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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 biogeochemistry, 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 50 mL of 0.1 M NiSO₄·7H₂O to 100 mL of 0.05 M Na₂S·9H₂O; (2) electrochemically, with a Ni foil and H₂S gas. At pH ≤ 5, millerite (β-NiS) was produced electrochemically and NiS mixtures, including heazlewoodite (Ni₃S₂) and polydymite (Ni₃S₄), 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 1.8) with conventional and synchrotron XRPD which could be assigned to a number of Ni sulfides. It has previously been referred to as “amorphous NiS” Jeong and Manthiram, 2001. Eight SAED reflections were collected which identified the material as godlevskite, orthorhombic NiS. HRTEM shows that the godlevskite particles are ca. 30 nm 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.

Reference

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Hafnium and neodymium isotope systematics in the rivers of eastern Tibet

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Hafnium and neodymium isotope systems are strongly coupled in terrestrial rocks but become decoupled during weathering and transport to the oceans, such that the seawater array has a different slope than the terrestrial array on an $\epsilon_{\text{Hf}}-\epsilon_{\text{Nd}}$ plot (Albarède et al., 1998; Vervoort et al., 1999). In order to understand the sources and processes involved in continental weathering, we investigated the two isotope systematics for the river suspended and bed material of the eastern Tibetan Plateau. Select samples from the Huang He (Yellow), Chang Jiang (Yangtze), Hong (Red), Mekong and Salween were studied.

The Hf and Nd concentrations in the solid were 1–45 ppb and 0.2–6 ppm, respectively, and in the dissolved load were 1–84 ppt and 10–390 ppt, respectively. While the Zr/Hf ratio in the suspended load is relatively constant at ~70, in the dissolved load it varies between 20 and 230. Thus, it is difficult to use the dissolved Zr as a proxy for dissolved Hf which occurs in much lower concentrations. The $\epsilon_{\text{Hf}}(0)$ values of all solid samples ranged from –20 to +6, but most fall between –10 and 0. The suspended load is more radiogenic than the silt or sand size fractions of the bed load. The highest values are seen for the suspended load of rivers draining igneous complexes in the Hong and Mekong river drainages and the lowest values for bed load draining sedimentary rocks in the Hong drainage.

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