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THE CHEMISTRY OF IRON  
SULPHIDE FORMATION AT LOW  
TEMPERATURES

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# 4. The chemistry of iron sulphide formation at low temperatures

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ABSTRACT—Six mineral iron sulphides are known: greigite, mackinawite, marcasite, pyrite, pyrrhotite and smythite. All six can be synthesised from aqueous solutions at low temperatures and pressure. An examination of the rates and products of the reactions between a variety of iron salts and sulphur species in aqueous solutions reveals that each iron sulphide is formed by a distinctive mechanism. Of critical importance is the nature of the sulphur-bearing reactant, especially since an investigation of the iron in all these compounds demonstrates that it is divalent. In particular, the presence of sulphide or polysulphide ion, or elemental sulphur as a reactant can determine the nature of the iron sulphide product.

However, the form of the reactant iron salt becomes important when it exerts any degree of structural control on the formation of the sulphide. Specifically, the relationship between siderite and the formation of smythite, and mackinawite and the formation of greigite, are decisive.

The data accrued on the mechanisms of formation of these minerals can be applied to determining the favourable physico-chemical conditions for the formation of each iron sulphide. However, the reversal of this process, that is the use of these minerals as environmental indicators, must be approached cautiously, since the fundamental requirements for the formation of each mineral may be satisfied by a number of environments. The possibility of using the experimental results in this way is discussed.

## ACKNOWLEDGEMENTS

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## INTRODUCTION

### *The mineral iron sulphides*

In their classic paper of 1912, ALLEN, CRENSHAW and JOHNSON investigated the chemistry of the iron sulphide minerals then known, pyrite, cubic  $\text{FeS}_2$ , marcasite, orthorhombic  $\text{FeS}_2$  and pyrrhotite, hexagonal or monoclinic  $\text{Fe}_{(1-x)}\text{S}$  (where  $x = 0$  to 0.125). X-ray analysis and advances in the methods of chemical investigation of natural materials have led to the discovery, since 1957, of three new iron sulphide minerals, smythite, greigite and mackinawite.

Smythite, first reported by ERD, EVANS and RICHTER (1957), from Indiana, U.S.A., has for formula  $\text{Fe}_3\text{S}_4$ . Smythite is rhombohedral and ferromagnetic, and is similar to pyrrhotite in that the two minerals have similar  $a_0$  values and  $c_0$ , smythite is six times that of pyrrhotite. Smythite has also been reported from the Kimmerian sedimentary iron ores of the Kerch Peninsular, U.S.S.R. (CHUKROV, GENKIN, SOBOLEVA and UPDOVA, 1965), and from silver-bearing veins at Cobalt, Ontario, Canada (TAYLOR, 1968). In each of its occurrences it is associated with rhombohedral carbonates, and fluid inclusion studies on calcite associated with the Indiana smythite indicate that it formed at a temperature of 25–40° C. It is probable that smythite is a widespread mineral, but its almost identical optical characters to monoclinic pyrrhotite make identification difficult in the absence of x-ray diffraction analysis.

Greigite,  $\text{Fe}_3\text{S}_4$ , is apparently a cubic dimorph of smythite. It was first described from a Tertiary lacustrine sequence in the U.S.A. by SKINNER, ERD and GRIMALDI (1964). It is a thiospinel of iron and is highly ferromagnetic. It has been reported from the Kimmerian sedimentary iron ores of the Kerch Peninsular, U.S.S.R. (KRAMM and SUKHITSKAYA, 1965) where it is associated with ferric oxyhydroxide. It has also been observed encrusting a mammoth's tooth in the U.S.S.R. (BOBROVNIK, 1967). It is generally referred to as 'melnikovite' in Russian literature, but, elsewhere, 'greigite' has been preferred because of the confusion that arises from the identification of a quasi-amorphous mixture of iron sulphides and possibly oxides commonly occurring in sediments as 'melnikovite'. Furthermore the adjective 'melnikovitic' has been used to describe certain forms of poorly crystallised pyrite.

Like smythite, greigite has probably been overlooked in the past because of its usual fine-grain size and oxide-like optical character.

MILTON and MILTON (1958) described the occurrence of a sulphide mineral, believed to be valleriite, from the Mackinaw mine, Washington, U.S.A. Subsequent electron probe microanalyses of this phase showed it to be copper-deficient, and to have a composition approaching  $\text{FeS}$  (BIRKS, BROOKS, ADLER

and MILTON, 1959). This new phase was described as mackinawite in 1964 (EVANS et al.).

It is a tetragonal sulphur-deficient iron sulphide,  $\text{FeS}_{(1-x)}$ , but difficulties arise in attempting to propose its exact range of composition because of its ability to take up large amounts of nickel and cobalt into its lattice. It has been described from the Outokumpu mine in Finland (KOUVO, VUORELAINEN and LONG, 1963) with a formula of  $(\text{Fe}_{0.97}\text{Ni}_{0.13}\text{Co}_{0.07})\text{S}$ . However, mackinawite has been shown to be identical with many pure ferrous sulphide phases that have been synthesised in the laboratory. 'Kansite', so-called 'cubic  $\text{Fe}_9\text{S}_8$ ', was first described from a sulphide corrosion product of steel pipes from a sour crude oil well in Kansas (MEYER, RIGGS, McGLASSON and SUDBURY, 1958), but it is now accepted as being identical to mackinawite. BERNER (1964) showed that his 'tetragonal iron sulphide' was also mackinawite.

The generally similar properties of mackinawite and valleriite have led to a reappraisal of the actual distribution of valleriite in deposits. TAKENO (1965) states that, whereas mackinawite is now apparently extremely common, valleriite is rare in comparison, and only been publicly authenticated from three localities (Loolekoop, South Africa; Kaveltorp, Sweden; Muskox Intrusion, Canada).

Both mackinawite and greigite have also been identified as the major constituents of the black iron sulphides of recent sediments (BERNER, 1964 and JEDWAB, 1967).

### *Scope of investigation*

The presence of six compounds of two elements in one system raises questions as to the nature of the elements in each compound and the reasons for their combination in each form. Furthermore, the apparently universal low temperature affiliations of the three new iron sulphides, together with the wide acceptance that much ore deposition, including the formation of the three earlier established minerals, can take place at low temperatures, has necessitated a new approach to the problem of iron sulphide chemistry.

The purpose of this investigation was therefore to examine in detail the chemistry and mechanisms of formation of the mineral iron sulphides, at low temperatures, in order to discover the conditions under which they may be formed.

### *Previous work*

Since 1957, there have been two major attempts to investigate the iron sulphides experimentally at low temperatures and pressures. KOROLEV and KOZORENKO (1965) added an aqueous sulphide to a solution of a ferrous salt at room temperature and heated the resultant unidentified product with the

remnant solution to 150° C. They synthesised pyrite, marcasite, pyrrhotite and greigite. During his extensive investigations BERNER (1964) added sulphide to various iron salts under a variety of pH, temperature and ageing conditions. He synthesised marcasite, pyrite, pyrrhotite, greigite and mackinawite. Both of these investigations were mainly concerned with the synthesis of recognisable phases, but BERNER included additional work on the experimental reproduction of complex natural conditions in order to examine the nature of the sulphide phases produced in sediments.

## METHODS

### *Introduction*

Although certain indications as to the possible controlling factors in the formation of iron sulphides may be gleaned from simple syntheses, this is essentially a by-product of such work. Syntheses tend to include factors which facilitate the formation of pure phases as well as those factors which control their formation. Furthermore, the reproduction of natural conditions also introduces many factors that confuse the interpretation of the mechanisms. In this investigation therefore, the reactions between various iron and sulphur species were observed. No attempt was made to synthesise pure phases, and the majority of the products were mixtures of two or more iron sulphides. Furthermore, the reactions were kept as simple as possible. Extraneous agents, that might accelerate crystallisation, but which have unknown effects on the chemistry of the iron and sulphur species, were excluded. For example, air, which BERNER employed to catalyse the formation of greigite, was not present in this experimentation, and rigorous precautionary measures were taken to exclude it.

