

## Transformation of mackinawite to greigite: An in situ X-ray powder diffraction and transmission electron microscope study

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### ABSTRACT

Synthetic mackinawite (tetragonal FeS) has been found to transform rapidly to greigite (Fe<sub>3</sub>S<sub>4</sub>) above ~373 K during heating experiments, as observed by in situ X-ray diffraction. Using monochromatic synchrotron radiation ( $\lambda = 0.60233 \text{ \AA}$ ), we measured the unit-cell parameters of both synthetic mackinawite between 293 and 453 K and of greigite formed from this mackinawite between 293 and 593 K.

The coefficients of thermal expansion for mackinawite are  $\alpha_1 = \alpha_2 = (1.36 \pm 0.11) \times 10^{-5}$ ,  $\alpha_3 = (2.98 \pm 0.12) \times 10^{-5}$ , and  $\alpha_{\text{vol}} = (5.67 \pm 0.19) \times 10^{-5}$  between 293 and 453 K. The coefficients of thermal expansion for greigite are  $\alpha_1 = \alpha_2 = \alpha_3 = (1.63 \pm 0.15) \times 10^{-5}$ , and  $\alpha_{\text{vol}} = (4.86 \pm 0.25) \times 10^{-5}$  between 293 and 593 K. On further heating in situ, we observed the reaction greigite  $\rightarrow$  pyrrhotite + magnetite.

Partial transformation of mackinawite to greigite was also observed using transmission electron microscopy (TEM) following in situ heating. Electron diffraction patterns show that (001) of mackinawite is parallel to (001) of greigite, and [110] of mackinawite is parallel to [100] of greigite. This orientation relationship confirms that the cubic close-packed S array in mackinawite is retained in greigite and implies that oxidation of some Fe<sup>2+</sup> in mackinawite drives rearrangement of Fe to form the new phase. Small regions of the crystallites show Moiré fringes resulting from the lattice mismatch between mackinawite and greigite. Electron diffraction patterns of mackinawite subjected to prolonged exposure to the atmosphere also show faint spots corresponding to greigite.

We propose that in these experiments surplus Fe is accommodated by reaction with either adsorbed O<sub>2</sub> or H<sub>2</sub>O to form amorphous nanophase Fe-O(H). Because greigite is so easily formed by oxidation from mackinawite, greigite should be an important precursor for pyrite nucleation, although any orientation relationship between greigite and pyrite remains to be determined.

### INTRODUCTION

The processes by which pyrite and marcasite are formed in sedimentary and hydrothermal systems are still only partially understood, despite considerable research. It is generally considered that the reaction sequence mackinawite  $\rightarrow$  greigite  $\rightarrow$  pyrite or marcasite is involved in sedimentary pyrite formation (Berner 1964; Bonev et al. 1989) and that this allows the relatively complex crystal structures of pyrite and marcasite to nucleate readily at low temperatures from the simpler crystal structures of mackinawite or amorphous FeS (Schoonen and Barnes 1991a, 1991b). The detailed sequence of crystallographic transformations, and chemical reactions of Fe and S, which allow formation of FeS<sub>2</sub> from mackinawite, are, however, still not resolved. In this paper, we examine in further detail the first part of this sequence, the transformation of mackinawite to greigite.

Mackinawite is a metastable mineral of composition Fe<sub>1+x</sub>S, where  $0.0 < x < 0.07$  (Vaughan and Craig 1978). Mackinawite possesses a layered structure similar to that found in litharge (tetragonal PbO), with Fe and S occupying the sites of O and Pb, respectively, in litharge (Lennie et al. 1995b). In nature, mackinawite occurs predominantly as a poorly crystalline precipitate formed by reaction of HS<sup>-</sup> ions with either Fe metal or Fe<sup>2+</sup> ions.

Greigite (Fe<sub>3</sub>S<sub>4</sub>), the thiospinel of Fe, was first reported as a mineral by Skinner et al. (1964), occurring as tiny grains and crystals in lacustrine sediments. Greigite has subsequently been found as inclusions within magnetotactic bacteria (Farina et al. 1990; Mann et al. 1990), which may, in part, account for its occurrence in sediments. In a study of the Fe-S system (Kissin and Scott 1982), greigite was not observed in hydrothermal synthesis experiments performed between 388 and 623 K, sug-

gesting metastability for this phase. Under vacuum, breakdown of greigite to pyrrhotite occurs at 555 K (Skinner et al. 1964).

There are no reports in the literature of either greigite or mackinawite synthesis from elemental Fe and S alone, and all reported greigite syntheses involve reactions of "FeS" precursors. Taylor et al. (1979b), in their review and further exploration of greigite synthesis, found that oxidants play an essential role in promoting the transformation of mackinawite to greigite. They proposed that this conversion proceeds by incorporation of S from the surface into the mackinawite S array, accompanied by outward diffusion and redistribution of Fe atoms. An intriguing transformation from mackinawite to greigite, induced by electron-beam heating of an FeS precipitate, has been proposed to occur by bulk diffusion of (amorphous) S into mackinawite (Horiuchi et al. 1970; Horiuchi 1971).

