

The Synthesis of Greigite from a Polysulfide Solution at about 100 °C

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Favorable synthesis conditions for greigite are examined in $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4\text{--Na}_2\text{S--Na}_2\text{S}_x$ systems at about 100 °C. It has been found that greigite formation is influenced by the pH adjustment and by the addition of sulfur. When the final pH is about 6.0 and the dissolved iron concentration is in the 10^{-3} – $10^{-1.5}$ M range, greigite is synthesized as a single phase. The unit-cell dimensions of greigite range from 9.840 to 9.877 Å, corresponding to variations in compositions between 45.4 and 42.9 atomic % Fe. The formula of synthetic greigite is represented as $\text{Fe}_{3+x}\text{S}_4$ ($x=0\text{--}0.4$).

Many reports have been published on the preparation of greigite, Fe_3S_4 , in an aqueous solution.^{1–3} However, it is not easy to synthesize greigite as a single phase, because greigite formation depends upon many factors, such as the temperature, the pH, the starting source materials, and the redox conditions.^{4,5} Recently, Horiuchi *et al.* studied the reaction of tetragonal FeS (mackinawite) with colloidal sulfur and observed the formation of cubic Fe_3S_4 in the semi-dry system by means of electron diffraction.⁶ From the results of this work, it was suggested that amorphous sulfur played an important role in Fe_3S_4 formation.

In an aqueous solution, free sulfur is frequently combined with sulfide ions and so changed into the form of polysulfide ions. Paying special attention to sulfur source materials, the present author attempted to prepare greigite from a polysulfide solution.

Experimental

All the chemicals used were of a guaranteed reagent grade. A polysulfide stock solution was prepared by reacting orthorhombic sulfur with a Na_2S solution in a nitrogen gas atmosphere for 2 h at about 100 °C. After the residual solid sulfur had been taken away by filtration, the polysulfide solution was kept in polyethylene bottles in a cold and dark place. Prior to the experiments, the concentrations of sodium and sulfur were determined by the methods of flame-

photometry and conventional gravimetry respectively. 0.20 M $\text{Na}_2\text{S}_{3.89}$ solution was used in the synthesis of greigite.

$\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$ and Na_2S were dissolved in a proper volume of distilled water in every other experiment. Less than 10 ml of a $\text{Na}_2\text{S}_{3.89}$ solution was added into large amounts of the Na_2S solution as a part of the sulfur source. Two hundred ml of a 0.0834 ± 0.0006 M $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$ solution were mixed with 200 ml of a 0.1468 ± 0.0006 M Na_2S solution containing polysulfide ions, as is shown in Fig. 1. Purified nitrogen gas was flowed through the solution at the rate of about 170 ml/min in order to avoid the contamination of products by air oxidation. A colloidal suspension of iron sulfides precipitated was heated at the boiling temperature (103 °C) for 15–20 h.

At the termination of each experiment, the final pH of solution was measured by means of a pH meter (TOA Electronics Ltd., HM-7A type). The concentration of ferrous ions in the clear supernatant solution was determined by the titration method using 1.67×10^{-2} M $\text{K}_2\text{Cr}_2\text{O}_7$ or a colorimetric method using 1,10-phenanthroline. The iron sulfide product was separated from the solution by a centrifuge, washed by water, aqueous ammonia, and acetone, dried in a vacuum, and identified by means of X-ray and electron diffraction. An X-ray diffractometer (Shimadzu VDR-11) and an electron microscope (100 kV: Hitachi 11 D) were employed to identify the specimens.

The compositions of the iron sulfide products were determined by the analytical method of Kolthoff and Sandell.⁷ About 200-mg portions of the specimens were decomposed into an ionic state on the basis of oxidation in the wet way using bromine with nitric acid. The sulfur was determined gravimetrically as BaSO_4 . After the dissolved iron had been reduced to Fe^{2+} ions with $\text{NH}_2\text{OH} \cdot \text{HCl}$, the iron content was determined by the spectrophotometric method,⁸ using 1,10-phenanthroline.

Results and Discussion

Greigite was obtained under the preferred synthesis conditions, listed in Table 1. Meanwhile, phase transformations were observed in the order of mackinawite, greigite, and pyrite (cubic FeS_2) with an increase in the amounts of the $\text{Na}_2\text{S}_{3.89}$ solution added. When the $\text{Na}_2\text{S}_{3.89}$ solution was not added, only mackinawite was formed. Greigite was produced as a single phase by the addition of 3–6 ml of the $\text{Na}_2\text{S}_{3.89}$ solution. Pyrite was formed together with greigite by the addition of 7–10 ml of the $\text{Na}_2\text{S}_{3.89}$ solution.