Apart from the difficulty of identification of the fine-grained mixed products of low temperature experimentation, the other great problem under these conditions is the general lack of equilibrium, and therefore the inability to apply simple thermodynamic interpretations to the results. As will be demonstrated below, evidence for the reversibility of many of the reactions is not forthcoming, and there are strong indications that some of the reactions are irreversible.

Of the six mineral iron sulphides only two, pyrite and members of the pyrrhotite group, are concerned in the phase relationships of the iron-sulphur system at temperatures above 325° C, conditions under which equilibrium tends to prevail. Furthermore, CLARK (1966) attempted to examine the reactions in the iron-sulphur system down to almost room temperature, but did not succeed in synthesising any other phase.

With this apparent lack of equilibrium conditions in the formation of the

majority of the iron sulphides, it is necessary to approach the problem of the conditions of formation from a kinetic rather than a thermodynamic viewpoint. That is, to establish the mechanism of the formation of each iron sulphide and then to examine the possible conditions under which the controlling factors may be present. BURKIN and RICKARD (1969b) report elsewhere the results of a detailed study of the kinetics and mechanism of the sulphidation of goethite, but during this investigation a qualitative semi-kinetic approach was used.

#### *Experimental procedure*

The reactions were performed in screw-topped sample bottles. The reactants employed were: ferrous sulphate, ferric chloride, synthetic goethite (prepared by the addition of sodium hydroxide to solutions of ferric chloride to pH = 8.5, and heating to 100° C) ferrous carbonate, sodium sulphide solution, sodium polysulphide solution (prepared by the reaction between sodium sulphide and sulphur together with subsequent filtration), and sodium thiosulphate. All reagents were of analytical grade, except ferrous carbonate and the laboratory-prepared reagents. The purity of the ferrous carbonate and the synthetic goethite was checked by x-ray powder diffraction analysis using a Debye-Scherrer 114.6 mm camera and CoK $\alpha$  radiation. No contaminants were detected in any of the samples by this method.

The sulphur solutions were poised at the required pH by the addition of hydrochloric acid or sodium hydroxide. The solution was then added to a solution or suspension of the iron salt, and the bottle was sealed under nitrogen. The use of nitrogen together with the extremely small gas space in the sealed bottles eliminated the risk of air oxidation. The pH and Eh were measured after the reaction and the readings taken when no further observable change was detected.

The pH was measured with a combined bulb-type glass electrode and a KCl-calomel reference electrode. The measurements were recorded on a Pye Universal pH meter. Agitation which had been continuous from the addition of the sulphur solution was arrested during measurement.

The products were identified by x-ray powder diffraction analysis using a 114.6 mm Debye-Scherrer camera and CoK $\alpha$  radiation. The products were not dried or removed from solution. This eliminated any possibility of the x-rayed material being in anyway different, through oxidation or drying, from the products in the reaction vessels. A sample of the product was taken up direct from the reaction vessel into a 0.3 mm bore Lindemann glass capillary, which was heat sealed. The capillary was mounted in the camera. The data obtained were compared where possible with standards, or otherwise with published results.



If samples were required dry for further experimentation or analysis, the products were filtered in sintered glass filters under an atmosphere of nitrogen. The precipitate was washed with water, alcohol and ether, and then placed in a vacuum dessicator. The dessicator was evacuated continuously for at least 24 hours and then sealed.

Attempts to identify the products through drying and mounting on a glass fibre or by using diffractometer smear mounts met with unqualified failure. The major problems were oxidation, and, with the smear mounts, lack of density of the samples and too low peak to background ratios to allow identification.

Chemical analysis of the samples was employed only as a rare adjunct to the x-ray analyses. The mixtures of products and the possibility of coprecipitation of the sulphur species, limited the usefulness of such analyses. Furthermore, electron probe microanalyses were attempted but were not successful due to a combination of factors, including the fine-grain size of the material, the difficulty of mounting the material because of its instability, and the presence of water in the samples.

Where possible, samples of the products were taken and dried and mounted in polished sections for optical analyses. However, the products were generally too fine-grained and unstable for successful analyses of their optical properties to be made.

In general the iron: sulphur ratio of the reactants was chosen such that the sulphur was in excess of the iron in the proportion of two moles of sulphur to one of iron. In the initial 65 ml of solution this was 0.925 M iron and 1.850 M sulphur. However, as controls, different iron-sulphur ratios were also employed, but in no case was there any evidence of any difference in the final sulphide product.

## RESULTS

### *Introduction*

The recorded pH and Eh values are not simple reflections of the conditions of formation of the products, since they could only be recorded at the conclusion of the reaction, and they therefore record metastable equilibria set up at the time of measurement. The recorded pH is, in fact, the final pH of the reaction.

In cases where the iron salt used was dissolved, the pH equilibrium time was of the same order as the reaction time. In these cases the initial pH of the solution was low (pH-2-3) and the measured pH records the maximum pH reached during the reaction. Therefore the pH measurements are, in this case, essentially relative.

In other reactions this pH fluctuation is unimportant, since the time for the

reaction mixture to reach the final pH is short (a few seconds) relative to the reaction time (a week). During this period only minor changes in pH occur, in the magnitude of tenths of a pH unit.

However, since the approach to this problem was mechanistic rather than thermodynamic, this lack of precision in these experiments does not affect the interpretation.

It could be argued that in such cases buffers should be used. However, experience in other experimental systems has shown that such buffers may react with the reactants and precipitate, especially in concentrations required in such concentrated solutions as those used in this experimentation. Since the approach was mechanistic, any such apparent refinement of the experimental technique would only add confusion and doubt to the interpretation.

Whereas the pH measurements can be easily interpreted and their importance assessed, the measured Eh does not measure the Eh of formation of the product. It is extremely difficult to interpret the Eh, since the equilibrium conditions it reflects are at the most transitory. Essentially, the Eh records two features of the reaction:

- the conditions under which the product retains some semblance of stability with respect to the solution—since it does not redissolve or oxidise,
- variations in the redox couple being measured, and variations in the concentrations of the redox reactants in solution.

The Eh therefore provides a guide. If there were any sudden change in the nature of the sulphide species, it should be reflected in the Eh. Furthermore, the removal of more or less dissolved iron or sulphur species from the solution, through precipitation as an iron sulphide, should also be reflected in the redox potential.

The Eh and pH results of this experimentation were plotted on a diagram with Eh and pH as ordinate and abscissa, for each particular reaction. The results are shown in Fig. 1.

A summary of the most important results of the various experiments performed are shown in Table 1.

The mechanisms and conditions of formation, together with data on the composition of each mineral iron sulphide are considered below.

