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Phase, morphology, elemental composition, and formation mechanisms of biogenic and abiogenic Fe-Cu-sulfide nanoparticles: A comparative study on their occurrences under anoxic conditions

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ABSTRACT

We report on a systematic study on the physicochemical attributes of synthetic Fe-Cu-sulfide nanoparticles (NPs) precipitated under conditions similar to the anoxic, low-temperature aqueous, sedimentary, soil, and subsurface environments where these NPs have been repeatedly identified. Characterizing the basic attributes of these NPs is the first step in understanding their behaviors in various processes including in the bio-availability of essential and toxic metals, environmental remediation, and resource recovery. Abiotic experiments are compared to biotic experiments in the presence of the sulfate-reducer *Desulfovibrio vulgaris* to elucidate biological controls on NP formation. First, the single-metal end-member NPs are determined by precipitation in a solution containing either aqueous Fe(II) or Cu(II). Limited differences are observed between biogenic and abiogenic precipitates aged for up to one month; the Fe-only experiments resulted in 4–10 nm mackinawite (FeS) NPs that aggregate to form nanosheets up to ~1000 nm in size, while the Cu-only experiments resulted in mixtures of covellite (CuS) NPs comprised of <10 nm fine nanocrystals, 20–40 × 6–9 nm nanorods, and ~30 nm nanoplates. The crystal sizes of biogenic mackinawite and covellite are, respectively, larger and smaller than their abiogenic counterparts, indicating a mineral-specific response to biological presence. Structural defects are observable in the fine nanocrystals and nanorods of covellite in both biogenic and abiogenic experiments, indicative of intrinsic NP instability and formation mechanism via particle attachment. In contrast, covellite nanoplates are defect free, indicating high stability and potentially rapid recrystallization following particle attachment. Next, mixed-metal sulfide NPs are precipitated at variable initial aqueous Fe-to-Cu ratios (2:1, 1:1, and 1:5). With an increasing ratio of Fe-to-Cu, Fe-rich covellite, nukundamite ($Cu_{5.5}FeS_{6.5}$), chalcopyrite ($CuFeS_2$), and Cu-rich mackinawite are formed. The Fe-rich covellite NPs are larger (100–200 nm) than covellite precipitated in the absence of Fe, indicating a role for Fe in promoting crystal growth. Chalcopyrite and nukundamite are formed through the incorporation of Fe into precursor covellite NPs while retaining the original crystal morphology, as confirmed by doping a covellite suspension with aqueous Fe(II), resulting in the formation of chalcopyrite and nukundamite within days. Additionally, in the biological systems, we observe the recrystallization of mackinawite to greigite (Fe_3S_4) after six months of incubation in the absence of Cu and the selective formation of chalcopyrite and nukundamite at lower initial Fe-to-Cu ratios compared to abiotic systems. These observations are consistent with NP precipitation that are influenced by the distinct (sub)micro-environments around bacterial cells compared to the bulk solution. Comparative TEM analyses indicate that the synthetic NPs are morphologically similar to NPs identified in natural environments, opening ways to studying behaviors of natural NPs using experimental approaches.

Keywords: Metal sulfide nanoparticle, mackinawite, covellite, chalcopyrite, greigite, biomineral