

Structure and properties of FeS in the early stages of formation

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Nanocrystalline iron sulphide phases (nominally FeS) are crucial for controlling the global S and Fe cycles through their dominant role in modern and ancient euxinic water columns and sediments. Furthermore, nanoparticulate FeS phases are believed to be the prime catalyst for prebiotic organic synthesis reactions. However, the early stages of FeS nanoparticle formation from solution and whether an amorphous precursor to mackinawite exists is still unknown. Here we combined a stepwise titration (pH 3.5-7.0) with *in situ* small angle X-ray scattering (SAXS), and *ex situ* X-ray diffraction (XRD) and transmission electron microscopy (TEM) to follow the very early stages of FeS nucleation growth and transformation to mackinawite.

Fast time resolved (1 frame/sec) SAXS data showed at pH below 4.5 the rapid formation of initial FeS particles that develop into mass fractal structures. However, the individual primary FeS particles remained stable, yet small (radius < 1nm) up to pH 6.2. The mass fractal dimensions of the aggregates increased rapidly to 2 in the initial stages of the reaction and continued increasing gradually but slower to 2.5 (> pH 5.8), indicating that loose, early agglomerates started compacting as a result of a slow growth of the FeS phases. *Ex situ* XRD of the material collected at pH 4.5 revealed diffraction peaks at 2θ 7.3, 9.1 and 11.7 degrees. These peaks do not correspond to known FeS phases and evidence the presence of a so far unknown intermediate FeS entity, suggesting that nucleation and growth of FeS phases in this system deviate from the classical theory. These transitional phases could be similar to the complex Fe_2S_2 or Fe_4S_4 clusters suggested by *ab initio* modelling [1]. Upon further increasing the pH to 7.0, eventually mackinawite peaks gradually formed until the system reached steady state.

[1] De Leeuw *et al* (2013) *MinMag.* **77** (5):965