### *Mackinawite*

Synthetic mackinawite, tetragonal  $\text{FeS}_{(1-x)}$ , was first identified by BERNER (1962a), who synthesised it by ageing the products of the reactions between iron phases and concentrated aqueous sulphide solutions. Eliminating those reactions where air was deliberately allowed into the reaction vessel or where

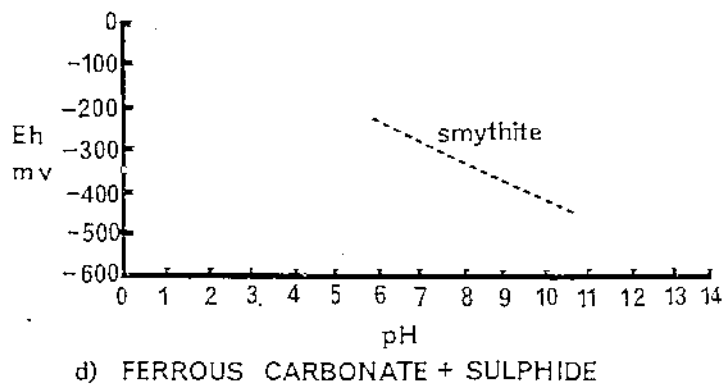
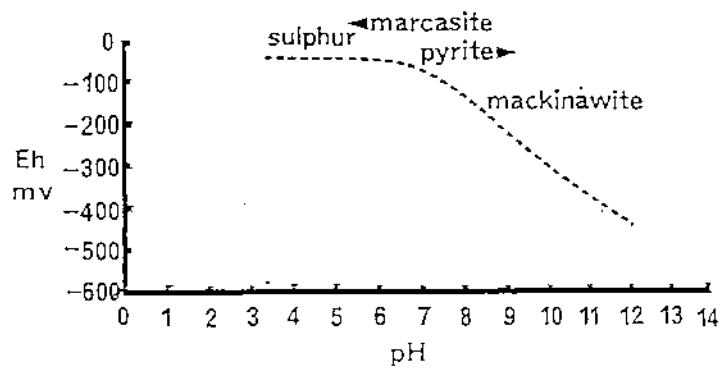
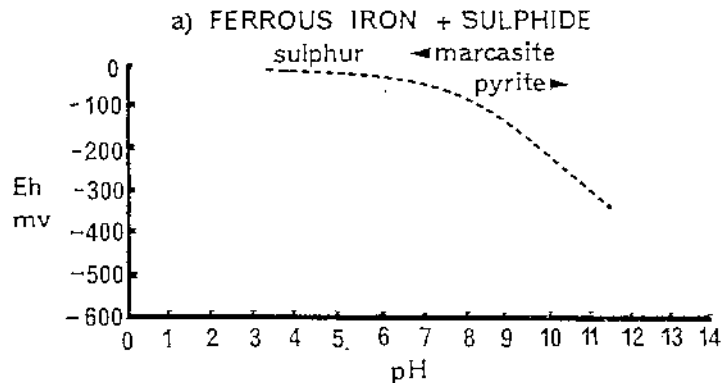
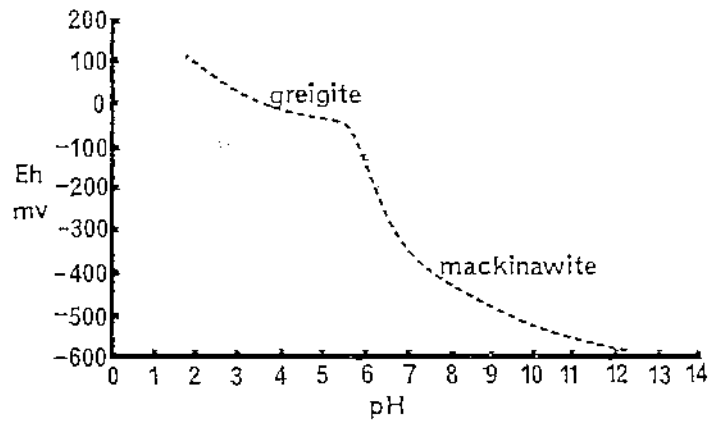


Fig. 1. Eh/pH conditions for the experimental syntheses of the iron sulphides.

Table 2. X-ray data for synthetic mackinawite

Synthetic mackinawite		Natural mackinawite <sup>1</sup>	
dÅ	I	dÅ	I
5.03	vs	5.03	vs
2.97	s	2.97	s
2.60	w	2.60	vw
2.28	m	2.31	s
1.838	mw	1.838	m
1.809	vs	1.808	s
1.720	mw	1.725	m
...	..	1.674	w
1.564	m	1.562	mw
1.403	vw	1.524	w
...	..	1.409	w
1.298	mw	1.300	mw
1.267	mw	1.258	mw
...	..	1.240	w
1.194	vw	1.190	vw
...	..	1.174	vw
1.129	w	1.133	mw
1.055	mw	1.055	mw
...	..	1.037	b
...	..	1.027	b
...	..	1.000	b

vs = very strong; s = strong; ms = medium strong; m = medium; mw = medium weak; w = weak; vw = very weak.

<sup>1</sup> KOUVO, VUORELAINEN and LONG, 1963.

peaks. In this experimentation, the material that was apparently equivalent to 'precipitated FeS' always gave one or more of the stronger characteristic mackinawite lines, especially the broad band at about 5 Å. Since it is improbable that a strictly amorphous iron sulphide exists, and since it has yet to be shown that this material, which has the same formula as mackinawite, has a different crystal structure, this material is referred to as mackinawite throughout this paper. It must be noted here, however, that the method of extraction of the sample for x-ray analysis, through sealing a suspension in a Lindemann glass capillary, probably gave better results for such finely-divided material.

Since mackinawite may be produced through the reaction between iron metal and aqueous sulphide solutions or between ferrous sulphate and sodium sulphide, it must be a simple *ferrous* sulphide. MORICE, REES and RICKARD (1969) have published Mössbauer analyses of this material which confirm this conclusion.

Table 1. Summary of results of experiments at 25° C in aqueous solution

Reaction	pH Range	Products (minor products in brackets)
Ferrous sulphate + sodium sulphide	3.4- 6.5	Greigite, (mackinawite)
	6.5-11.7	Mackinawite
Ferrous sulphate + sodium polysulphide	< 4.4	Sulphur
	4.4- 9.5	Pyrite, marcasite, (sulphur)
	> 9.5	Sodium iron sulphide
Ferrous sulphate + sodium thiosulphate	5.4-11.2	No reaction
Synthetic goethite + sodium sulphide	4.4- 7.0	Sulphur, Marcasite, Pyrite, (mackinawite)
	7.0- 9.0	Mackinawite
	> 9.0	Sodium iron sulphide
Synthetic goethite + sodium polysulphide	4 -11	Sulphur
Synthetic goethite + sodium thiosulphate	4 -11	Sulphur
Ferrous carbonate + sodium sulphide	6.5-10.3	Smythite, (mackinawite, siderite)
	6 - 8	No reaction
Mackinawite + sodium polysulphide	7	Pyrite, marcasite, (sulphur)

the reaction mixture was heated, BERNER (1964) synthesised mackinawite through the reaction between goethite and hydrogen sulphide (at pH = 4, and 6.5 with ammonium hydroxide) and through the reaction between steel or iron wire and hydrogen sulphide gas at pH = 4. It is unfortunately impossible to interpret those reactions in which air was allowed to take part because of a lack of knowledge of its precise effect on the reaction mixture. Also a lack of information as to the nature of the initial products reduces the applicability of the heating experiments. The pH of 4 for the hydrogen sulphide experiments probably does not reflect the pH of formation of the mackinawite but rather the pH of a solution saturated with hydrogen sulphide gas.

In the experimentation performed in this laboratory, mackinawite was formed through the reaction between ferrous sulphate and sodium sulphide at pH = 5.5-11.7, and goethite and sodium sulphide at pH = 7.2-11.4. The results are shown graphically in Fig 1a and c.

An x-ray analysis of this synthetic mackinawite is shown in Table 2. The mackinawite produced in these experiments has similar properties to the 'amorphous' or 'precipitated' iron sulphide of other investigators. There is no evidence that a strictly amorphous iron sulphide exists, and, by analogy with other base metal sulphide systems it is highly unlikely. Furthermore, there is no evidence that the initial precipitate, the 'precipitated FeS' of BERNER (1964, 1967), is a different iron sulphide phase from mackinawite, even if it is finely crystallised. BERNER has shown that his 'precipitated FeS' has an iron: sulphur ratio of about 1:1, and his published x-ray results do show small mackinawite

The results of previous analyses of mackinawite have been summarised (CLARK, 1966) and show that mackinawite is a sulphur-deficient iron sulphide with a formula varying between  $\text{Fe}_{1.04}\text{S}$  and  $\text{Fe}_{1.07}\text{S}$ . However, synthetic mackinawite produced in this laboratory contained adsorbed or coprecipitated sulphide and analysis gave an Fe:S ratio of 1:1.1. This is consistent with BERNER's (1964) results from titration experiments. If this material is filtered and dried and inserted into an evacuated pyrex tube and sealed, heating to temperatures as low as  $70^\circ\text{C}$  produces greigite very rapidly. X-ray analysis of the reactant confirms it as being mackinawite, with no greigite, and x-ray analysis of the product shows it to be greigite with minor remnant mackinawite. Therefore mackinawite reacts with coprecipitated or adsorbed sulphide to form greigite, in a semi-dried state.

