Structure changes of nanocrystalline mackinawite under hydrothermal conditions

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We investigated the structure changes and phase transformation from nanocrystalline mackinawite to pyrite 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 d001 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% Fe³⁺ was included in the nanocrystalline mackinawite to compensate the charge deficiency of Fe²⁺. 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 d001 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 Fe²⁺ was oxidized to Fe³⁺ 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 Fe³⁺ was reduced to Fe²⁺ 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 FeS₄ 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. 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: Nanoparticle, Iron monosulfide, Mackinawite, Greigite, Pyrite, Phase transformation

INTRODUCTION

For the emergence of life on Earth, ancient alkaline submarine hydrothermal vents could have provided a favorable environment for generating prebiotic organic molecules from CO₂, H₂, and CH₄ (White et al., 2015). In the Hadean submarine hydrothermal vent, the alkaline hydrothermal fluid at temperatures below 150 °C with pH values of about 9 had been erupted (Russell and Hall, 1997), and various sulfide minerals had been formed by the reaction between metal ions (e.g., Fe²⁺, Co²⁺, Ni²⁺, and...
Cu') and hydrogen sulfide ion (HS⁻) (Drobnar et al., 1990). Particularly, iron sulfide minerals such as mackinawite (FeS), greigite (Fe₃S₄), and pyrite (FeS₂) could be utilized in the synthesis of organic molecules essential for the origin of life called the 'iron-sulfur world hypothesis' (Wächtershäuser, 1988; Blöchl et al., 1992; Heinen and Lauwers, 1996). Bebie et al. (1998) described that since the surface of pyrite holds negatively charged, amino acids can be adsorbed on the pyrite's surface. It could consequently produce chains of amino acids, which are the fundamental building blocks of proteins.

In addition, hydrothermal mackinawite and greigite have attracted attention due to their structural affinities with hydrogenase, ferredoxin, acetyl coenzyme-A synthase, and carbon monoxide dehydrogenase (Russell, 2006; Russell and Hall, 2006; Mielke et al., 2011; Nitschke et al., 2013). These structural similarities provide an important evidence to support the possibility that the ancient hydrothermal mackinawite and greigite contributed to the synthesis of biogenic molecules.

The iron sulfide minerals, moreover, play a major role in cycle of sulfur in anaerobic lake and marine sediments (Berner, 1964a, 1964b; Rickard and Morse, 2005). Sulfate ion (SO₄²⁻) is reduced to sulfide ion (S²⁻) by the metabolic activity of sulfate-reducing bacteria, but it is re-oxidized to elemental sulfur (S⁰) and further oxidized to sulfate ion (SO₄²⁻) by the sulfur bacteria in the sedimentary environments. This biological sulfur cycle called 'sulfur cycle' is one of the most essential elemental cycles at the Earth’s surface (Kellogg et al., 1972; Ono et al., 2003; Fike et al., 2015). The sulfide ion produced in this cycle readily reacts with dissolved ferrous iron (Fe²⁺) to precipitate nanocrystalline mackinawite, which is finally grown to the most stable pyrite by the reaction with elemental sulfur in the anaerobic marine sediments (Huerta-Diaz and Morse, 1992; Wilkin and Barnes, 1996; Morse and Luther, 1999). Therefore, the formations of nanocrystalline mackinawite and pyrite are the primary geochemical reactions for fixing of sulfide ion and elemental sulfur in anaerobic lake and marine sediments.

Because of these important geochemical and microbiological phenomena, numerous studies have been performed to understand the crystal structure and phase changes of nanocrystalline mackinawite (Schoonen and Barnes, 1991a, 1991b; Rickard and Luther, 1997; Benning et al., 2000; Wolthers et al., 2003; Hunger and Benning, 2007; Csákberényi-Malasics et al., 2012; Sines et al., 2012). The structure of nanocrystalline mackinawite consists of distorted FeS₄ tetrahedral sheets, which is identical to the layer structure of well-crystalline mackinawite (Lennie et al., 1995; Wolthers et al., 2003; Ohfuji and Rickard, 2006). The structural difference between nanocrystalline mackinawite and well-crystalline mackinawite is the interlayer distance between FeS₄ tetrahedral sheets. The basal spacing (d₀₀₁) in the nanocrystalline mackinawite varies a fairly wide range from 5.1 to 6.8 Å. The well-crystalline mackinawite, on the other hand, shows the shortest d₀₀₁ value of 5.03 Å (Lennie et al., 1995; Wolthers et al., 2003; Ohfuji and Rickard, 2006; Jeong et al., 2008). Under the hydrothermal conditions at 120 °C, the nanocrystalline mackinawite crystallizes to the well-crystalline mackinawite, accompanied by contraction of the d₀₀₁ (Csákberényi-Malasics et al., 2012).

The nanocrystalline mackinawite transforms to greigite by the oxidation of ferrous (Fe²⁺) to ferric iron (Fe³⁺) (Lennie et al., 1997; Bourdoiseau et al., 2011; Csákberényi-Malasics et al., 2012). By supplying elemental sulfur, the nanocrystalline mackinawite crystallizes to pyrite accompanied with a small amount of greigite (Schoonen and Barnes, 1991a, 1991b; Hunger and Benning, 2007). The elemental sulfur could be therefore considered as a significant factor for greigite and pyrite formations at the Earth’s surface.

Despite these extensive studies of nanocrystalline mackinawite, the phase transformation process from mackinawite to pyrite has been still poorly understood due to its small crystallite size. The greigite and pyrite formations are necessary for understanding the mechanism of fixing elemental sulfur in the anaerobic lake and marine sediments. In order to clarify the detailed effects of sulfur on the phase transformation process from nanocrystalline mackinawite to pyrite, we performed hydrothermal experiments in the absence and presence of elemental sulfur, synchrotron X-ray diffraction (XRD) measurements, atomic Pair Distribution Function (PDF) analysis, Extended X-ray Absorption Fine Structure (EXAFS) analysis, and transmission electron microscopic (TEM) observation.

