

Structural change processes of iron sulfide nanoparticle under hydrothermal conditions

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We investigated the structure changes and phase transformations from nanocrystalline mackinawite to pyrite and greigite using hydrothermal experiments, synchrotron X-ray diffraction (XRD) technique, atomic Pair Distribution Function (PDF) method, Extended X-ray Absorption Fine Structure (EXAFS) analysis, and transmission electron microscopic (TEM) observation. The first hydrothermal ageing experiment was performed by heating the nanocrystalline mackinawite at 120 °C for 12 h. The nanocrystalline mackinawite remained essentially unchanged for 12 h. The d_{001} and FWHM values of XRD peaks decreased for the first 2 h and subsequently maintained almost constant. There was no linear relationship between lattice parameters and hydrothermal heating time. The crystallite size quickly increased by the heating of 2 h, leading to the increase of crystallinity and appearance of the medium-range order in the nanocrystalline mackinawite. The nanocrystalline mackinawite preferentially grew in the horizontal direction along the sheet structure. The Fe atoms were distributed in the tetrahedral sites with a site occupancy of approximately 80%. The pre-edge peak energy of Fe *K*-edge suggested that about 10% of $\text{Fe}^{3+} / \Sigma \text{Fe}$ was included in the nanocrystalline mackinawite to compensate the charge deficiency of Fe^{2+} . The second hydrothermal ageing experiment was performed by heating the nanocrystalline mackinawite at 120 °C under the presence of elemental sulfur for 24 h. The nanocrystalline mackinawite persisted up to 8 h of heating time. Thereafter, pyrite and greigite instead of the nanocrystalline mackinawite appeared. Finally pyrite became dominant. The d_{001} and lattice parameters of nanocrystalline mackinawite varied significantly compared with those heated under the absence of elemental sulfur. The pre-edge peak energy indicated that the Fe^{2+} was oxidized to Fe^{3+} by elemental sulfur acting as the oxidant during the phase transformation from nanocrystalline mackinawite to greigite. In the phase transformation to pyrite, on the other hand, the Fe^{3+} was reduced to Fe^{2+} by sulfur in mackinawite and greigite acting as the reductant. The EXAFS analysis revealed that the second peak from the Fe-Fe interaction appeared at the heating time of 2 h, implying the formation of sheet structure consisting of edge-sharing FeS_4 tetrahedra. Intensity of the second shell peak from the Fe-Fe interaction reduced after the heating time of 8 h. Instead, new peaks corresponding to the Fe-S and Fe-Fe interaction appeared after the heating time of 12 h. This result was strongly associated with formation of the disulfide bonds (S-S bonds) in pyrite. The third hydrothermal ageing experiment was performed by heating the nanocrystalline mackinawite at 140 °C. The nanocrystalline mackinawite persisted up to 2 h of heating time. After the heating for 4 h, greigite became dominant. The pre-edge peak energy indicated that the about 60% of $\text{Fe}^{2+} / \Sigma \text{Fe}$ was oxidized to Fe^{3+} . The EXAFS analysis suggested the shrinkage of FeS_4 tetrahedra. These results could be clearly explained by the phase transformation from the nanocrystalline mackinawite to greigite. Consequently, the elemental sulfur can be recognized as one of the most important factors to promote the phase transformation from mackinawite to pyrite in the reducing lake and marine sediments.

Keywords: iron sulfide nanoparticle, mackinawite, greigite, pyrite, elemental sulfur