Reference to Fig. 1a shows that although the reaction between ferrous sulphate and sodium sulphide gives mackinawite between  $\text{pH} = 6.5$  and  $11.7$ , the product of this reaction between  $\text{pH} = 3.4$  and  $6.5$  is greigite, with small amounts of mackinawite, especially at the higher end of this pH range. That is, greigite forms preferentially at lower pH values. As discussed above, these pH values do not reflect the pH of formation of the product where the time for reaching the measured pH is comparable with the time of formation of the product. In a precipitation reaction, as is observed between ferrous sulphate and sodium sulphide, this situation prevails. Therefore the real pH of the reaction varies from  $\text{pH} = 2-3$  to  $\text{pH} = 11.7$  for mackinawite and  $\text{pH} = 2-3$  to  $\text{pH} = 6.5$  for greigite. Thus the initial product should be identical in both cases, since this initial product is formed under essentially the same conditions. A close examination of the initial product of the greigite-producing experiments showed it to be non-magnetic and to give the strongest lines of mackinawite upon x-ray analysis. However, after standing one week at the more acid pH values of  $3.4$  to  $6.5$ , the product becomes highly magnetic and consists mainly of greigite. Therefore it must be concluded that the greigite is formed through the reaction between initial mackinawite and either sulphide in the solution or adsorbed or coprecipitated sulphide, in the same manner as was shown to occur in the heating of partially dry mackinawite. In no case was greigite observed to form directly from solution; in all cases an initial non-magnetic precipitate was present.

The solution reaction between mackinawite and excess sulphide was confirmed by ageing a mackinawite precipitate at  $\text{pH} = 8$  for three months. The resultant product was greigite.

Since no evidence has been found to support any proposal that hydrogen or hydroxide ions are present in the mackinawite formula, the pH can have no direct effect on the nature of the iron sulphide produced. As demonstrated above, the essential effect of pH variations is to vary the rate of the mackinawite-greigite transformation. It further seems that varying temperature can

have the same effect. This pH change can only affect the nature of the iron or sulphur species in solution or the nature of the initial mackinawite surface. The pH can have no effect on the iron species, and its effect on the sulphide species is simply to change dominant bisulphide ion (at pH greater than 7) to dominant hydrogen sulphide (at pH less than 7). Since the recorded pH does closely reflect the pH of transformation of mackinawite to greigite, the reaction rate change at pH = 6.5 is not coincident with the change in sulphide species, which occurs at pH = 7. However, the action of the pH is consistent with an assumption that the mackinawite surface has hydroxide or hydrogen ions adsorbed upon it, depending on pH. At higher pH values the surface would have hydroxide ions adsorbed upon it, and thus the prevailing bisulphide species would tend to be repelled. At lower pH values the surface would have hydrogen ions adsorbed upon it, which would not repel either hydrogen sulphide molecules or bisulphide ions. Therefore the rate of reaction would be faster at lower pH values. Preliminary results of infra-red spectrometric analyses of a mackinawite-like phase by Dr. R. HALLBERG (pers. comm.) do in fact demonstrate the presence of hydroxide ions.

The stability of mackinawite remains unclear. BERNER (1964) found that in the reaction between steel and aqueous sulphide at temperatures as low as 40–42° C both mackinawite and pyrrhotite were formed. Since a similar reaction at 20–25° C produced only mackinawite, it seems probable that the pyrrhotite was formed through a partial transformation of the initial low temperature mackinawite on heating. However, there is still the possibility of a separate reaction occurring to form pyrrhotite, and this evidence is not conclusive. CLARK (1966) and TAKENO (1965) suggested that inconsistencies in the thermal stability of mackinawite result from compositional variations, and CLARK suggested that natural mackinawite was stable up to 135° C.

In this laboratory, bacteriologically-produced mackinawite, the formation of which is described in another paper (RICKARD, 1969), was apparently partially transformed to pyrrhotite after ageing at 30° C for 9 months. The initial product of the reaction was mackinawite, and the final product included major pyrrhotite. Although it is possible to propose that the pyrrhotite was formed from a separate, slower reaction, it seems more reasonable that it was formed through the transformation of the mackinawite, particularly since examination of the products at intervals before the formation of pyrrhotite only revealed the presence of mackinawite and greigite; no other iron salts were detected.

It is possible therefore that pure mackinawite is a metastable phase in the iron-sulphur system being unstable with respect to pyrrhotite at all temperatures but with the reaction rate being temperature-dependent. The presence of cobalt, nickel and copper in the structure act to stabilise the mackinawite.

In conclusion, mackinawite—sulphur-deficient  $\text{FeS}_{(1-x)}$ —is the primary product of all reactions between an iron salt and a dissolved sulphide species

where topotaxy or epitaxy is not involved. It reacts further with sulphide to produce greigite. This reaction is apparently irreversible. There is no evidence to distinguish so-called 'amorphous FeS' or 'precipitated FeS' from mackinawite.

### *Greigite*

Although greigite, cubic  $\text{Fe}_3\text{S}_4$ , has probably been synthesised a number of times in the past, the first identification of a synthetic reaction product as pure greigite was made by UDA (1965), on heating the products of the reaction between ferrous ammonium sulphate and sodium sulphide to  $190^\circ\text{C}$  and quenching. Greigite also appeared in the experiments of BERNER (1964) and KOROLEV and KOZORENKO (1965).

The reaction between mackinawite and sulphide to give greigite has been described above.

Greigite was not detected in the reactions between goethite and sodium sulphide, which is consistent with the work of BERNER. However, the reason for this probably lies in the fact that, at the lower pH values of rapid greigite formation, large amounts of sulphur are produced when a ferric salt is sulphidised, masking any greigite that might be formed and resulting in the long term formation of marcasite and pyrite.

However, this experimentation, together with that of UDA, does not confirm BERNER's proposition that air is necessary for the formation of greigite. The careful precaution taken during these experiments against oxidation by air, rigorously exclude the possibility of its presence. Indeed, if air were admitted to the reaction vessels the products were pyrite and marcasite, or, in extreme cases, goethite and sulphur.

X-ray data for this synthetic greigite are shown in Table 3.

The composition of greigite has been given as  $\text{Fe}_3\text{S}_4$  (SKINNER, ERD and GRIMALDI, 1964). Although no deviations from this formula have yet been detected, insufficient greigite has been found naturally to confirm stoichiometry. Indeed, it would be surprising, in view of the well-known non-stoichiometry of the other compounds in this system, if greigite had a strict stoichiometric formula.

Since greigite has a similar structure and similar magnetic properties to magnetite it has been referred to as a ferroso-ferric sulphide in the past. Under the conditions of synthesis in this experimentation however, the heating of a mackinawite-sulphide precipitate or the reaction in solution between mackinawite and sulphide, the large amounts of ferric iron needed to satisfy the equation  $\text{FeS} \cdot \text{Fe}_2\text{S}_3$  cannot be formed.

This conclusion was confirmed by Mössbauer analyses of greigite, prepared in a similar manner to that recommended by UDA, which demonstrated that greigite was essentially a ferrous sulphide and contained no ferric iron.