**EXPERIMENTAL METHODS**

**Synthesis of iron monosulfide nanoparticle and hydrothermal ageing experiments**

In the study, deoxygenated water was utilized in the all experiments due to the high reactivity of the iron monosulfide nanoparticle toward oxygen. The deoxygenated water was prepared by bubbling N₂ gas to distilled water for 30 min. The black iron monosulfide suspension, colloidal FeS, was obtained by mixing 10 mL of 0.2 M (NH₄)₂Fe(SO₄)₂·6H₂O (FUJIFILM Wako Pure Chemical Corporation, purity; >99.0%) aqueous solution with 10 mL of 0.4 M Na₂S·9H₂O (FUJIFILM Wako Pure Chemi-
al Corporation, purity; >98.0%) aqueous solution in a glove box with an inert N\textsubscript{2} atmosphere. The hydrothermal ageing experiments were performed by heating the iron monosulfide suspension at 120 °C in the absence and presence of elemental sulfur. First, the iron monosulfide suspension was sealed with the deoxygenated water in a Teflon-lined stainless steel autoclave under N\textsubscript{2} atmosphere and then hydrothermally heated at 120 °C in an oven for 2, 4, 6, 8, and 12 h. After the hydrothermal heating experiments, the resulting solutions were filtered through 0.1 µm membrane filters (Merck Millipore Ltd). The obtained black solids were blow-dried with N\textsubscript{2} gas. Subsequently, they were kept in a vacuum desiccator until used. Second, the iron monosulfide suspension was transferred into the Teflon-lined stainless steel autoclave with 77 mg sulfur (0.12 M) powder (FUJIFILM Wako Pure Chemical Corporation, purity; >98.0%) and hydrothermally heated at 120 °C in the oven for 2, 4, 6, 8, 12, 16, 20, and 24 h. After quenching to room temperature, the pH values of the solutions were in a range between 9.96 and 10.18. The resulting solutions were filtered in the same way and stored in the vacuum desiccator.

**Synchrotron powder XRD measurements**

Synchrotron powder XRD measurements were performed at the BL-8B in Photon Factory (PF), KEK, Japan. In order to avoid any oxidation of the samples, they were inserted into the Lindemann glass capillary (\(\phi = 0.7\) mm) under N\textsubscript{2} gas atmosphere. The incident beam was monochromatized to a wavelength of 0.6868(5) Å using the Si(111) double crystal monochromator. The X-ray beam was collimated to 80 µm in diameter. The exposure time was set to 30 min. The obtained XRD data were analyzed with PDFIndexer software (Seto et al., 2010) to calculate the lattice parameters and relative phase fraction.

**Synchrotron X-ray total scattering measurements**

Synchrotron X-ray total scattering measurements were performed at beamline BL14B1 in SPring-8, Japan. 50 mg of the sample was loaded into a Kapton capillary tube with 2 mm inner diameter and 15 mm length under N\textsubscript{2} gas atmosphere. The incident beam was monochromatized to a wavelength of 0.20606(1) Å using the Si(311) double crystal monochromator. X-ray total scattering was measured at 20 K under vacuum (\(\sim 10^{-5}\) Torr). Data were collected in the Q range from 0.3 to 25 Å\(^{-1}\). The obtained X-ray total scattering data were transformed to the total scattering structure functions \(S(Q)\) and atomic Pair Distribution Functions (PDF) \(G(r)\) using PDFgetX2 program (Qiu et al., 2004). The refinements of lattice parameters, Fe site occupancy, and crystallite size were carried out by fitting the obtained PDF to the structure model of well-crystalline mackinawite (Lennie et al., 1995) using PDFgui software (Farrow et al., 2007).

**Transmission electron microscopy (TEM) observations**

Transmission electron microscopy (TEM) observations were performed using a field emission source transmission electron microscope (JEOL JEM-2100F) operating at accelerating voltage of 200 kV at National Institute for Materials Science (NIMS), Japan. The samples were dispersed in deoxygenated ethanol and dropped onto a Cu TEM microgrid (Okenshoji Co., Ltd) using a micropipette. The particle sizes were determined by analysis of the obtained TEM images using the ImageJ software (Schneider et al., 2012).

**Fe K-edge XAFS measurements**

Fe K-edge XAFS measurements were performed at BL-9C in PF, KEK, Japan. The XAFS station was equipped with the Si(111) double crystal monochromator. 4 mg of the sample was diluted with 150 mg of BN powder (FUJIFILM Wako Pure Chemical Corporation., purity >99%) and pressed into a pellet with a diameter of 10 mm. The pellets were transferred to polyethylene bags for measurements. The process was conducted in a glove box with an N\textsubscript{2} atmosphere. Ionization chambers filled with 100% N\textsubscript{2} and 15% Ar in N\textsubscript{2} were used to measure the incident and transmitted X-ray intensities, respectively. All spectra were collected in transmission mode at room temperature. The size of the X-ray incident beam at the sample was approximately 1.5 × 0.5 mm\(^2\). Energy measurement range was set from 6606.2 to 8211.3 eV. Energy calibration was carried out using spectrum of Fe foil. The obtained XAFS spectra were corrected and normalized using the Athena software (Ravel and Newville, 2005). The Fe\(^{3+}\)/Fe\(^{2+}\) contents were estimated based on the method by Bajt et al. (1994) from the energy of the pre-edge peak in X-ray absorption fine structure (XANES). The pre-edge peaks were fitted to Gaussian curves, whereas the backgrounds were fitted to 4th-order polynomials. Synthetic troilite (FeS) and greigite (Fe\(_3\)S\(_4\)) were used as calibration lines. The EXAFS spectra imported into Artemis software were fitted to theoretical models of well-crystalline mackinawite (Lennie et al., 1995) and pyrite (Willeke et al., 1992) using Atoms (Ravel, 2005) and FEFF6 code softwares (Rehr et al., 1991). The Fourier transformation and fitting ranges were set to \(3 \leq k \leq 14\) Å\(^{-1}\) and \(1.2 \leq r \leq 4.0\) Å, respectively.
RESULTS AND DISCUSSION