Mackinawite synthesized for our experiments transforms to hexagonal pyrrhotite when heated under vacuum in the temperature range 530–545 K (Lennie et al. 1995a). We use here the general term hexagonal pyrrhotite rather than troilite, as the troilite superstructure based on the NiAs unit cell breaks down above 413 K. Attempts to measure directly the kinetics of pyrrhotite formation by heating X-ray diffraction proved unsuccessful. Instead, transformation to greigite above 373 K was observed in this experiment. In the present study, we examine this transformation in more detail, using in situ high-temperature X-ray powder diffractometry (XRD) and transmission electron microscopy (TEM).

#### EXPERIMENTAL PROCEDURE

The procedure for synthesizing mackinawite is described elsewhere (Lennie et al. 1995b) and involves reaction of Fe wire with HS<sup>-</sup> ions in an acetate-buffered sodium sulfide solution. The mackinawite formed was rinsed, vacuum dried, and sealed under vacuum in borosilicate glass tubes to prevent oxidation before experimentation. Chemical analysis of this synthetic mackinawite gave the following composition: Fe, 49.67 at%; Ti, 0.09 at%; Mn, 0.14 at%; S, 50.10 at% (Lennie et al. 1995a).

#### CuK $\alpha$ powder diffraction

Initial high-temperature X-ray powder diffraction studies were made using a conventional laboratory CuK $\alpha$  X-ray source ( $\lambda = 1.54018 \text{ \AA}$ ) in a Siemens D5000 X-ray powder diffractometer. The diffractometer was fitted with an Anton-Parr TTK50 camera, which comprises a computer-controlled heated sample holder enclosed in a pressure cell with mylar windows; the pressure cell can be evacuated. The sample stage is kept stationary and both X-ray and detector arms move in a  $\theta$ - $\theta$  configuration.

Samples were prepared for XRD by quickly loading in air the mackinawite powder from the sealed borosilicate tubes used for synthesis directly into the well of the sample holder and then carefully levelling the surface of the sample flush with the top of the sample holder using light

pressure from a glass slide. The sample and holder were placed in the pressure cell, which was sealed and evacuated to  $\sim 5 \times 10^{-3}$  mbar. A series of XRD patterns, in the range  $10$ – $70^\circ 2\theta$ , were collected from the sample under vacuum as the sample was heated in increments of 50 K between room temperature and 473 K. Because of the relatively poorly crystalline nature of the powder, a count time of 25 s per  $0.05^\circ 2\theta$  step was used, giving a total time of 8.3 h to collect each diffraction pattern. The sample was maintained under vacuum for the full series of patterns.

#### High-resolution synchrotron powder diffraction

High-resolution powder diffraction data were recorded at Station 9.1 on the 5.0 Tesla wiggler beam line of the Daresbury Laboratory Synchrotron Radiation Source. Monochromatic radiation of wavelength  $0.60233 \text{ \AA}$  was selected from a channel-cut Si(111) monochromator, the wavelength being calibrated from the positions of seven reflections from an Si NBS 640b sample. The synchrotron wavelength was selected to be well above the Fe K absorption edge to reduce possible photo-oxidation of Fe. A description of the high-resolution powder diffractometer is given in Bushnell-Wye and Cernik (1992).

Samples of mackinawite from sealed borosilicate tubes were opened within an He-filled polyethylene glove bag sealed around the diffractometer sample chamber and were loaded onto a flat plate aluminum sample holder (15 mm diameter, 1 mm deep) of the instrument. The sample chamber was continually purged with He during data collection. Because of experimental difficulties in loading, the sample was not perfectly flat within the sample holder, and electrostatic effects associated with the glove bag meant that the sample could not be ground to as fine a powder as would normally be preferred. Nonetheless, data of sufficient quality for unit-cell-parameter determinations were obtained.

Diffraction data were first collected at room temperature between  $5$  and  $25^\circ 2\theta$  ( $d = 6.91$ – $1.39 \text{ \AA}$ ) at steps of  $0.01^\circ 2\theta$ ; no sample degradation with exposure to synchrotron radiation was observed at room temperature. While maintaining the He atmosphere by a continuous purge, the sample was heated in a series of temperature steps using a controlled-heating chamber surrounding the sample stage. Scans were again recorded from  $5$  to  $25^\circ 2\theta$ ; the scan time was 30 min. Two separate samples of synthetic mackinawite were studied. Successive scans of the first sample were taken as it was heated stepwise up to 698 K. The second mackinawite sample was heated stepwise to 473 K, then cooled in steps back to room temperature, with scans acquired during both heating and cooling.

#### Transmission electron microscopy

Approximately 0.1 mg of mackinawite from a sealed tube opened in air was dispersed in acetone onto a carbon-coated copper grid and loaded into a low-background analysis holder of a Philips CM200 transmission electron

microscope operating at 200 kV. The microscope was fitted with a Tracor Northern energy-dispersive detector with an ultrathin window. Identification of mackinawite grains was made both from selected-area diffraction (SAD) patterns and by energy-dispersive analysis, for which pyrite ( $\text{FeS}_2$ ) was used as a standard. The sensitivity factor  $k_{\text{FeS}}$  derived from the pyrite was found to be  $1.37 \pm 0.10$  for analyses in weight percent.

