

## Crystal structural changes of iron sulfide nanoparticle with grain growth

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In anaerobic marine sediments and lake sediments, an iron sulfide nanoparticle is produced with vital activities of sulfate-reducing bacteria. The iron sulfide nanoparticle is known as precursor of mackinawite (FeS), greigite (Fe<sub>3</sub>S<sub>4</sub>), pyrrhotite (Fe<sub>1-x</sub>S), and pyrite (FeS<sub>2</sub>), but the phase transition mechanism and crystal structure change with grain growth have not been elucidated yet. In this study, hydrothermal experiment, scanning electron microscope (SEM) observation, synchrotron X-ray powder diffraction (XRD) experiment, and X-ray absorption fine structure (XAFS) measurement were performed to clarify the structural change and the phase transition mechanisms from the iron sulfide nanoparticle to mackinawite and to greigite.

The black suspensions consisting of flake-like crystal with size of several 10 nm showed clear diffraction peaks of mackinawite corresponding to (001), (101), (200), and (112). The diffraction pattern has additional broad diffraction peaks corresponding to (111), (211), (220), and (312). The mackinawite possesses lattice constants  $a = 3.67$  (1),  $c = 5.55$  (5), which exhibit a remarkable expansion along the c-axis direction compared to that of the well-crystalline mackinawite ( $a = 3.67$ ,  $c = 5.03$  Å). The crystallite size estimated from Scherrer equation was 2.83 nm. The black suspensions, therefore, are indicated to be disordered nanocrystalline mackinawite. The lattice expansion along the c-axis direction would result from intercalation of water molecules and residual strain of FeS<sub>4</sub> tetrahedral sheets. The size of black suspensions was increased to several 100 nm with heating at 120°C. XRD pattern of the heated mackinawite showed additional clear diffraction peaks corresponding to (111), (211), (220), and (312). The lattice constants calculated are  $a = 3.671$  (1) - 3.673 (3),  $c = 5.212$  (9) - 5.23 (1) Å. With the heating, the c lattice constant is decreased, and the crystallite size is increased to 6.56 - 7.57 nm. In addition, small peaks of greigite were detected in the XRD pattern. The ratio of greigite to mackinawite was increased with heating time. XANES analysis revealed that the oxidation state of Fe was increased from 1.89 to 2.00 with the heating time from 5 hours to 7 days. It is suggested that the greigite formation is caused by the oxidation of Fe<sup>2+</sup>, because the oxidation of Fe<sup>2+</sup> is closely associated with the ratio of greigite to mackinawite in the sample. The first proximity, the coordination number, and bond distances are Fe-S bonding, about four, and about 2.24 Å, respectively. They remain unchanged with the heating time. This result suggests that the greigite is not formed with phase transition from mackinawite but caused by both partial phase transition of mackinawite and dissolution-reprecipitation of mackinawite. This study provides fundamental data of the mineral formation and structural behavior of iron sulfide nanoparticle, mackinawite, and greigite in anaerobic aqueous environments.

Keywords: iron sulfide nanoparticle, mackinawite, greigite, synchrotron powder XRD, XAFS