

Pathways of mackinawite 'FeS' formation

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Quantifying the initial stages of solution-based nucleation and the mechanisms leading to iron sulphide phase formation are both critical to understanding the role of iron sulphides in the global S and Fe biochemical cycles. Furthermore, nanoparticulate iron sulphides, due to their high surface reactivity and affinity for heavy metals are crucial phases used in various remediation and industrial catalytic applications. A plethora of previous studies proposed that the first solid phase that forms in aqueous media in the Fe-S system is a nanophase mackinawite-type material; however, neither the exact formation mechanism, nor the structure or reactivity of such a primary FeS entity that is believed to nucleate and grow from aqueous media have so far been quantified. Here we present results from a study in which we characterized the formation of FeS phases from aqueous solutions and followed their aging and crystallization to mackinawite.

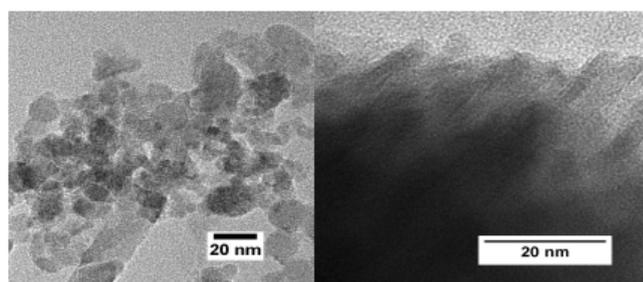


Fig 1. Mackinawite morphologies from titration and rapid-mix experiments.

Our results revealed that immediately after mixing of a ferrous iron and sulphide rich solution a precursor phase on the way to mackinawite was formed. This precursor differs from that of mackinawite in that it has characteristic d-spacing of ~ 12 , 9 and 7 Å (compared to 5.03 Å in mackinawite). Depending on experimental approach (e.g., titration, direct mixing or diffusion; see image below) this nanophase transforms to mackinawite via different pathways. The crystallization to mackinawite can be controlled through various ways to stabilize the nano-sized precursor phase. This may have potential interesting new applications.