Following transfer of the grid to a heating, double-tilt holder, the sample was heated to  $\sim 473$  K, as recorded by a thermocouple adjacent to the sample, for 4 h. SAD patterns were obtained from the same grains as previously studied, relocation being facilitated by the use of a numbered copper grid. Following heating, the sample was cooled, transferred again to the analysis holder, and individual grains reanalyzed (the construction of the heating holder prevented reliable in situ analysis). Diffraction patterns and images were recorded photographically at both ambient and elevated temperatures.

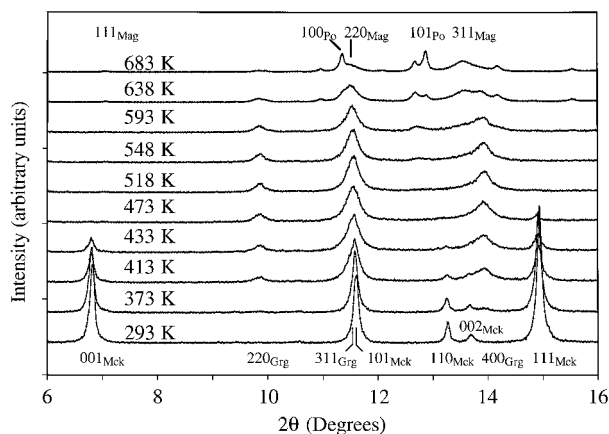
## RESULTS

### $\text{CuK}\alpha$ powder diffraction

The diffraction patterns obtained from this experiment showed reflections from mackinawite, and a small amount of  $\alpha$ -Fe at low temperatures (296 and 323 K), but reflections corresponding to those reported for greigite began to emerge when the sample temperature reached 373 K. As these new reflections increased in intensity, the mackinawite reflection intensities decreased. The intensity of the new reflections increased with increasing temperature until, at 473 K, mackinawite reflections were absent except for a very small signal at the position of the 001 mackinawite reflection. There was no change in the intensity of the Fe reflections during the experiment. At this stage, the sample had been exposed to  $\text{CuK}\alpha$  X-rays for  $\sim 42$  h. No reflections corresponding to hexagonal pyrrhotite or to Fe-O(H) phases were observed during this experiment. This transformation was of sufficient interest to warrant repeating the experiment with the high-resolution heating powder diffractometer at the Daresbury Laboratory using synchrotron radiation.

### High-resolution synchrotron powder diffraction

Both samples in this experiment showed transformation to greigite on heating while bathed in the synchrotron X-ray beam. The temperature evolution of the diffraction patterns is shown in Figure 1. Greigite reflections emerged at 373 and 343 K in the first and second experiments, respectively, and the mackinawite was completely transformed at 473 K, after  $\sim 5$  h exposure to the X-ray beam. At this temperature, no additional reflections were observed, except for  $\alpha$ -Fe remaining from the mackinawite synthesis. On heating beyond 533 K, the greigite began to decompose, as revealed by the emergence of reflections corresponding to poorly crystalline hexagonal pyrrhotite. The transformation to pyrrhotite was still not complete at 683 K, at which temperature some additional



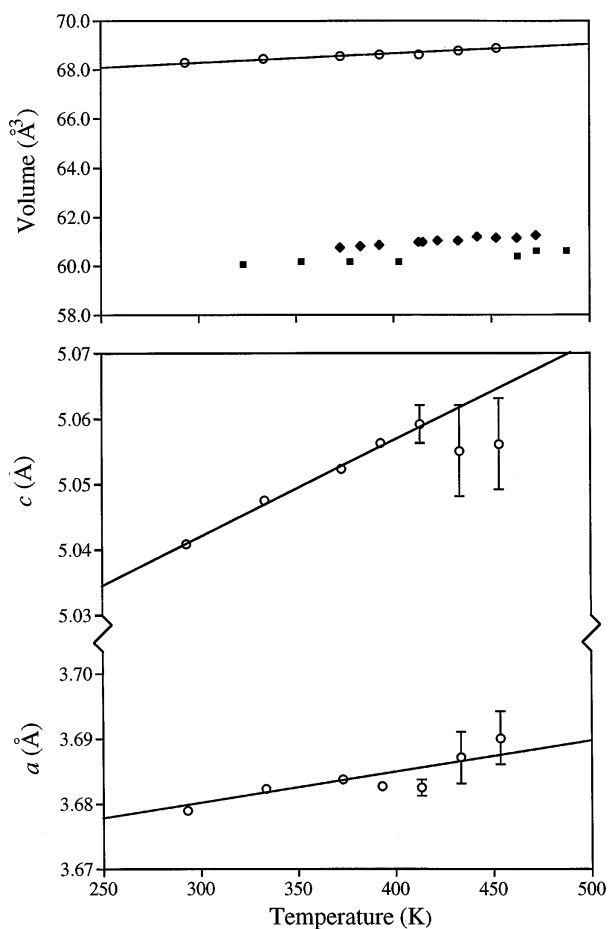
**FIGURE 1.** Powder diffraction patterns obtained with increasing temperature from synthetic mackinawite using synchrotron radiation ( $\lambda = 0.60233$  Å). An He atmosphere was maintained to prevent oxidation of the mackinawite. Greigite reflections emerge at 373 K and increase in intensity as mackinawite reflections decrease in intensity. Breakdown of greigite to a mixture of pyrrhotite and magnetite can be observed in the diffraction patterns above 518 K. Successive diffraction patterns are shifted up the intensity axis to facilitate comparison. Mackinawite (Mck), greigite (Gr), pyrrhotite (Po), and magnetite (Mag) reflections are indicated.

small and very broad reflections corresponding to microcrystalline magnetite were observed.