Table 3. X-ray data for synthetic greigite

Synthetic greigite		Natural greigite <sup>1</sup>	
dÅ	I	dÅ	I
5.66	m	5.72	8.0
3.46	ms	3.50	31.5
2.97	vs	2.98	100.0
2.83	m	2.86	3.9
2.45	vs	2.47	54.8
2.30	mw	2.26	1.2
1.991	mw	2.02	9.2
1.893	s	1.901	28.6
1.739	vs	1.746	76.8
1.612	vw	1.671	0.9
1.556	vw	1.5625	4.2
1.507	vw	1.5058	9.3
1.478	mw	1.4863	1.5
1.417	mw	1.4253	3.6
.....	..	1.3826	0.7
.....	..	1.3204	3.6
1.283	mw	1.2859	12.8
1.228	w	1.2349	9.2
.....	..	1.2097	0.3
.....	..	1.1975	0.2
.....	..	1.1640	0.3
1.140	w	1.1401	1.8
1.099	mw	1.1051	16.4
.....	..	1.0844	0.6
.....	..	1.0544	2.1
.....	..	1.0351	7.1
1.005	m	1.0080	30.9

vs = very strong; s = strong; ms = medium strong; m = medium; mw = medium weak; w = weak; vw = very weak.

<sup>1</sup> SKINNER, ERD and GRIMALDI, 1964.

This is consistent with the other thiospinels with which greigite is isostructural: linnaeite ( $\text{Co}_3\text{S}_4$ ), polydymite ( $\text{Ni}_3\text{S}_4$ ), siegenite ( $\text{Co}_2\text{Ni}_3\text{S}_4$ ), violarite ( $\text{FeNi}_2\text{S}_4$ ), carrolite ( $\text{CuCo}_2\text{S}_4$ ) and daubréelite ( $\text{FeCr}_2\text{S}_4$ ). Although it might be argued that the cobalt in these compounds could be trivalent, the contention that the isostructural polydymite contains trivalent nickel is highly improbable.

Furthermore, it has been shown by BURKIN and RICKARD (1969a), in their examination of the preparation and properties of ferric sulphide, that ferric iron—sulphide bonding is extremely unstable.

It might also be proposed that greigite is a ferrous sulphide-ferrous poly-

sulphide mixture,  $2\text{FeS}\cdot\text{FeS}_2$ . Although the Mössbauer evidence cannot be interpreted to exclude this possibility, wet chemical evidence indicates that it is unlikely. Apart from the lack of an oxidising agent in sufficient concentration to oxidise half of the sulphide to polysulphide, the reactions between mackinawite and polysulphide, and between ferrous iron in solution and polysulphide, have been shown to result in the formation of marcasite and pyrite (see below). This is particularly pertinent in view of the fact that these polysulphide solutions necessarily contained sulphide ions, and therefore these experiments contained all the necessary ingredients for the formation of a ferrous sulphide-polysulphide, if such a compound existed.

Furthermore, although it has been suggested that greigite is unstable with respect to pyrrhotite and pyrite, experiments in this laboratory on heating suspensions of greigite to temperatures of  $180^\circ\text{C}$  gave partial transformation to pyrrhotite within three hours. Neither pyrite nor marcasite were detected in the products of these heating experiments.

The stability of greigite is not well known, but there is no clear evidence to suggest that it rapidly decomposes below  $180^\circ\text{C}$  at least. However, since greigite has not been formed through reactions between iron and sulphur at any temperature and because of its dependence on the prior existence of mackinawite for its formation, greigite is, perhaps, a non-equilibrium phase in the iron-sulphur system. It may be metastable at all temperatures with respect to pyrrhotite, the reaction rate being temperature-dependent.

### *Smythite*

The only reported synthesis of smythite, rhombohedral  $\text{Fe}_3\text{S}_4$ , is that of RICKARD (1968), during this investigation. Experiments by this and other investigators under a variety of conditions between a number of iron and sulphur species all failed to produce smythite. RICKARD produced smythite through the sulphidation of the rhombohedral ferrous carbonate, siderite, and thus concluded that the pre-existence of siderite was a necessary factor in the formation of smythite.

Further results of this experimentation are shown in Fig. 1d, and x-ray data for synthetic smythite are shown in Table 4.

In no case was pure smythite formed. At more acid pH values more ferrous iron was dissolved and the reaction between this and aqueous sulphide resulted in the formation of mackinawite. This effect was further enhanced by the evolution of carbon dioxide gas which intimately agitated the siderite suspension, increasing the rate of dissolution of the ferrous iron. At more alkaline pH values the reaction did not go to completion within the reaction time employed and remnant siderite was left with the smythite.

Using identical arguments as for greigite (above) it can be shown that,

Table 4. X-ray data for synthetic smythite

Synthetic smythite		Natural smythite <sup>1</sup>		Natural mackinawite <sup>2</sup>	
dÅ	I	dÅ	I	dÅ	I
11.6	s	11.5	6	....	..
5.78	m	5.75	1/2	.....	..
5.05	m	....	..	5.03	vs
3.62	mw	3.82	2	....	..
2.98	s	{ 3.00	6	2.97	s
		{ 2.96	1/2		
		{ 2.86	1/2		
2.80	ms	{ 2.83	2	....	..
		{ 2.75	4		
2.59	mw	2.56	6	2.60	vw
		{ 2.45	2		
2.31	s	{ 2.29	1/2	2.31	s
		{ 2.26	6		
2.14	mw	2.16	4	....	..
1.967	mw	1.979	7	....	..
1.875	s	1.897	8	....	..
1.839	m	....	..	1.838	m
1.808	ms	....	..	1.808	s
1.732	vs	1.732	10	1.725	m
		{ 1.687	1/2	1.674	w
1.674	mw	{ 1.672	4		
		{ 1.577	1/2	1.562	mw
1.552	w	{ 1.546	1/2		
1.525	vw	....	..	1.524	w
		{ 1.435	2	....	..
1.426	m	{ 1.427	6		
1.350	w	1.351	1/2	....	..
1.298	m	1.306	2	1.300	mw
		{ 1.280	2	1.258	mw
1.260	mw	{ 1.254	1/2		
		{ 1.154	4	1.133	mw
1.132	w	{ 1.102	1/2		
1.056	m	1.065	1/2	1.055	ms
1.039	vw	1.037	2	1.037	$\beta$

vs = very strong; s = strong; ms = medium strong; m = medium; mw = medium weak; w = weak; vw = very weak.

<sup>1</sup> ERD, EVANS and RICHTER, 1957.

<sup>2</sup> KOUVO, VUORELAINEN and LONG, 1963.

through lack of oxidising agents and because of the transformation to pyrrhotite on heating, smythite is not a ferroso-ferric sulphide nor a ferrous sulphide-polysulphide, but is strictly dimorphic with greigite as a simple ferrous sulphide.

Like greigite it was partially transformed to pyrrhotite within three hours at 180° C in an aqueous suspension, and it therefore probably has similar relationships with pyrrhotite as greigite.

*Structural controls on the formation of greigite and smythite*

During detailed experiments on the synthesis of equilibrium iron sulphides at various compositions and temperatures, GRØNVOLD and HARALDSON (1952) came to the conclusion that the maximum degree of iron-deficiency possible in pyrrhotite at temperatures less than 360° C is  $\text{Fe}_7\text{S}_8$ . Generally, this conclusion is consistent with analyses of natural pyrrhotites.

Greigite and smythite are therefore of particular interest in this context since these apparently simple ferrous sulphides have an iron-deficiency exactly twice the maximum proposed for pyrrhotite, according to their stoichiometric formulae of  $\text{Fe}_3\text{S}_4$ . Although no evidence has yet been produced to indicate non-stoichiometry in these compounds, it is probable that both will show divergences from the ideal formulae when more specimens are examined. This is especially true in the case of smythite, since a structural analysis of smythite (ERD, EVANS and RICHTER, 1957) has shown that smythite consists of slabs with a pyrrhotite-like structure stacked so that  $2_0\text{pyrrhotite} = 2_0\text{smythite}$ , but  $6_0\text{smythite} = 6_0\text{pyrrhotite}$ . There is also some evidence of a large rhombohedral superlattice, probably resulting from an ordering of iron vacancies.

