Nanoparticulate nickel sulfides formed in low temperature aqueous solutions

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The nature of the nickel sulfides formed in low temperature aqueous solutions is not well-understood. The material has some intrinsic interest to mineralogy, geochemistry and materials science as well as to biogeochemisty, especially as a possible catalyst involved in the origin and early evolution of life.

We synthesized Ni sulfide under anoxic conditions at 25°C: (1) chemically, by the addition of 50mL 0.1M $NiSO_4 \cdot 7H_2O$ to 100mL 0.05M $Na_2S \cdot 9H_2O$; (2) electrochemically, with a Ni foil and H_2S gas. At pH≤5, millerite (β-NiS) was produced electrochemically and NiS mixtures, including heazlewoodite (Ni_3S_2) and polydymite (Ni_3S_4), were obtained chemically. At pH >11, α-NiS was obtained from the chemical reaction. At pH 6-9, the product produced only two broad peaks (d = ca. 2.7 and 1.8Å) with conventional and synchrotron XRPD which could be assigned to a number of Ni sulfides. It has previously been referred to as "amorphous NiS" [1]. Eight SAED reflections were collected which identified the material as godlevskite, orthorhombic NiS. HRTEM shows that the godlevskite particles are ca. 30nm in diameter and plate-like. SAXS analyses show that the material is 6-8.5 nm thick.

Godlevskite is structurally related to makinawite, tetragonal FeS, and is found naturally in similar parageneses - associated with the monosulfide solid solution products of high temperature nickel ores. Mackinawite is the black FeS precipitate from the reaction between Fe(II) and S(-II) in aqueous solution. It appears that, geochemically, godlevskite is the Ni analogue of mackinawite.

References

[1] Jeong Y.U. and Manthiram A. (2001) *Inorg. Chem.* **40**, 73-77.