The second mackinawite sample examined by synchrotron radiation was heated stepwise to 463 K to achieve transformation to greigite, then cooled stepwise from 403 K to room temperature to allow measurement of greigite unit-cell parameters; the greigite structure was retained on cooling.

Unit-cell parameters were refined from these synchrotron diffraction data for mackinawite and for the emergent greigite using the programs PKFIT and REFCEL (Murray et al. 1990). Angles of reflection were identified by PKFIT, and unit-cell parameters were refined from measured  $2\theta$  positions of Bragg reflections using the REFCEL least-squares program. A table of original measured and indexed reflection positions is available from the first author. Refined unit-cell parameters of mackinawite and greigite were fitted to a straight line using a Marquardt weighted least-squares minimization routine following the method of Holland and Redfern (1997). This gave unit-cell parameters in the temperature range 293–453 K for mackinawite:  $a = (3.6647 \pm 0.0013) + [(5.01 \pm 0.39) \times 10^{-5}] T$  Å;  $c = (4.9971 \pm 0.0019) + [(1.50 \pm 0.06) \times 10^{-4}] T$  Å;  $V = (67.11 \pm 0.04) + [(3.87 \pm 0.13) \times 10^{-3}] T$  Å<sup>3</sup>, where  $T$  is the temperature in Kelvins. The unit-cell parameters for greigite are  $a = (9.811 \pm 0.007) + [(1.61 \pm 0.15) \times 10^{-4}] T$  Å;  $V = (944.4 \pm 1.1) + [(4.66 \pm 0.24) \times 10^{-2}] T$  Å<sup>3</sup> in the temperature range 293–593 K. Plots of these data are shown in Figures 2 and 3.

The (instantaneous isobaric) thermal expansion is re-

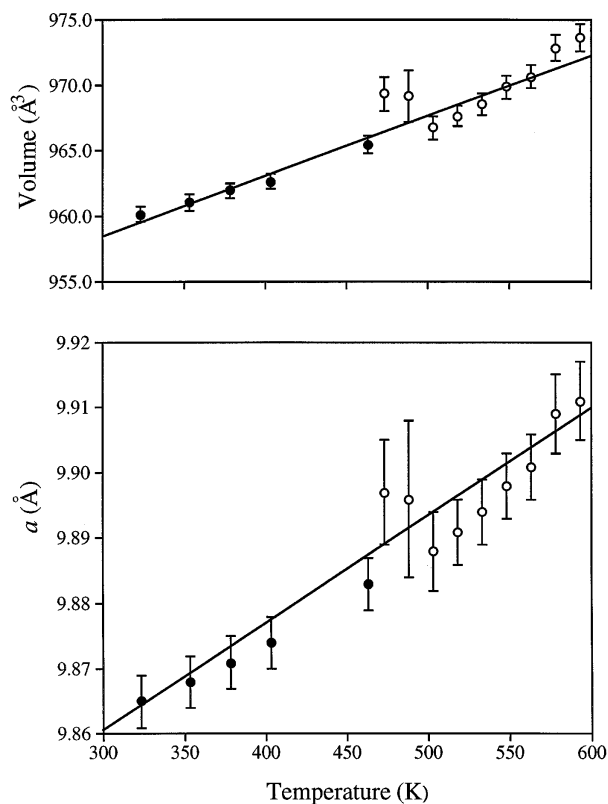


**FIGURE 2.** Unit-cell parameters of synthetic mackinawite ( $\text{Fe}_{1+x}\text{S}$ ) derived from synchrotron X-ray diffraction patterns, showing the increase of the parameters with temperature between 273 and 473 K. Error bars are  $\pm 1$  standard deviation and for some data points are smaller than the symbol. For comparison, unit-cell volumes of stoichiometric hexagonal pyrrhotite (based on the NiAs-type subcell) are shown as diamonds between 373 and 473 K (Kruse 1992). Unit-cell volumes of greigite between 273 and 473 K (per two  $\text{Fe}_{0.75}\text{S}$  formula units for comparison with the mackinawite unit cell) are shown as squares. The lines are least-squares fits to the experimental data, weighted as described in the text.

lated to the unit-cell parameter  $x$  and may be approximated as  $\alpha_x = (1/x_0)(dx/dT)_p$ , where  $x_0$  is a reference unit-cell constant at 298 K. We have taken  $x_0$  to be the value of the relevant unit-cell parameter at 298 K as derived from the weighted least-squares analysis given above.