It is therefore possible that the role of the rhombohedral carbonate is to control the arrangement of the iron sites in the smythite lattice, allowing the formation of a compound with iron deficiencies double that possible where no such control exists. The structural relationships of pyrrhotite and smythite would be consistent with the proposal that such a control operates in the formation of smythite.

It has been demonstrated that there is no experimental evidence to show that greigite may form directly from solution. It seems that in every case there is evidence for the prior presence of mackinawite. It may therefore be that mackinawite acts in the case of greigite in a similar way as does siderite with smythite, being a necessary precursor to greigite since it assists in the organisation of the iron sites in the distorted spinel structure.

*Pyrite and marcasite*

Pyrite and marcasite have been synthesised from solution very many times. The most often quoted experiments were those of ALLEN, CRENSHAW and JOHNSON (1912), which were repeated in later years by LUNDQVIST (1947). No major advances have been made in the understanding of the mechanisms and conditions of formation of these compounds, apart from the fact that it has

been realised that they may be formed as well-crystallised forms at 25° C and 1 atmosphere pressure.

Pyrite and marcasite are dimorphs. Structurally, pyrite is cubic and marcasite orthorhombic, but both have their sulphur atoms paired in the so-called 'dumb-bell' arrangement. This is in agreement with considerations as to the probable oxidation states of the elements in pyrite and marcasite, which indicate that they are ferrous polysulphides. Although the formal lattice charge distributions in marcasite and pyrite are the same, the Mössbauer investigation by MORICE, REES and RICKARD (1969) demonstrates that marcasite is less ionic than pyrite, implying that the resultant charge on the marcasite sulphide ions is lower than that on the pyrite sulphide ions.

The chemistry of marcasite and pyrite formation has, in the past, been studied by rather irrational techniques. Apart from the higher temperature syntheses, most syntheses have required the presence of either ferric iron or oxygen, neither of which are involved in the pyrite or marcasite formulae. Widespread misapprehensions have arisen about these two minerals mainly through their natural abundance, their distinctive optical characters, and the unfortunate situation that arises from their chemistry in that errors in experimental technique, as, for example, in the faulty sealing of reaction vessels, tend to result in their formation.

Experiments in this laboratory show that, at temperatures below 150° C, in aqueous solutions and in the absence of oxidising agents, pyrite and marcasite will not form through the reaction between a dissolved ferrous salt and an aqueous sulphide. However, the addition of a sodium polysulphide solution to a solution of ferrous sulphate gave pyrite and/or marcasite under all conditions where the polysulphide did not decompose spontaneously. The results are shown in Fig. 1b.

Pyrite was synthesised at pH values between 4.4 and 9.5. At pH values below 4.4 the polysulphide solution decomposed to sulphur instantaneously. At pH values above 9.5 an unidentified compound was formed. This compound was air-stable, black and moderately ferromagnetic. It is believed to be a sodium iron sulphide, but its exact composition is unknown. X-ray data for this compound are shown in Table 5, and x-ray data for synthetic pyrite in Table 6.

Pyrite was minor to marcasite at pH = 4.4. As the pH increased, marcasite decreased, until, at pH = 9.5, marcasite was completely absent. This absence of marcasite at pH = 9.5 is important. It demonstrates that the product of the reaction between ferrous iron and polysulphide is pyrite, since the reaction pH was not restricted to pH = 9.5 but ranged over the whole spectrum of pH values from the initial pH of the ferrous sulphate solution to the final recorded pH of 9.5, as the polysulphide solution was added. The absence of marcasite in the products of such a reaction indicates that marcasite was not formed

Table 5. *X-ray data for unidentified compound*  
(possibly a sodium iron sulphide)

1		2	
dÅ	I	dÅ	I
8.22	vs	8.1	10
6.35	vs	6.1	4
5.39	vs	5.37	9
....	..	4.02	4
2.918	s	2.94	4
2.754	s	2.76	6
2.554	s	....	..
2.357	w	....	..
2.059	w	....	..
1.860	w	....	..
1.469	s	....	..

vs = very strong; s = strong; w = weak.

<sup>1</sup> Compound produced in this laboratory.

<sup>2</sup> Compound produced by ERD, EVANS and RICHTER, 1957.

Table 6. *X-ray data for synthetic pyrite*

Synthetic pyrite		Natural pyrite <sup>1</sup>	
dÅ	I	dÅ	I
3.34	mw	3.128	36
2.713	vs	2.709	84
2.424	s	2.423	66
2.212	s	2.212	52
1.918	ms	1.916	40
1.638	vs	1.633	100
1.565	mw	1.564	14
1.504	m	1.503	20
1.461	m	1.445	24
1.243	w	1.243	12
1.213	mw	1.211	14
1.183	mw	1.182	7
1.155	mw	1.155	6
1.106	mw	1.106	6
1.044	m	1.043	27
1.007	mw	1.006	8
0.9906	mw	0.9892	6
0.9555	m	0.9577	12
.....	..	0.9030	15

<sup>1</sup> A.S.T.M. 6-0710.

vs = very strong; s = strong; ms = medium strong; m = medium; mw = medium weak; w = weak.

during this reaction, even at the lower pH values. Therefore pyrite is the product of the reaction aqueous ferrous iron and polysulphide at all pH values from 2-3 to 9.5. Marcasite must have been formed through a separate, slower reaction that occurs more readily at lower pH values.

An examination of the chemistry of the various iron and sulphur species present in the reaction mixture indicates two conclusions:

- that, at more acid pH values, elemental sulphur is more likely to form, through the decomposition of the polysulphide solution,
- that the initial polysulphide solution must have contained relatively large amounts of sulphide ions, as well as the polysulphide ions.

However, the addition of sulphur to dissolved ferrous iron did not, at 25° C, result in any detectable reaction. The addition of sulphide to ferrous iron, on the other hand, has been demonstrated to result in the formation of mackinawite (above, under Mackinawite).

A sample of mackinawite was prepared, and checked for purity by the methods described above. The sample was then dried and inserted into a sealed evacuated pyrex tube with an equal weight of 'flowers of sulphur'. This analytical grade sulphur was shown by x-ray methods to be pure finely-divided rhombic sulphur. The products of this reaction at 150° C for 48 hours were major pyrite, with minor marcasite and pyrrhotite. At 100° C for 24 hours the products were marcasite and pyrrhotite, pyrite not being detected. At 70° C for 24 hours the products were major marcasite and sulphur. However, the large amount of remnant sulphur present obscured any other possible minor phase present.

Therefore the reaction between mackinawite and sulphur results in the formation of marcasite at low temperatures, with pyrite becoming more important at higher temperatures. This temperature dependence of marcasite and pyrite formation is in agreement with the conclusions of ALLEN, CRENSHAW and JOHNSON, and results from the transformation of marcasite to pyrite rather than the immediate formation of the more stable phase, since marcasite was present with the pyrite at the higher temperature. The formation of pyrrhotite is in agreement with the earlier mentioned results from the equilibration of mackinawite at elevated temperatures.

The results of these experiments indicated that the formation of marcasite depended on the the reaction between sulphur and a pre-existing iron sulphide, mackinawite. It is possible that the reaction between sulphur and greigite would give a similar result, since, as has been described above, the heating of mackinawite gives greigite rapidly, and therefore greigite may have also been involved in the reaction to form marcasite. However, this has not been confirmed.

The results of these experiments on the formation of marcasite were confirmed by adding a polysulphide solution to a mackinawite suspension at a pH of approximately 7. The products were pyrite and marcasite with rhombic sulphur. The similarity of this result with that from the reaction between dissolved ferrous iron and polysulphide indicates that similar reactions were proceeding: an oxidation of mackinawite by sulphur to give marcasite and an exchange reaction between the sulphide of mackinawite and polysulphide ion to give pyrite.