The analytical results of the products showed that the S/Fe atomic ratio of iron sulfides increased linearly with an increase in the amount of polysulfide solution

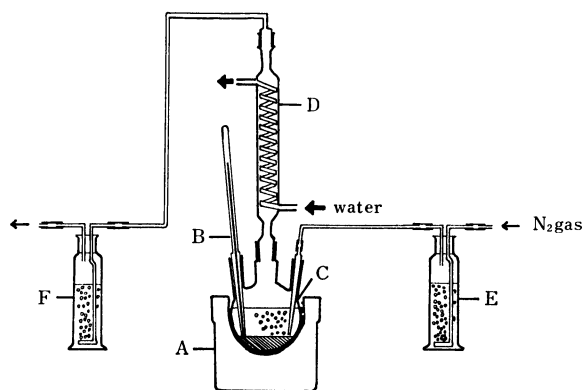


Fig. 1. Schematic diagram of the reaction vessel for synthesis of iron sulfides. A: Heating mantles. B: Mercury thermometer. C: 500 ml of round bottom flask with four necks. D: Dimroth condenser. E and F: Washing gas bottles. E is filled with 40 per cent pyrogallol–NaOH solution to remove oxygen in nitrogen gas. H_2S gas which is expelled from the vessel is absorbed in F, filled with 10 per cent NaOH solution.

TABLE 1. EFFECT OF SULFUR FROM A 0.20 M $\text{Na}_2\text{S}_{3.89}$ SOLUTION UPON PRODUCTS, ON HEATING FOR 15–20 h AT ABOUT 100 °C

Source materials			Final pH	Product
$\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ in g	$\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ in g	$\text{Na}_2\text{S}_{3.89}$ in ml		
6.5401	7.0269	—	6.38	mackinawite
6.4972	7.0227	3	6.00	greigite
6.5807	7.0733	5	6.10	greigite
6.5988	7.0158	5.5	6.01	greigite
6.6023	7.0279	6	6.03	greigite
6.5211	7.0322	10	6.00	greigite + pyrite

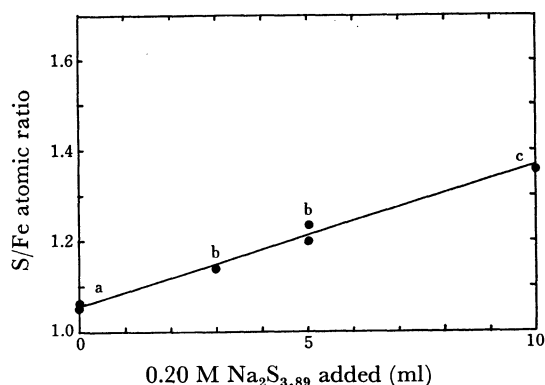


Fig. 2. Relation of S/Fe atomic ratio of products with 0.20 M $\text{Na}_2\text{S}_{3.89}$ solution added. Products: a=mackinawite, b=greigite, c=greigite + pyrite.

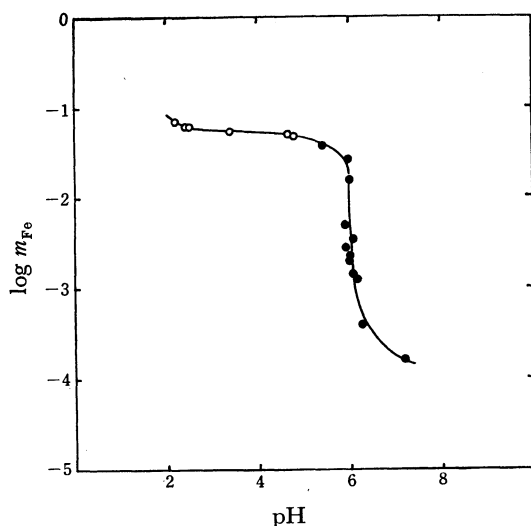


Fig. 3. Relations of the final pH with iron concentration in solutions. The pH is adjusted with variation of mixing ratio of $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$ and Na_2S (●), and addition of 1.13 M H_2SO_4 (○).

added (Fig. 2). The dissolved iron content in the clear supernatant solution increased by the order of 2.5, from 10^{-4} to $10^{-1.5}$ M/l, corresponding to the pH change from 7 to 5.8 (Fig. 3). The final pH values of the solutions associated with greigite ranged from 5.8 to 6.1.

The region of greigite formation was consistent with the conspicuous increase in the solubility of mackinawite. These results indicate that (1) forms of the resulting iron sulfide are controlled systematically by the amounts of sulfur added and by the pH of the solution and (2) the region of greigite formation as a single phase in solutions is restricted to the extremely narrow pH range between 5.8 and 6.1.