Thus, for mackinawite, the coefficients of thermal expansion are  $\alpha_1 = \alpha_2 = (1.36 \pm 0.11) \times 10^{-5}$ ,  $\alpha_3 = (2.98 \pm 0.12) \times 10^{-5}$ , and  $\alpha_{\text{vol}} = (5.67 \pm 0.19) \times 10^{-5}$  in the temperature range 293–453 K. For greigite, the coefficients of thermal expansion are  $\alpha_1 = \alpha_2 = \alpha_3 = (1.63 \pm 0.15) \times 10^{-5}$  and  $\alpha_{\text{vol}} = (4.86 \pm 0.25) \times 10^{-5}$  in the temperature range 293–593 K.

With the use of data obtained at 683 K, an NiAs-type



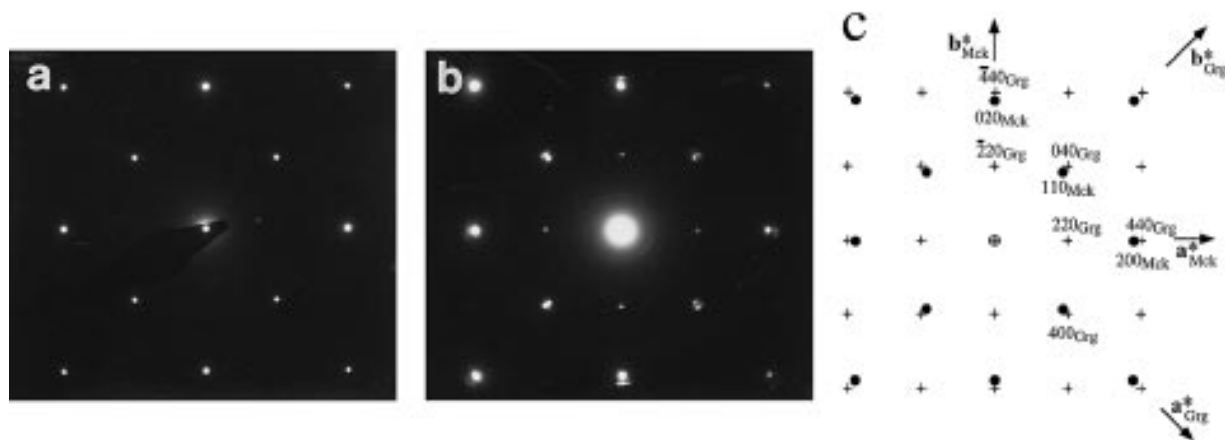
**FIGURE 3.** Unit-cell parameters of (cubic) greigite ( $\text{Fe}_3\text{S}_4$ ) obtained from synthetic mackinawite, showing the expansion of the unit cell with temperature. Error bars are  $\pm 1$  standard deviation. Open circles represent data obtained on heating, solid circles represent data obtained on cooling of the second sample. The lines are least-squares fits to the experimental data, weighted as described in the text.

unit cell of dimensions  $a = 3.510(1)$ ,  $c = 5.708(5)$  Å, and  $V = 60.91(6)$  Å<sup>3</sup> was refined from reflections corresponding to hexagonal pyrrhotite. Unfortunately, it was not possible to determine the chemical composition of this pyrrhotite.

### Transmission electron microscopy

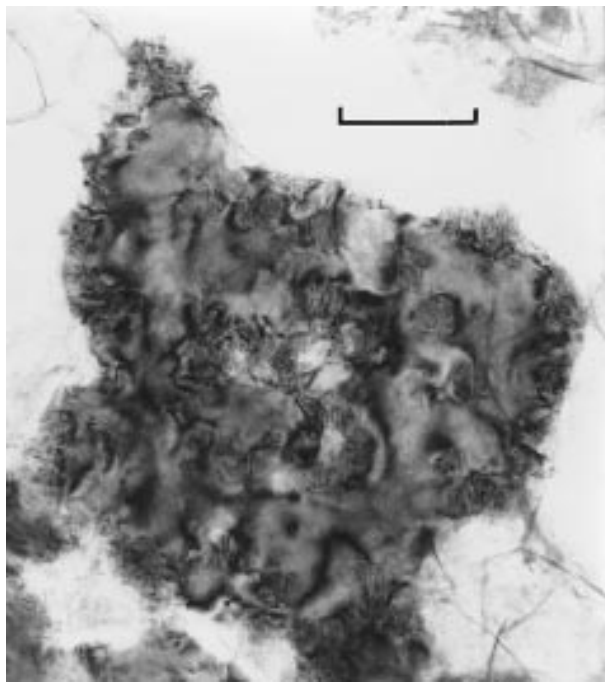
Examination of synthetic mackinawite using TEM showed irregularly shaped single crystals with dimensions of approximately 0.8  $\mu\text{m}$  that often occurred in aggregates on the carbon-coated copper grid. Some regions of the grid contained fibrous particles that contained Fe only, these being particles remaining from synthesis. They resulted in weak powder diffraction rings, confirming their identification. Quantitative energy-dispersive measurements were made on three individual mackinawite particles, care being taken to avoid areas containing fibrous Fe. The analyses gave an average Fe:S atomic ratio of 0.99, with an estimated standard deviation of 0.02.

