes in geological environments.

Thermodynamic data are critical to making accurate inferences from pentlandite compounds and to enhance thermodynamic formation models of ore deposits, but several basic thermodynamic properties of the endmember species remain insufficiently constrained, and there are no calorimetric studies of their mixing energetics. We have synthesized and characterized pentlandite samples of various compositions and measured their enthalpies of formation by oxidative high temperature solution calorimetry. We discuss the impact of compositional variations between Ni-Fe-Co and Ni-Fe-Ag on the structure and thermodynamic stability of these synthetic pentlandite-type compounds. These findings are applied to understand differences in pentlandite group minerals from various mineralization types (e.g., magmatic sulfide, orogenic gold, direct metamorphic remobilization, Iron oxide copper-gold, unconformity, and porphyry related).

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