Synchrotron XRD study

The first hydrothermal ageing experiment was performed by heating the iron monosulfide suspension at 120 °C. Figure 1a shows the evolution of XRD pattern of the iron monosulfide nanoparticle for 12 h. Before the hydrothermal treatment, the iron monosulfide suspension showed a characteristic broad XRD profile. The peak positions were in approximately agreement with those of nanocrystalline mackinawite (Jeong et al., 2008). As already reported by many authors, the XRD peak positions of mackinawite have been distributed over a wide range depending on the degree of crystallinity, crystallite size, particle size, and its preparation condition (Lennie et al., 1995; Wolthers et al., 2003; Ohfuji and Rickard, 2006; Jeong et al., 2008; Sines et al., 2012). Wolthers et al. (2003) showed that the \( d_{001} \) decreased as increasing the mackinawite crystallinity. For instance, in the disordered mackinawite (MkA), the \( d_{001} \) is 6.60 Å (Wolthers et al., 2003). In the well-crystalline mackinawite, on the other hand, the \( d_{001} \) is 5.0328 Å (Lennie et al., 1995). In the iron monosulfide suspension synthesized in the study, the \( d_{001} \) was 5.50 Å. This basal spacing was nearly the same with that of disordered mackinawite (MkB), \( d_{001} = 5.48 \) Å (Wolthers et al., 2003). It has been also recognized that in mackinawite the \( c \) lattice parameter exhibits a wide range from 5.0 to 6.8 Å although the \( a \) lattice parameter falls within a small range between 3.7 and 4.0 Å (Lennie et al., 1995, 1997; Mullet et al., 2002; Wolthers et al., 2003; Jeong et al., 2008). In the present study, the \( a \) and \( c \) lattice parameters refined from the XRD data were 3.671(16) and 5.26(5) Å, respectively. The \( a \) lattice parameter was fairly close to that of well-crystalline mackinawite \( a = 3.6735(4) \) Å, but the \( c \) lattice parameter was considerably larger than that of well-crystalline mackinawite \( c = 5.0328(7) \) Å. The lattice expansion relative to the well-crystalline mackinawite would be caused by lowering crystallinity and by decreasing particle size (Wolthers et al., 2003). Since the iron monosulfide suspension obtained in the study possessed the lower crystallinity and the smaller particle size such like nanocrystalline mackinawite (Ohfuji and Rickard, 2006; Jeong et al., 2008), it was regarded as the nanocrystalline mackinawite. As it can be clearly seen in the Figure 1a, the FWHM values of XRD peaks were decreased by the hydrothermal heating for 2 h. Thereafter until the end of the hydrothermal experiment for 12 h, crystal structure of the mackinawite remained essentially unchanged. The result reflects that the crystallinity increased rapidly for the first 2 h, and then remained nearly unchanged up to the

![Figure 1](image-url)

**Figure 1.** Evolutions of XRD patterns of nanocrystalline mackinawite hydrothermally heated at 120 °C (a) in the absence of elemental sulfur, and (b) in the presence of elemental sulfur and variation of phase fraction for nanocrystalline mackinawite, greigite and pyrite as a function of hydrothermal heating time.
end of the experiment for 12 h. It is noteworthy that notwithstanding mackinawite crystallinity increased with ageing time in the previous studies (Rickard and Luther, 1997; Wolthers et al., 2003), the XRD intensity never increased continuously with the hydrothermal heating time in the present study. After the hydrothermal heating for 8 h, however, a small amount of greigite could be detected in the nanocrystalline mackinawite. As mentioned later, the Fe₃⁺/ΣFe contents almost remained unchanged in spite of the occurrence of greigite. Very recently, Li et al. (2018) performed the ageing experiment of the mackinawite under ‘acidic’ hydrothermal condition at 120 °C. The authors confirmed that the mackinawite quickly transformed to greigite after 1 h and then completely transformed to pyrrhotite (Fe₉S₁₀) through smythite (Fe₉S₁₁) for 6 h of ageing time. The authors conducted the hydrothermal experiment under the ‘acidic condition’ to hydrolyze thioacetamide, which was used as a source of sulfide ions. Since mackinawite is unstable under acidic condition (Özverdi and Erdem, 2006), it must be dissolved in the Li’s experiment (Li et al., 2018). In the present hydrothermal experiment, on the other hand, the nanocrystalline mackinawite remained up to at least 12 h under alkaline condition, which was accompanied by a very small amount of greigite. The result was perfectly consistent with the hydrothermal experiment performed at neutral pH (Csákberényi–Malasics et al., 2012). Therefore, the mackinawite is most stable between neutral and alkaline conditions, but it is extremely unstable under acidic condition (Özverdi and Erdem, 2006).

The second hydrothermal ageing experiment was performed by heating the nanocrystalline mackinawite under the presence of elemental sulfur at 120 °C for 24 h. Figure 1b exhibits the evolution of XRD pattern of the nanocrystalline mackinawite. The characteristic broad XRD pattern of mackinawite was observable until the hydrothermal heating of 6 h. The mackinawite seemed to persist up to 8 h of heating time. The most remarkable result was that the XRD peaks corresponding to pyrite appeared after 6 h heating and subsequently evolved gradually with increasing the ageing time. A small amount of greigite was confirmed at the hydrothermal heating of 8 h. After the further heating for 12 h, the XRD peaks of mackinawite completely diminished. Pyrite instead of the nanocrystalline mackinawite finally became dominant. The phase fraction versus heating time inserted in Figure 1b indicates that the nanocrystalline mackinawite underwent the phase transformation to pyrite together with a small amount of greigite. This result was consistent with the previous hydrothermal experiment (Hunger and Benning, 2007).

Figure 2 shows variations of the d₀₀₁ value and lattice parameters for the nanocrystalline mackinawite hydrothermally heated under the absence and presence of elemental sulfur. At the hydrothermal heating under the absence of elemental sulfur for 2 h, the d₀₀₁ decreased from 5.50 to 5.34 Å and subsequently maintained almost constant up to the hydrothermal heating for 12 h (Fig. 2a). The a lattice parameter slightly increased by the hydrothermal heating in the absence of elemental sulfur for 4 h and then maintained substantially constant up to the end of the hydrothermal experiment (Fig. 2b). The c lattice parameter, on the other hand, decreased after 2 h of heating, and then maintained substantially constant up to the end of the hydrothermal experiment (Fig. 2b). The c lattice parameter, on the other hand, decreased after 2 h of heating, and then maintained constant (Fig. 2c). Surprisingly, there were no linear relationships between lattice parameters and the hydrothermal heating time.

