# Phase, size and shape variations of biogenic versus abiogenic Fe-Cu-sulfide nanoparticles

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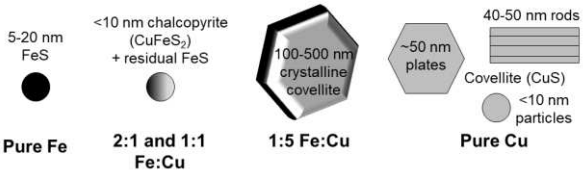
Metal sulfide nanominerals are key components in the biogeochemical cycling of sulfur and metal contaminants. In nature, these minerals precipitate in complex environments containing microbes and two or more dominant metal ions, leading to physicochemical properties that may not be captured in simplified lab experiments. We therefore designed a study to provide a more direct link between experiments and natural systems, with the specific aim of characterizing the properties of sulfide nanoparticles precipitated in anoxic mixtures of Fe and Cu solutions in the presence and absence of microbes. Biogenic precipitation was induced using a sulfate reducer *Desulfovibrio vulgaris* as the sulfide producers, and was compared to abiogenic precipitation in which sulfide was added through slow titrations at ambient temperatures.

In general, the phase, shape and size of the nanominerals were primarily controlled by the aqueous Fe-to-Cu ratios, as characterized by TEM and XRD. 'Pure Fe' and 'pure Cu' systems produced nano-precipitates of FeS and covellite (CuS), respectively, while mixed systems resulted in mostly chalcopyrite ($CuFeS_2$) or larger CuS minerals. Subtle




differences were attributed to microbial activities in biogenic experiments. Abiogenic FeS was identified as nanocrystalline mackinawite with approximately equidimensional dimensions, while biogenic FeS showed preferential growth along the c-axis. At 1:1 Fe:Cu ratio, biogenic system exclusively precipitated $CuFeS_2$ while abiogenic system was less selective, producing a mixture of $CuFeS_2$, CuS and FeS. No difference was however observed for biogenic and abiogenic CuS. Overall, our study provides a more complex view for the Fe-Cu-sulfide nanomineral precipitation system that can be taken as a basis for comparison to the environment.