

Characteristics of mackinawite, tetragonal FeS.

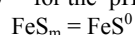
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Mackinawite, tetragonal FeS_m, is a key mineral in ore deposits and in sediments. It is possibly the last widespread simple sulfide mineral discovered. FeS_m is metastable and its relatively rapid formation from aqueous solution [1] is an example of a modified Ostwald's Step Rule [2].

Its textbook composition is Fe_{1+x}S. However, the non-stoichiometry is caused by the substitution of metals such as Cu, Ni and Cr in mackinawite associated with the monosulfide solid solution in magmatic ore deposits. Analyses of the synthetic phase has been plagued by a lack of reproducibility. The problems include: (a) FeS_m dissolution in acid can produce black rhombic sulfur which leads to underestimation of FeS:S. This can be overcome with the addition of a reductant like Ti(III) citrate; (b) Low analytic totals which are caused partly by (a) but may also be due to contaminants involved in the syntheses. The composition is stoichiometric Fe_{1.00±0.01}S, in agreement with precision XRD results. The material is not hydrated.[3]

The solubility of FeS_m is described by a pH dependent reaction and a pH-independent reaction. The intrinsic solubility product is 10^{-5.7} for the pH independent reaction



where FeS⁰ is a monomeric representation of aqueous Fe_xS_x clusters [4]. The pH-independent reaction describes FeS_m solubility in environmentally important neutral to alkaline solutions. The free Fe²⁺ concentration in sulfidic solutions at pH = 8 in equilibrium with FeS_m is < 0.1% of the total dissolved Fe (II). FeS_m only forms where {Fe(II)} {S(-II)} is high and thus its distribution in normal marine sediments appears limited [5].

Precipitated FeS_m is nanoparticulate and occurs as tabulate crystals, 2 - 11 nm long and 2 - 4 nm thick. The smallest particles contain *ca* 150 FeS molecules and may represent the first condensed phase in the system. The material is not amorphous, as has been widely reported. Apparent XRPD amorphism is due to small particle size. The mean specific surface area is 380 ± 10 m² g⁻¹. The d₁₀₀ lattice expansion is ≤ 3% of the bulk consistent with lattice relaxation in the nanoparticles. [6]

References

- [1] Rickard D. (1995) *Geochem. Cosmochim. Acta.* **59**, 4367 - 4379. [2] Luther G.W. III and Rickard D. (2005) *J. Nano. Res.* **7**, 389-407. [3] Rickard D., Griffith A., Oldroyd A., Butler I. B., Lopez-Capel E., Manning D. A. C., Apperley D.C. (submitted) *Chem. Geol.* [4] Rickard D. (in press) *Geochem. Cosmochim. Acta* [5] Rickard D. and Morse J.W. *Mar. Chem.* **97**, 141-197 [6] Ohfuji H. and Rickard D. (2006) *EPSL* **241**, 227-233.



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References

[1] Author A.B. (date) *GCA* **97**, 128-134.

[2] Arhenius X.Y., Steno R.S., Galileo T.U., and da Vinci V.W. (date) *GCA* **103**, 22-33.