By the hydrothermal heating under the presence of elemental sulfur, the d₀₀₁ decreased drastically from 5.45 to 5.15 Å for the first 2 h (Fig. 2d). The a lattice parameter continuously increased with heating time (Fig. 2e), but the c lattice parameters decreased progressively (Fig. 2f). Compared with the result of the heating experiment performed in the absence of elemental sulfur, not only the d₀₀₁ value but also the a and c lattice parameters were significantly varied with the heating time. Generally, in mackinawite the c lattice parameter is readily varied with
the degree of crystallinity and crystallite size (Lennie et al., 1995, 1997; Mullet et al., 2002; Wolthers et al., 2003; Jeong et al., 2008). The result of our study implies that the sharp decrease of $d_{001}$ and drastic increase of the $a$ lattice parameter would be associated with the phase transformation from mackinawite to pyrite.

**PDF analysis**

Second, we performed X-ray total scattering measurements to investigate the evolution of short to medium range atomic order in the nanocrystalline mackinawite by the hydrothermal heating under the absence of elemental sulfur. The variation of the PDF patterns and fitted results with mackinawite are exhibited in Figure 3. The PDF fitting results of nanocrystalline mackinawite are listed in Table 1. Since the all experimental data could be approximately fitted with the well-crystalline mackinawite (Lennie et al., 1995), it could be considered that crystal structure of the nanocrystalline mackinawite had a mackinawite-like local structure. After the hydrothermal heating for 2 h, the $R_w$ value of PDF fit was improved from 36.7 to 28.3% (Table 1). In the PDF pattern of 0 h, the residual difference from 12 to 20 Å was particularly larger than that of 2 h. This fact suggests that medium-range atomic arrangement of the initial nanocrystalline mackinawite, the black iron monosulfide suspension, was more disordered than that of nanocrystalline mackinawite heated for 2 h. Therefore, the improvement of $R_w$ values from 0 to 2 h indicates that the degree of medium-range atomic order ranging from 12 to 20 Å increased by the hydrothermal heating, although the short-range order of nanocrystalline mackinawite was almost unchanged (Fig. 3). Jeong et al. (2008) reported that in nanocrystalline mackinawite there are many crystal defects such as edge dislocations and curvatures, which are only limited along the grain boundaries. Ohfuji and Rickard (2006) also described that the ends of the mackinawite (001) fringes are highly irregular and that individual crystals appear to lack of sharply defined outlines. It could be therefore inferred that in the nanocrystalline mackinawite the disordered regions would be rearranged, and the medium-range order was significantly enhanced by the hydrothermal treatment.

Figure 4 displays the variation of crystallite size and structural parameters as a function of hydrothermal heating time. By hydrothermally heating the nanocrystalline mackinawite at 120 °C, the crystallite size quickly increased from 2 to 4 nm for the first 2 h, but thereafter it remained essentially constant up to the end of the hydrothermal experiment for 12 h. The variation in crystallite size was within the small range that has been observed by TEM (Ohfuji and Rickard, 2006). This growth of crystallite size seems to result in the increase of crystallinity and appearance of the medium-range order in the nanocrystalline mackinawite (Figs. 1 and 3). Here, it is very important to distinguish the results between the PDF method and conventional XRD method. In general, lattice parameters obtained from the XRD patterns utilize structural information on long-range order and periodicity of atomic array.

![Figure 3. Evolution of PDF pattern of nanocrystalline mackinawite hydrothermally heated at 120 °C in the absence of sulfur source.](image)

| Time (h) | Crystallite size (nm) | $a$ (Å) | $c$ (Å) | S atomic coordinate $z$ | Fe site occupancy | $R_w$ | Bond length Fe-S (Å) | Interatomic distance Fe-Fe (Å) |
|---------|----------------------|---------|---------|-------------------------|-----------------|-------|---------------------|---------------------|
| 0       | 2.1 (4)              | 3.68 (4) | 5.14 (9) | 0.248 (9)              | 0.80 (19)       | 0.367 | 2.24 (6)            | 2.60 (3)            |
| 2       | 3.6 (8)              | 3.69 (2) | 5.12 (5) | 0.248 (6)              | 0.84 (13)       | 0.283 | 2.24 (3)            | 2.61 (1)            |
| 4       | 3.6 (8)              | 3.69 (2) | 5.14 (6) | 0.245 (6)              | 0.79 (13)       | 0.318 | 2.24 (3)            | 2.61 (1)            |
| 6       | 3.4 (8)              | 3.70 (2) | 5.14 (7) | 0.247 (7)              | 0.80 (15)       | 0.279 | 2.24 (4)            | 2.61 (2)            |
| 8       | 3.6 (9)              | 3.69 (2) | 5.14 (7) | 0.244 (6)              | 0.81 (14)       | 0.272 | 2.23 (4)            | 2.61 (2)            |
| 12      | 3.6 (1.0)            | 3.70 (3) | 5.14 (7) | 0.245 (7)              | 0.79 (14)       | 0.321 | 2.24 (4)            | 2.61 (2)            |