It has been suggested (VOLKOV and OSTROUMOV, 1957) that, because of the differing reactivities of the sulphur atoms in thiosulphate, thiosulphate may be instrumental in the formation of pyrite. However, experiments in this laboratory showed no reaction between dissolved ferrous iron, or mackinawite, and thiosulphate.

The reaction between thiosulphate, or polysulphide, and goethite results in the decomposition of the sulphur-bearing compounds with the formation of sulphur, no iron sulphides were detected.

The relationship that exists between the presence of elemental sulphur and the formation of marcasite is in agreement with the results of all the present experimental work and is consistent with most of the results from past investigations. The formation of marcasite will be favoured at lower pH values because elemental sulphur is more likely to be a reactant species under these conditions. However, elemental sulphur may exist metastably under a variety of conditions, since its rate of dissolution in low concentrations of solvents will be slow. Thus marcasite may be formed outside acid conditions. The reaction between mackinawite and elemental sulphur is relatively fast at 25° C in aqueous solutions, since water can act as a carrier for the elemental sulphur, whereas slightly higher temperatures are needed to complete the reaction between well-crystallised sulphur and mackinawite in experimental time.

The results of the reaction between sodium sulphide and goethite are shown in Fig. 1c. The results agree broadly with those of BERNER, inasmuch as mackinawite, with relatively broad lines and admixed with sulphur, was the major product of the reaction between pH = 7 and pH = 9. Below pH = 7 however, down to the pH of dissolution of the precipitate at pH = 4.4, marcasite was the major product. The marcasite was admixed with pyrite, but at these more acid pH values marcasite was dominant. Above pH = 9 the unidentified compound, possibly a sodium iron sulphide, which occurred under similar conditions in the ferrous iron-polysulphide experiments, was the major product. The formation of marcasite is consistent with the conclusions reached during the earlier experiments with polysulphide and ferrous sulphate described above. BURKIN and RICKARD (1959b) have examined the kinetics and mechanism of the sulphidation of goethite and have demonstrated that mackinawite is the primary product of such a process. The further reaction be-



tween mackinawite and sulphur or polysulphide will then result in the formation of marcasite and pyrite.

As the pH of the solution becomes more alkaline, sulphur becomes less apparent, until, under the conditions of formation of the sodium iron sulphide, elemental sulphur is not detected in the precipitate. At these pH values, sulphur reacts with excess sulphide and hydroxide in the solution to form polysulphide ions. This was confirmed by the colour of the solution and the formation of the sodium iron sulphide in an identical manner to that which occurs with polysulphide added directly to ferrous iron.

The formation of the polysulphides is not limited to these elevated pH values. Even though, at acid pH values, the polysulphide will tend not to form, since sulphur is stable, more polysulphide will form with the higher pH. However, the problem still remains as to the reason for the preservation of mackinawite in the pH = 7-9 region, where it would be expected that either pyrite or marcasite should form. This is explicable in exactly the same manner as the limitation of the rapid conditions of formation of greigite to lower pH values. If the surface of the mackinawite is covered with adsorbed hydroxide ions above pH = 6.5 (see under Mackinawite) then polysulphide ions would tend to be repelled. At more acid pH values surface hydrogen ions would tend to attract the polysulphide anions with the resultant formation of pyrite. However, the instability of polysulphide under these conditions would not allow major pyrite to form. The reaction, although it proceeds at all pH values, is experimentally slow at high pH values.

The formation of pyrite from the sulphidation of goethite at pH values of about 8 has been shown in the bacteriological experiments (RICKARD, 1969). At these higher pH values the initial product of the reaction was mackinawite, but pyrite was found to be the major product of the reaction after six months ageing. Organic matter may have catalysed this reaction.

The differences in conditions of formation of the dimorphic iron polysulphides, pyrite and marcasite, in aqueous solution, depend on differences in their mechanisms of formation. Whereas pyrite forms through the direct precipitation reaction between dissolved ferrous iron and polysulphide, marcasite depends on the reaction between sulphur and a pre-existing iron sulphides, in these experiments, mackinawite. It also seems that mackinawite can react with polysulphide to give pyrite. The reasons for the difference in mineral type resulting from these reactions is probably that, whereas the reactions of pyrite formation are polysulphide-sulphate or sulphide exchange reactions, the reaction between sulphur and mackinawite is essentially a solid state oxidation. Whereas the former may reach equilibrium under low temperatures and pressures the latter cannot, and the non-equilibrium phase, marcasite, is produced.

*Pyrrhotite*

The pyrrhotite group together with pyrite form the stable equilibrium phases of the iron-sulphur system. The interrelationships of the various members of the pyrrhotite group at high temperatures are well known, but the low temperature interrelationships are less well defined because of the high degree of uncertainty about the reaching of equilibrium. However, CLARK (1966) has succeeded in synthesising troilite and monolinic pyrrhotite through the reaction between iron and sulphur at temperatures as low as 45° C.

Pyrrhotite may be synthesised from aqueous solutions but this generally requires high temperatures (BERNER, 1964) or very long periods of time. As has been described above, pyrrhotites were formed during this investigation through the heating of greigite and smythite at temperatures as low as 180° C in very short periods of time. BERNER has shown that mackinawite is apparently converted to pyrrhotite, specifically troilite, at temperatures as low as 40–45° C, and as mentioned before, pyrrhotite reflections were isolated from a bacteriologically-produced mackinawite precipitate after nine months at 30° C. The formation of pyrrhotite, in the heating of mackinawite and sulphur during experiments to examine the formation of marcasite, was also probably caused by the transformation of mackinawite.

Insufficient data were provided by the pyrrhotites produced during these experiments to allow an accurate identification of the structure and composition to be made.

It therefore seems that the three sulphides, mackinawite, greigite and smythite are probably unstable with respect to pyrrhotite, and that pyrrhotite will be formed on prolonged ageing of these materials, or, more rapidly, on heating aqueous suspensions.

## DISCUSSION

This investigation has been essentially concerned with the six well-established mineral iron sulphides. As has been discussed when considering mackinawite, such forms as 'kansite', 'tetragonal FeS', 'amorphous FeS' and 'precipitated FeS' are considered to be identical with mackinawite at various degrees of crystal size. Furthermore, BERNER (1964) has shown that the common iron sulphides of sediments, 'hydrotroilite' and 'melnikovite' (in the non-Russian sense), are mixtures of one or more of the established sulphides and are not valid mineral species.

It is possible, however, that other iron sulphide forms occur initially in the mackinawite-producing reactions, such as BAAS BECKING'S (1956) disulphydryl iron. However, as pointed out by BERNER (1962b), there is no evidence for the existence of such a species and all the experimental evidence tends to preclude

