The structure of disordered mackinawite

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ABSTRACT

Synthetic Fe^{2+} monosulfide, FeS_{am}, displays a disordered tetragonal mackinawite structure. It is nanocrystalline, with an average primary particle size equivalent to a crystallite size of 4 nm and a corresponding specific surface area of 350 m^2/g. It can be described in terms of a mixture of two end-member phases with different long-range ordering, which we refer to as MkA and MkB. MkA has an average primary particle size of 2.2×1.7 nm and lattice parameters $a = b = 4.0$ Å, $c = 6.6 \pm 0.1$ Å. MkB has an average primary particle size of 7.4×2.9 nm and lattice parameters $a = b = 3.7$ Å, $c = 5.5 \pm 0.2$ Å. A typical disordered mackinawite precipitate consist of 30% MkA and 70% MkB and the proportion of MkA decreases with age. Lattice expansions relative to crystalline mackinawite ($a = b = 3.7$ Å, $c = 5.0$ Å) may be explained by intercalation of water molecules between the tetrahedral sheets and by lattice relaxation due to small crystallite size.

The formation of two phases of FeS_{am} is consistent with competing pathways involved in its formation from aqueous solution. MkA may be equivalent to sheet-like precipitated aqueous FeS clusters. The reactivity of FeS_{am} is dependent on the proportion of the two end-member phases. These in turn are dependent on the conditions of formation, especially pH, and the age of the precipitate. These observations partly explain the reported differences in FeS_{am} reactivity in experimentation and in the environment. The structural model has implications for the behavior of natural acid volatile sulfides in scavenging elements from solution in natural environments.