Note: Mackinawite crystallizes into the tetragonal $P4_{2}^{n}mm$ with the atoms located at special positions: Fe(0, 0, 0) and S(0, 1/2, z).
arrangement. By contrast, those determined from the PDF $G(r)$, which is the Fourier transform of the reciprocal space total scattering structure function $S(Q)$, include structural information on short- and medium-range order of atomic arrangement (Toby and Egami, 1992; Billinge and Kanatzidis, 2004; Egami and Billinge, 2013). Figure 4 clearly shows that there were little variations in the $a$ and $c$ lattice parameters of nanocrystalline mackinawite. Especially, compared with the $c$ lattice parameter determined from the XRD patterns (Fig. 2c), it was almost unchanged throughout the hydrothermal heating experiment. Local atomic structure of the nanocrystalline mackinawite seemed to be unaffected by the hydrothermal treatment. The Fe-S bond length, Fe-Fe interatomic distance, and site occupancy factor of Fe were also approximately unchanged with the hydrothermal treatment (Figs. 4d-4f). The Fe-S bond lengths of 2.23–2.24 Å and Fe-Fe interatomic distances of 2.60–2.61 Å were nearly identical with those in well-crystalline mackinawite (Lennie et al., 1995), but we would like to emphasis that the Fe atoms were distributed in the tetrahedral sites with a site occupancy of approximately 80% (Fig. 2f). The result was quite reasonable because there must be numerous structural defects in nanocrystalline mackinawite (Ohfuji and Rickard, 2006; Jeong et al., 2008). Although significant structural defects would pose S deficiency in the nanocrystalline mackinawite as well, the refinement of site occupancy factor for S atom suggested no significant deviation from the full occupation. The Fe deficiency would be associated with the following three structural features; (1) a negatively charged FeS$_4$ tetrahedral sheet, (2) an incorporation of H atoms into the tetrahedral site, and (3) a partial oxidation of ferrous (Fe$^{2+}$) to ferric iron (Fe$^{3+}$) to compensate the missing charge. We considered the three possibilities. First, Wolthers et al. (2003) described that the lattice expansions may be explained by intercalation of water molecules between the tetrahedral sheets. If a polar molecule of water has been intercalated between the negatively charged FeS$_4$ tetrahedral sheets, the interlayer distance would have been more expanded. Furthermore, the water molecules could be hardly dehydrated because they are stabilized by a hydrogen bond between the sheets. This is a clear contradiction to the characteristic feature of mackinawite that it possesses the variable $d_{001}$ value. The lattice expansion along the c-axis direction might be explained by the adsorption of cations on the surface of the negatively charged FeS$_4$ tetrahedral sheets. The adsorption property of mackinawite has been known as the most important mineral features. Indeed, Wilkin and Beak (2017) reported that the c lattice parameter slightly increased when Ni ions were intercalated into the FeS$_4$ tetrahedral sheet. However, the most expanded c lattice parameter was 5.10 Å at most. It was therefore unlikely that the lattice expansion along the c-axis was ascribed to the negatively charged FeS$_4$ tetrahedral sheets. The PDF and EXAFS studies (mentioned later), however, showed that the Fe had a nearly identical tetrahedral coordination with that in the well-crystalline mackinawite. The results implied that the FeS$_4$ tetrahedron itself was hardly expanded by the hydrothermal heating. In addition, the pH values were actually maintained constant at around 10 throughout the all hydrothermal experiments. Namely, few hydrogen ions were contained in the solutions. Consequently, few H atoms are incorporated in the FeS$_4$ tetrahedral coordination. The partial oxidation of Fe$^{2+}$ in the tetrahedral site will be discussed in the section of XANES and RSF analyses.

**TEM observation**

Figure 5 shows TEM images of the nanocrystalline mackinawite before and after the hydrothermal heating under the absence of elemental sulfur. We clearly observed the
characteristic lattice fringes corresponding to \(d\)-spacing of \((001)\) plane of mackinawite. Before the hydrothermal treatment, the thickness of single crystals was from 1.8 to 2.2 nm, and the length was from 2.2 to 5.5 nm. After the hydrothermal heating of 8 h, the thickness and length increased to 3.3–4.4 nm and 15–20 nm, respectively. The average thickness and length enlarged by two to four times by the hydrothermal treatment. It is apparent that the nanocrystalline mackinawite preferentially grew in the length (horizontal) direction along the sheet structure rather than in the thickness (vertical) direction. In the study, however, the particle size observed by TEM was obviously larger than that obtained from the PDF analysis. The particle size measured by the TEM implies the linear dimensions of a particle separated with sharp boundaries. The particle size obtained by the PDF analysis is, on the other hand, determined from the PDF intensity falloff indicating the coherent atomic arrangement disappears. Therefore, since the nanocrystalline mackinawite must include disordered arrangement regions (Ohfuji and Rickard, 2006; Jeong et al., 2008), the particle size determined by the PDF method must become smaller than that determined by the TEM observation.

XANES and RSF analyses

We investigated the Fe K-edge X-ray absorption near-edge structure (XANES) spectra to determine the distribution of valence states of iron in the nanocrystalline mackinawite. Figure 6a gives the evolution of pre-edge peak in Fe K-edge XANES spectra of the nanocrystalline mackinawite hydrothermally heated under the absence of elemental sulfur. The pre-edge peak position was almost unchanged by the hydrothermal heating of 12 h. The \(\text{Fe}^{3+}/\Sigma\text{Fe}\) content fluctuated around 10% (Fig. 6b). Mullet et al. (2002) investigated the content of \(\text{Fe}^{3+}/\Sigma\text{Fe}\) in the mackinawite by Transmission Mössbauer Spectroscopic analysis and reported that the mackinawite contained up to...
20% Fe\(^{3+}\). The Fe\(^{3+}\) content was therefore within an acceptable range for mackinawite. It could be explained reasonably by considering that the Fe\(^{3+}\) compensated the charge deficiency of Fe\(^{2+}\) in the structure. Assuming that the Fe\(^{3+}\) content in the mackinawite was 20%, the chemical formula of nanocrystalline mackinawite could be described as \((\text{Fe}_0.70\text{Fe}_{0.20})\text{S}_2\). Therefore, the Fe site occupancy was estimated to be 0.90. The Fe site occupancies estimated from PDF analysis were distributed around 0.79 and 0.84 (Table 1), which were roughly consistent with those determined by the XANES spectra.

Taking into account the Fe deficiency in mackinawite, the van der Waals forces between the Fe\(_\text{S}_3\) tetrahedral sheets will be reduced because the atom density per unit volume became lowered. In general, van der Waals forces are proportional to the Hamaker constant (A), which is given by \(A = \pi^2 \times C \times \rho^2\), where C is the London dispersion constant and \(\rho\) is the molecular density per unit volume. In the nanocrystalline mackinawite, atom density in the Fe\(_\text{S}_4\) tetrahedral sheets was reduced by the Fe deficiency. The lowering the atomic density would lead to the expansion between the sheets. Although Wolthers et al. (2003) have already reported that the lattice expansion along the c-axis is due to the lowering crystallinity and decreasing particle size. Indeed, it might be mainly attributed to the Fe deficiency caused by the structural defects (Ohfuji and Rickard, 2006; Jeong et al., 2008).