At room temperature, single crystals of approximately stoichiometric FeS showed selected-area electron diffrac-



**FIGURE 4.** (a) Electron diffraction pattern obtained from mackinawite parallel to (001) before heating. The space group of mackinawite is  $P4/nmm$ . The  $n$ -glide plane parallel to (001) results in the systematic absence of  $hk0$  reflections for which  $h + k \neq 2n$  (where  $n$  is an integer). (b) Electron diffraction pattern from mackinawite parallel to (001) after heating to 473 K, showing extra

spots because of the partial transformation. (c) Schematic diagram of the pattern in **b**; mackinawite spots are shown as solid circles, and greigite spots are shown as plus signs. The orientation relationship is  $(001)_{\text{Mck}} \parallel (001)_{\text{Grg}}$ ,  $[110]_{\text{Mck}} \parallel [100]_{\text{Grg}}$ . Note that because greigite has the spinel structure,  $hk0$  reflections are present only if  $h + k = 4n$ .



**FIGURE 5.** TEM image of a mackinawite grain after heating to 473 K in the TEM. The scale bar is 0.2  $\mu\text{m}$ . The fibrous material near the grain is  $\alpha$ -Fe from the starting material. Moiré fringes result from the lattice mismatch between mackinawite and greigite parallel to (001). The fringe spacing is  $\sim 37$  Å, similar to the fringe spacing of 35 Å calculated from the lattice mismatch between the  $d$  values for greigite (440) and mackinawite (200) planes. The fringes are perpendicular to the  $g$  vectors for these two planes.

tion patterns consistent with mackinawite lying with (001) parallel to the carbon film. An example of this pattern is shown in Figure 4a. Occasionally, a square pattern of faint, diffuse spots was also present in the pattern. The  $d$  value of these diffuse reflections corresponded to about 3 Å.

After heating to 473 K, a grain that had been previously analyzed was reexamined. Partial transformation was indicated by the appearance of additional diffraction spots, consistent with greigite. The new pattern is shown in Figure 4b. The new reflections are consistent with an orientation relationship between the two phases such that  $(001)_{\text{Mck}}$  is parallel to  $(001)_{\text{Grg}}$  and  $[110]_{\text{Mck}}$  is parallel to  $[100]_{\text{Grg}}$  (see Fig. 4c). Thus, the cubic close-packed S arrangement of mackinawite is retained in greigite. There is no diffraction evidence for the formation of  $\alpha$ -Fe, nor for known Fe-O(H) phases upon transformation. Quantitative energy-dispersive analysis of this and six other grains that had been heated in the electron microscope gave an average Fe:S atomic ratio of  $1.00 \pm 0.07$ . Thus, there was no detectable change in the Fe:S ratio of the mackinawite after heating. Residual mackinawite was present after all heating experiments at 473 K in the TEM, even after heating for 4 h.

In TEM images of heated samples, greigite manifests itself as small regions of Moiré fringes, approximately  $50 \times 50$  Å, nucleating within the mackinawite crystal and around the edges of grains. An example of an image of this type is shown in Figure 5. Some mackinawite grains with longer exposure to the atmosphere at room temperature also showed additional electron diffraction spots resulting from greigite.

## DISCUSSION

Unit-cell-expansion data for mackinawite derived from the XRD experiments show that both  $a$  and  $c$  unit-cell

parameters increase with temperature up to 453 K. This is consistent with the behavior on heating of both  $t\text{-Fe}_{1+x}\text{Se}$  and  $t\text{-Fe}_{1+x}\text{Te}$ , the isostructural iron chalcogenide compounds (Grønvold 1968; Grønvold et al. 1954). We would expect that, on further heating above 453 K under vacuum, the mackinawite unit cell continues to expand until transforming, by a diffusion mechanism (Lennie et al. 1995a), to hexagonal pyrrhotite between 530 and 545 K.

The unit-cell volume of mackinawite at 530 K, calculated from our measurements, would be approximately  $69 \text{ \AA}^3$ . Stoichiometric hexagonal pyrrhotite has a volume of  $61.814 \text{ \AA}^3$  (with two formula units per NiAs-type unit cell) at 533 K (Kruse 1992), giving a reduction in molar volume of about 10% for the mackinawite-to-hexagonal pyrrhotite transformation.

In the experiments described above, we observed either partial or complete transformation of mackinawite to greigite at temperatures well below that of the mackinawite-to-hexagonal pyrrhotite transformation. The heating X-ray diffraction experiments show increasing greigite reflection intensities accompanied by decreasing mackinawite reflection intensities, indicative of a kinetically controlled solid-state transformation. Greigite does not revert to mackinawite on cooling.

In addition, the electron diffraction patterns clearly show an orientation relationship between mackinawite and greigite. From the relative orientations of these two phases derived from the electron diffraction patterns, it can be seen that a cubic close-packed S array is common to these two phases. The greigite S array shows a contraction relative to that of mackinawite. The relationship between the two crystal structures, derived from the electron diffraction evidence, is illustrated in Figure 6. From our measured unit-cell parameters, we calculate that the volume occupied by the cubic close-packed S array in greigite at 373 K is about 12% smaller than that in mackinawite, representing a substantial enthalpic stabilization of greigite relative to mackinawite because of the overall density increase. This is similar to the volume reduction of the mackinawite-to-hexagonal pyrrhotite transformation. The greigite unit cell shows isotropic expansion until the breakdown of hexagonal pyrrhotite begins at about 533 K; we observed also the emergence of very broad reflections that can be indexed to a magnetite unit cell.