It was found that the correct pH adjustment of the solution was important in preparing greigite as a single phase. However, the rapid pH change upon the addition of mineral acids was not suitable for its synthesis. In order to acidify solutions mildly and gradually from the alkaline side in the heating process, proper mixing ratios of $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$ and Na_2S solutions, described above, were selected. Pure greigite was formed when (1) $2 m_{\text{SO}_4^{2-}} > m_{\text{Na}^+}$ and (2) $m_{\text{S}^{2-}} + m_{\text{HS}^-} > m_{\text{Fe}^{2+}}$ (all the iron was transformed initially into the form of precipitated FeS).

After the solution had been dried in a vacuum, synthetic greigite was obtained as a fine sooty black powder with strong magnetic properties. The grain size of greigite was calculated to be 200–300 Å on the basis of the measurement of the half-width of the diffraction peak. Fresh greigite synthesized in acidic solution sometimes showed a pyrophoric property. When exposed to the atmosphere, it was burned with fumes of S_2 and SO_2 , being thus completely altered to a mixture of magnetite (Fe_3O_4) and hematite (Fe_2O_3).

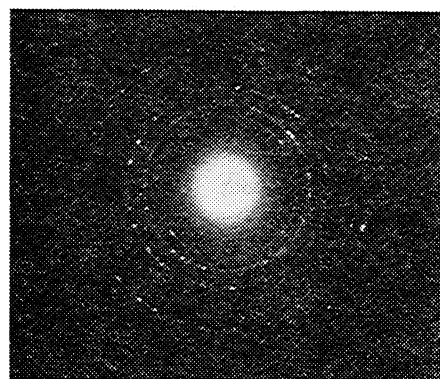


Fig. 4. Electron diffraction pattern of synthetic greigite.

Figure 4 shows a typical electron-diffraction pattern from a synthetic greigite. This pattern contains only the reflections allowed for the spinel structure, with the space group $\text{Fd}\bar{3}\text{m}$. Both the d-spacings and the relative intensities observed are listed in Table 2 in comparison with the X-ray data of natural greigite. There is a close correspondence of d-spacings and intensities between synthetic greigite and the natural mineral.⁹⁾

The product, stable in air was examined by the X-ray powder diffraction method, and its composition was determined by chemical analysis. The compositions of synthetic greigite ranged from 45.4 to 42.9 atomic per cent of iron and explicitly showed a deviation from stoichiometric Fe_3S_4 . The chemical formula of synthetic greigite was given by $\text{Fe}_{3+x}\text{S}_4$ ($x=0-0.4$). With respect to the compositions, this iron-rich greigite ($\text{Fe}_{3+x}\text{S}_4$) was analogous to natural iron-rich smythite ($\text{Fe}_{3+x}\text{S}_4$), which

TABLE 2. ELECTRON-DIFFRACTION DATA FOR SYNTHETIC GREIGITE IN COMPARISON WITH X-RAY DIFFRACTION DATA FOR MINERAL GREIGITE (Skinner, Erd, and Grimaldi (1964))

<i>hkl</i>	Synthetic greigite		Natural greigite	
	<i>d</i> _{obsd}	<i>I</i> ^{a)}	<i>d</i> _{obsd}	<i>I</i>
111	5.68	w	5.720	8
220	3.51	s	3.500	30
311	3.00	vs	2.980	100
222	2.88	w	2.855	4
400	2.49	vs	2.470	55
331	2.29	w	2.260	2
422	2.03	w	2.017	10
333, 511	1.91	vs	1.901	30
440	1.75	vs	1.746	75
531			1.671	1
620	1.57	vw	1.563	4
533	1.50	w	1.506	10
622			1.488	2
444	1.43	w	1.425	8
711, 551	1.39	vw	1.383	1
642	1.32	vw	1.320	4
731, 553	1.29	vw	1.286	12
800	1.23	vw	1.235	10
733			1.210	1
644			1.198	1
822, 660			1.164	1
751, 555	1.14	vw	1.140	2
840	1.10	w	1.105	16
753, 911			1.084	1
664			1.054	2
931	1.03	vw	1.035	8
844	1.01	w	1.001	30

a) Intensities were estimated visually. vs=very strong, s=strong, w=weak, vw=very weak.

was found at Silverfields Mine, Cobalt, Ontario.¹⁰⁾

The cell edges of synthetic greigite ranged from

9.840 Å to 9.877 Å with corresponding variations in the compositions. They increased with a decrease in the iron content in the compositional range between 45.4 and 42.9 atomic % Fe.

The density determination with a pycnometer was made at 25 °C on synthetic greigite. The specific gravities of Fe_{3.33}S₄ and Fe₃S₄ were 4.60 and 4.02 respectively.

The results presented above may be indicative of the possibility that excess iron occupies an interstitial site in the spinel structure. Further detailed researches on the crystal structure are, however, necessary for a better understanding of the nonstoichiometry of greigite.

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