Since the phase transformation from mackinawite to greigite involves the oxidation of Fe\(^{2+}\) to Fe\(^{3+}\), many researchers have speculated that anoxic water acts as the oxidant under anoxic solution condition (Schoonen and Barnes, 1991a, 1991b; Rickard and Morse, 2005; Rickard and Luther, 2007; Jeong et al., 2008; White et al., 2015). It has consequently been proposed that greigite is formed by the following oxidation reaction:

\[
4\text{FeS} + 2\text{H}_2\text{O} \rightarrow \text{Fe}_2\text{S}_3 + \text{Fe(OH)}_2\text{aq} + \text{H}_2 \quad (1)
\]

or

\[
4\text{FeS} + 2\text{H}_2\text{O} \rightarrow \text{Fe}_2\text{S}_3 + \text{FeOOH}_\text{aq} + 1.5\text{H}_2 \quad (2).
\]

If Fe\(^{3+}\) has been contained in mackinawite, however, the phase transformation from mackinawite to greigite would have occurred directly without the oxidation of Fe\(^{2+}\). In this study, greigite might be directly formed from the Fe\(^{3+}\)-bearing mackinawite on the following decomposition reaction:

\[
\text{Fe}_{1/2(2-3x)}\text{Fe}^{3+}_x\text{S} \rightarrow (1 - 2x)\text{FeS} + 1/2x\text{Fe}_2\text{S}_4
\]

\[
(0.09 \leq x < 0.14) \quad (3),
\]

where \(x\) denotes the amount of Fe\(^{3+}\) in mackinawite. The reaction continuously varies depending upon the \(x\) value. A small amount of greigite was formed by the hydrothermal heating under the absence of elemental sulfur (Fig. 1a). Despite the formation of greigite, the Fe\(^{3+}/\Sigma\text{Fe}\) contents almost remained unchanged (Fig. 6b). Therefore, the decomposition reaction of (3) would be supported by this fact that a small amount of greigite was formed with the Fe\(^{3+}\)-bearing nanocrystalline mackinawite.

Figure 6c shows the evolution of pre-edge peak in Fe K-edge XANES spectra of the nanocrystalline mackinawite hydrothermally heated in the presence of elemental sulfur. The pre-edge peak position was gradually shifted to the higher energies. The Fe\(^{3+}\) content approached the maximum value at the hydrothermal heating of 8 h by the formation of greigite, but it decreased to the initial level by the pyrite formation (Fig. 6d). In the sulfur-rich hydrothermal condition, the phase transformation from mackinawite to greigite can be explained by the following oxidation reaction:

\[
3(\text{Fe}_{1/2(2-3x)}^{3+}\text{Fe}^{3+}_x\text{S}) + (1 - 2x)\text{S} \rightarrow (1 - 1/2x)\text{Fe}_2\text{S}_4 \quad (0.09 \leq x < 0.17) \quad (4),
\]

where \(x\) denotes the amount of Fe\(^{3+}\) in mackinawite. In mackinawite, Fe\(^{2+}\) is oxidized to Fe\(^{3+}\) by the elemental sulfur acting as the oxidant. The Fe\(^{3+}\)/\(\Sigma\text{Fe}\) content significantly increased at the hydrothermal heating of 8 h with the formation of greigite (Fig. 6d), which would suggest that the oxidation reaction of (4) had progressed. It is necessary to bear in mind that S atoms in pyrite occur in pairs with covalent disulfide (S-S) bonds. In pyrite structure, the S atoms possess the larger valence state of −1 than the formal valence of −2. Thus, the Fe\(^{3+}\)-bearing mackinawite can transform to pyrite on the following reaction:

\[
\text{Fe}_{1/2(2-3x)}^{3+}\text{Fe}^{3+}_x\text{S} + (1 - x)\text{S} \rightarrow (1 - 1/2x)\text{Fe}_2\text{S}_2 \quad (5).
\]

In this phase transformation, the Fe\(^{3+}\) is reduced to Fe\(^{2+}\) by sulfur in mackinawite acting as the reductant. The phase transformation from greigite to pyrite occurs on the following reaction:

\[
\text{Fe}_2\text{S}_3 + 2\text{S} \rightarrow 3\text{FeS}_2
\]
In the phase transformation from greigite to pyrite, the Fe$^{3+}$ is reduced to Fe$^{2+}$ by sulfur in greigite acting as the reductant. These reductions of Fe$^{3+}$ in both mackinawite and greigite were reflected to the variation of Fe$^{3+}$/ΣFe content in the heating time between 8 and 24 h, but we would like to emphasize that the Fe$^{3+}$/ΣFe content was apparently larger than the phase fraction of greigite estimated from XRD measurement (Fig. 1b). In particular, by the hydrothermal heating for 24 h in the presence of elemental sulfur, the Fe$^{3+}$/ΣFe content was still more than 10% (Fig. 6d), but the phase fraction of greigite estimated from XRD measurement was only 2% (Fig. 1b). There are therefore the following two possibilities to explain the observed contradiction: one is that there was the Fe$^{3+}$–bearing amorphous iron monosulfide (Csákberényi–Málasics et al., 2012) in the sample and the other is that the Fe$^{3+}$ was contained in pyrite. These two possibilities will be discussed in the next section.

The evolution of Radial Structure Function (RSF) profiles and EXAFS fit results of the nanocrystalline mackinawite hydrothermally heated in the absence of elemental sulfur are given in Figure 7a and Table 2, respectively. The RSF profiles apparently consisted of two shells. The first shell corresponds to the Fe–S bonds in the FeS$_4$ tetrahedral site. The distance of 2.256(6) Å was quite close to that determined by PDF fitting. The second shell was ascribed to the Fe–Fe interaction between the neighboring FeS$_4$ tetrahedra. The variations of Fe–S bond length, coordination number, Fe–Fe interatomic distance, and Fourier transform (FT) magnitude of the Fe–Fe peak are shown in Figures 8a–8d, respectively. During the hydrothermal treatment without elemental sulfur, the Fe–S...
The bond length of about 2.26 Å and the CN of 4 remained nearly constant within the standard deviation, which suggested that the local atomic structure around Fe was never changed with the hydrothermal heating. The result was in good agreement with that of PDF analysis. Furthermore, the Fe–S bond length was exactly consistent with that of 2.2558(9) Å in well-crystalline mackinawite (Lennie et al., 1995). Therefore, the Fe possessed a nearly identical tetrahedral coordination with that in well-crystalline mackinawite. The Fe–Fe interatomic distance, on the other hand, varied in the range of 2.66 to 2.70 Å (Table 3), which was apparently larger than that of 2.5976(3) Å in well-crystalline mackinawite (Lennie et al., 1995). The FT magnitude of the second shell peak increased significantly after the hydrothermal heating of 2 h (Fig. 8d). This result apparently indicated that the coordination number of Fe–Fe was increased. Namely, it implied the formation of a sheet structure consisting of edge-sharing FeS4 tetrahedra and the appearance of the medium-range order in the nanocrystalline mackinawite. This result was in excellent agreement with that of our PDF analysis.