On the basis of the evidence described above, we propose that in our experiments greigite forms by rearrangement of Fe cations within the cubic close-packed S array of mackinawite. Greigite crystallites so formed are smaller than those of mackinawite, as shown by the broader X-ray reflections of greigite. To achieve the transformation by rearrangement of Fe requires oxidation of some  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  and removal of excess Fe formed in the following reaction:  $4\text{FeS} \rightarrow \text{Fe}_3\text{S}_4 + \text{Fe}$ . Surplus Fe must be removed either as  $\text{Fe}^0$  or as ions:  $\text{Fe}^{2+} + 2e^-$  or  $\text{Fe}^{3+} + 3e^-$ .

We note here the similarity between our proposed mechanism and that used to account for the oxidation of magnetite ( $\text{Fe}_3\text{O}_4$ ) to maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ). This is a one-

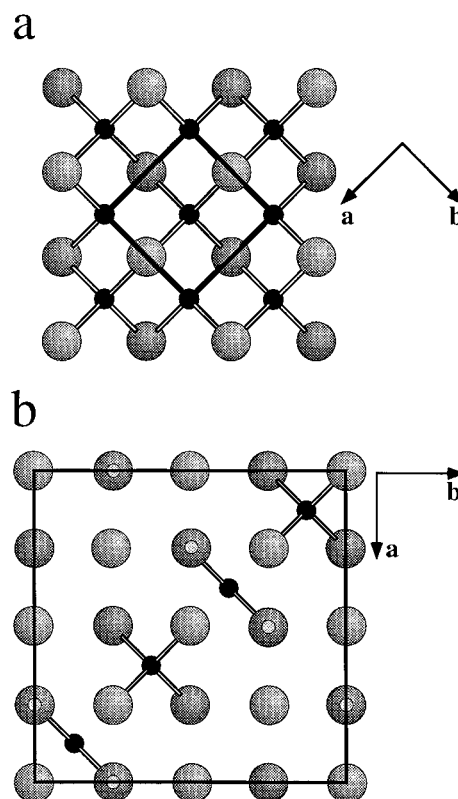


FIGURE 6. Mackinawite (a) and greigite (b) crystal structures projected onto (001), illustrating the orientation relationship observed in the electron diffraction pattern. S atoms are shown by large circles,  $^{54}\text{Fe}$  by small dark circles, and  $^{56}\text{Fe}$  by small light circles. The mackinawite  $a$  axis is at a  $45^\circ$  angle to that of greigite, and  $a_{\text{Mck}} \approx \sqrt{2/4}a_{\text{Gr}}$ . The unit cells are shown by heavy black lines.

phase topotactic reaction in which the oxide-ion array remains cubic close packed and O layers are added as Fe cations migrate to the surface (Feitknecht and Lehmann 1959). Here, free  $\text{O}_2$  at the magnetite crystal surface is reduced by electrons from  $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^-$ . The rate of oxidation is controlled by diffusion of Fe cations through the O array to the crystal surface (Gallagher et al. 1968). The magnetite particle size is important for this reaction; the oxidation temperature increases with particle size from 393 to 483 K.

Transformation to greigite in our XRD experiments occurs above  $\sim 373 \text{ K}$ , similar to the temperature range of the magnetite-to-maghemite oxidation. In our experiments, a reactant is required to satisfy the redox requirements of surplus electrons and ions. The probable reactants to act as electron acceptors are O from surface-adsorbed  $\text{O}_2$  or  $\text{H}^+$  from adsorbed  $\text{H}_2\text{O}$ . Some electron diffraction patterns showed that mackinawite had partially transformed to greigite in air, which suggests that  $\text{O}_2$  is the agent for the transformation. The presence of diffuse reflections with  $d \approx 3 \text{ \AA}$  in some samples exposed to the atmosphere also suggests the presence of

epitaxial iron (hydr)oxide on the surface of these grains; 3 Å is the approximate distance between Fe atoms in edge-sharing FeO<sub>6</sub> octahedra found in many iron (hydr)oxides (Murray 1979).

Despite prolonged heating at 473 K in the TEM vacuum, we did not observe complete transformation of mackinawite to greigite. This suggests a limited supply of oxidant and tends to rule out photoreduction to Fe<sup>0</sup> as a mechanism for accommodating excess Fe. The high vacuum (~10<sup>-7</sup> mbars) in the TEM and the large surface area exposed to it would rapidly remove O<sub>2</sub> or H<sub>2</sub>O desorbed from the specimen surfaces during heating.

The behavior in the TEM contrasts with the XRD experiments, which all showed complete transformation to greigite with no residual mackinawite remaining at the highest temperatures. This lack of scattered X-ray intensity from mackinawite could disguise the persistence of a small proportion (<2 wt%) of, possibly nanophase, mackinawite, although this would still not reconcile the microstructural observations from the TEM and XRD experiments. We do not believe, therefore, that differences in spatial selectivity (and hence detection limits of minor phases) can explain the contrast between TEM and XRD experiments. Instead, we suspect that the persistence of mackinawite in the TEM experiments, and the lack of it in the XRD experiments, reflects differences in high-temperature environments, in particular the O<sub>2</sub> fugacity.

