Phase change process of iron sulfide nanoparticle from amorphous to crystalline with grain growth

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1. Introduction

In anaerobic marine sediments, sulfate-reducing bacteria (SRB) acquires metabolic energy by reducing sulfate ions (SO_4^{2-}) to sulfide ions (S^{2-}). Sulfide ions are, furthermore, oxidized from sulfur (S^0) to sulfate ions by the metabolic activity of sulfur bacteria (SB). These series of reaction are called geochemical sulfur cycle and considered as one of the most important elemental cycle. In the reaction, a part of the sulfide ions is readily reacted with ferrous ions (Fe^{2+}) to produce iron sulfide nanoparticle (FeS), and which grows to more stable mackinawite (FeS). In the previous study, it was reported that the crystal growth from iron sulfide nanoparticle to mackinawite occurred in hydrothermal aging experiment at 120°C (Csákberé nyi-Malasics et al., 2012). Despite its importance as a precursor of mackinawite, phase change process of the iron sulfide nanoparticle from amorphous to crystalline has not been elucidated yet. In this study, synchrotron X-ray total scattering measurement and atomic Pair Distribution Function (PDF) analysis were performed to clarify the crystal structure change of iron sulfide nanoparticle with grain growth.

2. Experimental method

At first, iron sulfide nanoparticle suspension was synthesized by the mixing 10 mL of 0.2 M $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ solution with 10 mL of 0.4 M $Na_2S \cdot 9H_2O$ solution in N_2 gas atmosphere. The synthesized suspensions were heated in a Teflon container at 120°C for 2, 4, 6, 8 and 12 hours, respectively. After the end of heating experiments, the solid phases were dried by blowing N_2 gas and stored in vacuum. Synchrotron X-ray total scattering measurements were performed at beamline BL14B1 in SPring-8. The incident beam was monochromatized to a wavelength of 0.20606 Å. X-ray total scattering data at 20 K and 300 K were collected in the Q range between 0 and 25 $Å^{-1}$. Atomic Pair Distribution Function (PDF) analysis was applied to X-ray total scattering data.

3. Results and discussion

The PDF pattern of iron sulfide nanoparticle synthesized in the study almost disappeared at about 2 nm. Those of samples heated for 2, 4, 6, 8, 12 h are, on the other hand, were continuously observed up to 4 nm. This result showed that the particle size of iron sulfide nanoparticle was grown to 4 nm by the heating at 120°C. The Fe-S and Fe-Fe distances obtained by the PDF analysis are 2.25 and 2.65 Å, respectively, which suggests that the local atomic structure around Fe, ie FeS_4 tetrahedra, in iron sulfide nanoparticle almost remains unchanged by particle growth. Compared with the structure model of mackinawite, the iron sulfide nanoparticle would consist of disordered arrangement of FeS_4 tetrahedra. This is consistent with the structure model of iron sulfide nanoparticle proposed by the previous study (Wolthers et al., 2003; Ohfuji and Rickard, 2006; Jeong et al., 2008). In the presentation, we will discuss structure change associated with medium-range atomic order and propose phase change process from amorphous to crystalline by particle growth.

Keywords: atomic Pair Distribution Function , iron sulfide nanoparticle, mackinawite