Figure 7b presents the evolution of RSF profiles of the nanocrystalline mackinawite hydrothermally heated in the presence of elemental sulfur. Based on the result of XRD measurement, the RSF profiles of the heating time from 0 to 6 h were fitted with well-crystalline mackinawite structure (Lennie et al., 1995), while those of the heating time from 12 to 24 h were fitted with pyrite structure (Willeke et al., 1992). The RSF of 8 h heating time exhibited the medium profile between mackinawite and pyrite. Table 3 gives the EXAFS fit results with mackinawite and pyrite. The most remarkable result was that the R factor of 24 h heating time dropped to 0.005, indicating that the product exactly matched the ideal pyrite structure. The perfect coincidence between the observed and calculated RSF profiles implied that no Fe3+-bearing amorphous iron monosulfide (Csákberényi-Malasics et al., 2012) was included in the product. Therefore, the Fe3+ must be present in the pyrite structure. It has been reported that the pyrite’s surface is rich in Fe3+ as a result of rupture of the disulfide bonds (S–S bonds) (Nesbitt et al., 1998; Nesbitt et al., 2000; Chernyshova, 2003; Mattila et al., 2004). Pyrite nanoparticles with large surface area must bear a more Fe3+ than pyrite with the larger particle size. In the present study, the average crystallite size of the pyrite was determined to be 14(2) nm using

![Figure 8](image_url)

**Figure 8.** Variations of (a) Fe–S bond length, (b) coordination number, (c) Fe–Fe atomic distance and (d) FT magnitude of Fe–Fe peak obtained from the RSF in the absence of elemental sulfur, and variations of (e) Fe–S bond length and (f) coordination number obtained from the RSF in the presence of elemental sulfur.

| Time (h) | Fe–S |  | Fe–Fe |  |
|---------|------|--|------|--|
|         | R (Å) | CN | σ² (Å²) | R (Å) | CN | σ² (Å²) | ΔE₀ (eV) | R factor |
| 0       | 2.255 (7) | 3.6 (5) | 0.006 (1) | 2.70 (2) | 0.4 (4) | 0.006 (6) | 5.2 (9) | 0.020 |
| 2       | 2.259 (4) | 4.2 (3) | 0.0064 (6) | 2.698 (7) | 1.0 (3) | 0.0064 (19) | 6.2 (5) | 0.007 |
| 4       | 2.255 (4) | 4.1 (3) | 0.0059 (6) | 2.692 (7) | 1.0 (3) | 0.0049 (17) | 6.4 (7) | 0.0107 |
| 6       | 2.262 (5) | 3.9 (4) | 0.0050 (7) | 2.690 (7) | 1.0 (3) | 0.0052 (17) | 6.8 (6) | 0.0081 |
| 8       | 2.258 (5) | 4.7 (4) | 0.0064 (7) | 2.68 (3) | 0.2 (3) | 0.0061 (6) | 6.0 (1.4) | 0.0420 |

| Time (h) | Fe–S1 |  | Fe–Fe |  |
|---------|------|--|------|--|
|         | R (Å) | CN | σ² (Å²) | R (Å) | CN | σ² (Å²) | ΔE₀ (eV) | R factor |
| 12      | 2.257 (8) | 5.7 (7) | 0.006 (1) | 3.47 (3) | 6 | 0.009 (3) | 3.85 (2) | 12 | 0.0095 (9) | 4.9 (1.7) | 0.036 |
| 16      | 2.261 (7) | 5.3 (6) | 0.0055 (8) | 3.48 (2) | 6 | 0.009 (3) | 3.86 (2) | 12 | 0.0096 (8) | 5.3 (1.2) | 0.026 |
| 20      | 2.259 (7) | 5.6 (7) | 0.0056 (9) | 3.47 (3) | 6 | 0.008 (3) | 3.86 (2) | 12 | 0.0089 (8) | 4.8 (1.4) | 0.033 |
| 24      | 2.264 (3) | 6.4 (3) | 0.0046 (3) | 3.47 (1) | 6 | 0.0058 (9) | 3.855 (5) | 12 | 0.0067 (4) | 5.4 (6) | 0.005 |

**Table 3.** EXAFS fit results of nanocrystalline mackinawite and pyrite hydrothermally heated under the presence of elemental sulfur.
Scherrer’s equation. The size was so small that the particle carried a higher charge. The Fe$^{3+}$/ΣFe content of more than 10% (Fig. 6b) in pyrite must be therefore due to the smaller particle size. The Fe–S bond length of 2.2558(9) Å in well-crystalline mackinawite (Lennie et al., 1995) is practically indistinguishable from that of 2.2640(7) Å in pyrite (Willeke et al., 1992) because they are too close to each other. However, the magnitude of the first peak corresponds to the first shell coordination around Fe. The substantial increase of the first peak intensity at the heating time of 12 h was therefore ascribed to the phase transformation from mackinawite to pyrite.

The second peaks observed in both RSF profiles were derived from the Fe–Fe interaction (Figs. 7a and 7b). Appearance of this peak at 2 h was due to the formation of a sheet structure consisting of edge-sharing FeS$_4$ tetrahedra and to the appearance of the medium-long range order in the nanocrystalline mackinawite. Under hydrothermal heating in the presence of elemental sulfur, the second shell peak was reduced after 8 h (Fig. 7b). Instead, new peaks corresponding to the Fe–S and Fe–Fe interaction appeared after 12 h (Fig. 7b). The appearance of these peaks could be strongly associated with the formation of the disulfide bonds (S–S bonds) in pyrite. The formation of the S–S bonds was greatly affected by the presence of elemental sulfur. The appearance of greigite was confirmed by the XRD measurements, but the amount of greigite was below 10% (Fig. 1b). Greigite has the inverse spinel cation distribution, in which half of the Fe$^{2+}$ enters the tetrahedral site, while the other half and the Fe$^{3+}$ occupy the octahedral site. In greigite, the Fe–S bond lengths in the tetrahedral and octahedral sites are 2.15(4) and 2.46(4) Å, respectively (Skinner et al., 1964). Therefore, the peaks corresponding to greigite might be masked by the strong first shell peak from mackinawite or pyrite. In addition, Jeong et al. (2008) reported that a few percent of greigite could not contribute to the RSF profile of nanocrystalline mackinawite. Figures 8e and 8f exhibit the variations of Fe–S bond distance and coordination number. The Fe–S bond distance of about 2.26 Å seemed to remain unchanged during the phase transformation from mackinawite to pyrite because these bond lengths were indistinguishable from each other. On the other hand, the coordination number of about four started to increase at the heating time of 8 h and finally approached to about six at the heating time of 12 h. Thereafter, the coordination number of about six was maintained almost constant within the experiment error. The results obtained from the RSF profile analysis were in excellent agreement with the result from XRD measurement.