In the CuKα powder diffraction experiment, transformation of mackinawite to greigite may have resulted from the limited exposure of mackinawite to O<sub>2</sub> during sample preparation or from O<sub>2</sub> or H<sub>2</sub>O contamination during the experiment (5 × 10<sup>-3</sup> mbar vacuum). In the synchrotron experiment, in which sample transfers were designed to minimize oxidation, He was used to limit oxidation, although no drying of He was performed prior to use. Despite these measures, the transformation from mackinawite to greigite still proceeded rapidly above about 373 K.

Two reactions for the transformation of mackinawite to greigite can thus be presented: 12FeS + 2O<sub>2</sub> → 3Fe<sub>3</sub>S<sub>4</sub> + Fe<sub>3</sub>O<sub>4</sub> and 12FeS + 4H<sub>2</sub>O → 3Fe<sub>3</sub>S<sub>4</sub> + Fe<sub>3</sub>O<sub>4</sub> + 4H<sub>2</sub>. Similar reactions could be described using other Fe-O(H) phases.

We did observe the appearance of very broad reflections corresponding to magnetite on further heating in the synchrotron experiment. This suggests that excess Fe generated during the transformation to greigite is accommodated as nanophase amorphous Fe-O(H); we did not observe powder diffraction evidence corresponding to Fe-O(H) phases following transformation of mackinawite to greigite below 473 K in either X-ray or TEM experiments. The energy-dispersive analysis of mackinawite crystals in the TEM showed no obvious excess S, either before or after transformation, indicating that S-induced transformation was not the mechanism operating in these experiments.

The ready transformation of mackinawite to greigite in the X-ray experiments may explain the "breakdown" temperatures for mackinawite observed near 413 K (Tak-

eno and Clark 1967; Takeno 1965a, 1965b; Clark 1966; Zôka et al. 1972) and attributed to the formation of hexagonal pyrrhotite. The breakdown may instead have been due to greigite formation by oxidation of mackinawite.

Although the transformation of mackinawite to greigite appears to be kinetically controlled, accurate kinetic measurements of this reaction remain to be established. Such kinetics would be a complex function of Fe oxidation state, the type and availability of oxidant, the temperature, and the cation-diffusion process. These factors would make reliable establishment of kinetic parameters, such as by time-temperature-transformation measurements, difficult.

### GEOCHEMICAL IMPLICATIONS

Although mackinawite is metastable with respect to troilite-hexagonal pyrrhotite, kinetic factors prevent rapid transformation of mackinawite to hexagonal pyrrhotite and thus allow mackinawite to persist in nature for enough time to be an important phase in the low-temperature Fe-S system. Because mackinawite is so easily transformed to greigite, it seems reasonable, as other researchers have proposed (Berner 1967; Sweeney and Kaplan 1973; Rickard 1975; Krupp 1994), to assume that greigite is an intermediate phase in the formation of pyrite, marcasite, or both from mackinawite in low-temperature sedimentary and hydrothermal systems.

Schoonen and Barnes (1991a, 1991b, 1991c) proposed that, at temperatures below ~523 K, direct nucleation of FeS<sub>2</sub> from solution is extremely slow in comparison with formation by sulfidation of monosulfide precursors. Sulfidation proceeds rapidly in the presence of S as the polysulfide or zerovalent S form (Rickard 1975; Luther 1991), in contrast to sulfidation of amorphous FeS by H<sub>2</sub>S or HS<sup>-</sup>, which proceeds at an insignificantly slow rate at 338 K (Schoonen and Barnes 1991b). However, at or above 373 K, sulfidation with H<sub>2</sub>S as the S source proceeds at a faster rate (Drobner et al. 1990; Schoonen and Barnes 1991c; Taylor et al. 1979a, 1979b), with reduction of H<sup>+</sup> to H<sub>2</sub> balancing the redox requirements of the reaction.

We suggest that greigite forms a suitable precursor for the formation of FeS<sub>2</sub>, with little rearrangement of Fe. Thus, at least two reaction steps in the formation of FeS<sub>2</sub> from the monosulfide are clearly required: oxidation of Fe<sup>2+</sup> in mackinawite with subsequent migration of Fe<sup>3+</sup> to nucleate greigite, followed by addition of S to greigite, accompanied by reduction of Fe<sup>3+</sup> to Fe<sup>2+</sup>, to form pyrite or marcasite. It may be that, in the first step, S instead of O catalyzes the formation of greigite.

Because pH influences low-temperature formation of pyrite and marcasite (Murowchick and Barnes 1986), suggesting surface controls on crystallization (Tossell et al. 1981), we propose that the greigite surface is important in FeS<sub>2</sub> formation. Recent studies of the surface structure of magnetite, the iron oxide spinel (Weiss et al. 1993; Barbieri et al. 1994; Condon et al. 1994), may provide new information that can be used in the development of

mechanistic models of how S is added to the greigite surface to form FeS<sub>2</sub>.

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