**IMPLICATIONS**

**Nanocrystalline mackinawite at the Hadean alkaline hydrothermal vents**

It has been thought that amino acids could be polymerized on the pyrite’s surface, which has been recognized as the surface metabolism hypothesis (Wächtershäuser, 1988; Blöchl et al., 1992; Heinen and Lauwers, 1996; Bebie et al., 1998). Mackinawite and greigite have attracted attention because they would be the main products in ancient alkaline hydrothermal vents, and because they could contribute to the synthesis of bioorganic molecules. Furthermore, they have structural affinities with Fe–S clusters in the bioorganic molecules such as ferredoxin. The present study has two important implications. First, the structure of nanocrystalline mackinawite is most stable under alkaline conditions in the absence of elemental sulfur. No phase transformation from nanocrystalline mackinawite to pyrite occurs without elemental sulfur. The noteworthy finding is that the elemental sulfur must be an essential element to promote the phase transformation from nanocrystalline mackinawite to pyrite. Although hydrogen sulfide ion could be the most dominant sulfur specie at the Hadean submarine hydrothermal vent (Russell and Hall, 1997), it would be dissolved to the elemental sulfur and hydroxide under oxygen-limiting conditions; 2HS$^- + O_2 \rightarrow 2S^0 + 2OH^-$ (Janssen et al., 1998). Therefore, the nanocrystalline mackinawite initially precipitated at the Hadean alkaline hydrothermal vent could be transformed to greigite and pyrite.

Next, the Fe–S bond distance and Fe–Fe atomic distance in nanocrystalline mackinawite were good agreement with those in the several ferredoxins (Fe–S = 2.23–2.27 Å and Fe–Fe = 2.66–2.76 Å) (Teo et al., 1979). This result would support the Wächtershäuser’s surface metabolism hypothesis that the synthesis of bioorganic molecules is catalyzed by the nanocrystalline mackinawite around the Hadean submarine hydrothermal vents.

**Formation of iron sulfide minerals in anaerobic sediments**

Nanocrystalline mackinawite is the most abundant iron sulfide mineral in anaerobic marine and lake sediments, but it gradually converts to pyrite by the reaction with elemental sulfur released by sulfur bacteria. This conversion was directly confirmed by our experiment in which the nanocrystalline mackinawite transformed to pyrite under the presence of elemental sulfur. The elemental sulfur is the most effective element to produce covalent disulfide (S–S) bonds in the iron sulfide mineral and to
change the coordination environment of Fe from FeS$_4$ tetrahedra to FeS$_6$ octahedra, resulting in the formation of long-range atomic order of pyrite. This study suggests that the Fe$^{3+}$-bearing mackinawite can transform to pyrite through the reduction reaction of (5), in which Fe$^{3+}$ is reduced to Fe$^{2+}$ by sulfur in mackinawite acting as the reductant.

Greigite is also one of the abundant iron sulfide mineral in the anaerobic sediments. It has been known that greigite is formed from the nanocrystalline mackinawite by the oxidation from Fe$^{3+}$ to Fe$^{4+}$. In the oxidation process, the following four oxidants have been assumed; anaerobic water, slight oxygen, hydrogen sulfide ion (H$_2$S$_{aq}$ and HS$^-$), and elemental sulfur. This study suggested that the Fe$^{3+}$ in the nanocrystalline mackinawite was partially oxidized to Fe$^{3+}$ by elemental sulfur, resulting that a small amount of greigite was formed by the oxidation reaction of (4). Thereafter, the Fe$^{3+}$ was re-reduced to Fe$^{2+}$ by sulfur in greigite acting as the reductant through the reduction reaction of (6). So, in the anaerobic sediments, the sulfur behaves as both oxidant and reductant during the pyrite formation by controlling the valence state of Fe.

CONCLUSIONS

In the nanocrystalline mackinawite prepared in the present study, the $d_{001}$ was 5.50 Å. The $a$ and $c$ lattice parameters were 3.671(16) and 5.26(5) Å, respectively. The first hydrothermal ageing experiment was performed by heating the nanocrystalline mackinawite at 120 °C in the absence of sulfur source for 12 h. The nanocrystalline mackinawite remained essentially unchanged up to the end of the hydrothermal experiment for 12 h. The $d_{001}$ and FWHM values of XRD peaks decreased for the first 2 h and subsequently maintained almost constant until the end of the hydrothermal experiment. There was no linear relationship between lattice parameters and hydrothermal heating time. The PDF analysis showed that the crystallite size quickly increased by the heating time of 2 h, leading to the increase of crystallinity and appearance of the medium-range order in the nanocrystalline mackinawite. In the nanocrystalline mackinawite, the Fe atoms were distributed in the tetrahedral sites with a site occupancy of approximately 80%. The Fe K-edge XANES analysis suggested that Fe$^{3+}$ was included in the nanocrystalline mackinawite. The Fe$^{3+}$-bearing mackinawite transformed to greigite without the oxidation of Fe$^{2+}$. The TEM observation revealed the nanocrystalline mackinawite preferentially grew in the length (horizontal) direction along the sheet structure rather than in the thickness (vertical) direction.

The second hydrothermal ageing experiment was performed by heating the nanocrystalline mackinawite at 120 °C in the presence of elemental sulfur for 24 h. The nanocrystalline mackinawite persisted up to 8 h of heating time. Instead of the nanocrystalline mackinawite, pyrite and greigite appeared. Finally pyrite became dominant. Compared with first ageing experiment, the $d_{001}$ value and the lattice parameters of nanocrystalline mackinawite were significantly varied with the heating time. In the phase transformation to greigite, the Fe$^{2+}$ was oxidized to Fe$^{3+}$ by elemental sulfur in mackinawite acting as the oxidant. 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. These oxidation and reduction were reflected to the pre-edge peak energy of Fe K-edge XANES. The results of EXAFS analysis indicated that S–S bonds formation and coordination change from FeS$_4$ tetrahedra to FeS$_6$ octahedra occurred, resulting in the formation of long-range atomic order of pyrite.

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