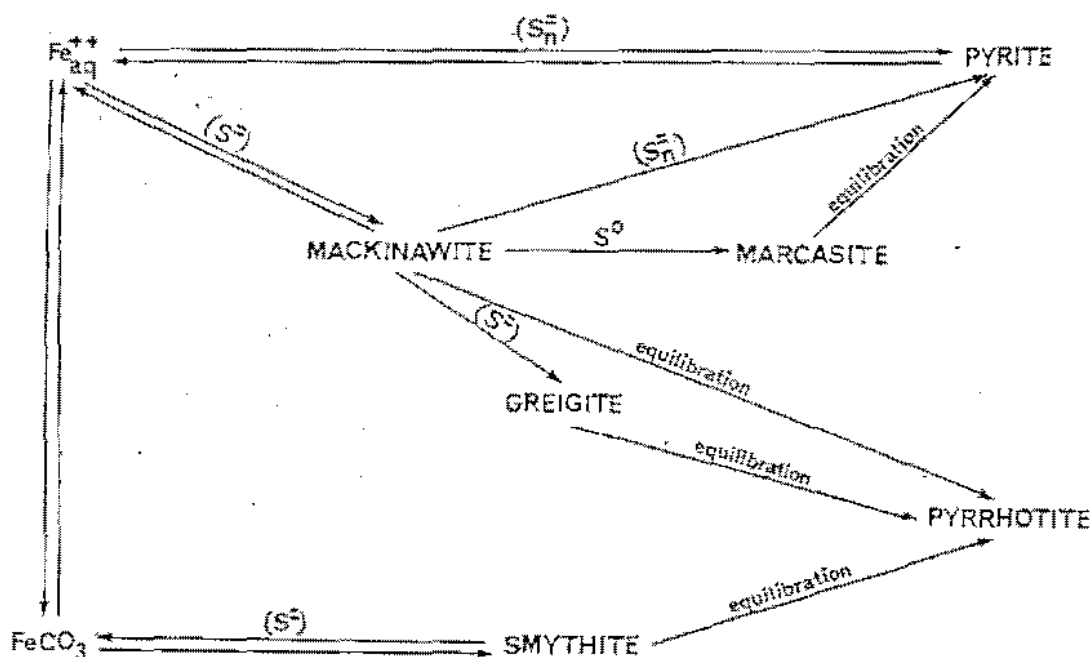
the possibility of its formation. Furthermore, the comparison of the iron sulphides with the iron oxides cannot be used to predict any possible transitory form of iron sulphide. For example, it would seem improbable that a form  $\text{FeSOH}$  could be produced analogous with  $\text{FeOOH}$ , since this would require the formation of a ferric sulphide hydrate. BURKIN and RICKARD (1969a) have demonstrated that, although ferric sulphide can be produced as a discrete chemical compound, its extreme instability makes it improbable that it is formed naturally. The comparison of greigite with magnetite has been demonstrated above to be erroneous.

It must be concluded that there is, at present, no evidence to suggest that a well-defined transitory phase predates the formation of mackinawite, and there is no obvious analogy that allows one to be predicted.

A diagrammatic summary of the major interrelationships of the iron sulphides in aqueous solutions is shown in Fig. 2. Of the 10 reactions involving iron sulphides, only three are reversible: the reactions between ferrous iron and sulphide to form mackinawite, ferrous iron and polysulphide to form pyrite, and ferrous carbonate and sulphide to produce smythite. The equilibration reactions and the mackinawite—greigite,—marcasite and —pyrite transformations are all irreversible.

Water apparently plays an essential role in the formation of mackinawite. This mineral has not yet been prepared in the absence of excess water, although the product of any dry reaction between iron metal and hydrogen sulphide has not been examined. It is possible that the water act as a carrier for sulphide ions and that metastable mackinawite is essentially a transition complex intermediate to the formation of pyrrhotite. The role of water in the formation of greigite and smythite is less clear. Greigite has been formed from mackinawite with adsorbed sulphide, which was partially dried and only contained about 10 per cent water. Smythite however, was not formed by the passage of gaseous hydrogen sulphide over dry ferrous carbonate; the reaction was too slow and only superficial sulphidation occurred at 25° C, after one week. Since the reaction between mackinawite and sulphur has been shown to give the more oxidised sulphide, marcasite, water may be important in the formation of greigite as a solvent for sulphide ions, catalysing a reaction which, when dry, may not result in the formation of greigite before the equilibration of mackinawite to pyrrhotite. It may also act to catalyse the formation of smythite, particularly by the removal of carbonate from the reaction surface.

Although KULLERUD (1967) has suggested that marcasite may be stabilised by the presence of bisulphide groups in its structure, evidence for this contention is still not forthcoming. It seems that water may be important in the formation of marcasite in that it allows a reaction between iron and sulphur to proceed rapidly at temperatures where the marcasite-pyrite transformation is relatively slow. This would explain why, in the examination of the Fe-S-O-H



$S^0$  = sulphur;  $(S^{2-})$  = sulphide;  $(S_n^{2-})$  = polysulphide

Fig. 2. Summary of the major iron sulphide interrelationships in aqueous solution (reactions involving ferric iron not considered).

system (KULLERUD, 1967), both marcasite and pyrite were formed, and not marcasite alone, at temperatures below about 400° C.

Throughout the above description of experimentation, results and interpretations, it is apparent that the rates of the reactions concerned are of extreme variability. From a geological point of view the problem of reaction rate is important since this determines the possible time of persistence of the various phases. The direct precipitation reactions, including the reactions between dissolved ferrous iron and sulphide or polysulphide giving mackinawite or pyrite, are extremely rapid. This is typical of many reactions involving dissolved ions. However, the reaction rate of heterogeneous reactions, particularly those involving one or more solid phases, is dependent on parameters other than simple concentration, temperature and pressure. Of particular importance is the surface area of the solid phase. Kinetically, the surface area of a solid phase is proportional to its activity in a heterogeneous system. Increase in surface area increases not only the area for reaction but also the area for removal of undesirable products. At the low temperatures and pressures of this experimentation and the relatively high concentrations of reactants (compared to most natural environments) the rate of precipitation of mackinawite and pyrite was far higher than the rate of crystallisation. Therefore extremely fine-grained products ensued, with enormous surface areas. This

was of particular importance with regard to mackinawite which can undergo two further reactions: the equilibration to pyrrhotite and the reaction with more sulphide to form greigite. Even under the conditions described above, the rate of equilibration of mackinawite to pyrrhotite is extremely slow, and therefore large crystals of mackinawite should be stable for geologically significant time spans at low temperatures.

The reasons for the inconsistent data that has been published as to the breakdown temperature of mackinawite may not only be compositional variations but also crystal size. Furthermore, the rate of reaction with respect to the formation of greigite has been shown above to be pH dependent and to be slow in alkaline conditions, even with the fine-grain sizes involved. Similarly the transformation of greigite and smythite to pyrrhotite is not observed under experimental conditions at 25° C and takes a relatively long time under heating at various temperatures. Thus greigite and smythite can be preserved under geological conditions for very long periods of time.

The marcasite-pyrite transformation is also dependent on crystal size with regard to the rate of the reaction. Under experimental conditions, as has been pointed out by ALLEN, CRENSHAW and JOHNSON (1912), and during this experimentation, marcasite tends to be preferentially formed under lower temperatures. It is assumed that, at the higher temperatures, marcasite is formed but is rapidly transformed to pyrite. However, experiments by KULLERUD (1967) indicate that this transformation occurs completely only above 400° C within the experimental time limitations. The inconsistencies of these results may be explicable in terms of crystal size being an important rate-controlling factor.

#### CONCLUSIONS

The six mineral sulphides of iron may be formed at low temperatures and in aqueous solutions from a variety of distinctive mechanisms. The nature of the mechanism determines the conditions of formation of the sulphide. The major controlling factor is the oxidation state of the sulphur-bearing reactant, since the oxidation state of the iron is ferrous in all these minerals. In particular, the presence of aqueous sulphide or polysulphide ion, or elemental sulphur, can decide the nature of the final product. The form of the pre-existing iron salt becomes important when it exerts some degree of structural control on the product. In this context the presence of ferrous carbonate or siderite to give smythite, and the possible relationship between the prior presence of mackinawite and the formation of greigite, are important.

The results suggest that the iron sulphide minerals may be used as indicators of the physico-chemical conditions prevailing in the environment at the time of their formation. However, since the fundamental requirements

for their formation may be satisfied in a variety of ways, the use of these minerals for this purpose is subject to a number of limitations.

The presence of mackinawite, for example, indicates low temperature and neutral to alkaline conditions in the environment at the time of its formation, since mackinawite re-reacts rapidly at more acid pH values or higher temperatures to form greigite or pyrrhotite. However, the presence of mackinawite discloses nothing about the nature of the reactant iron salt, and only indicates that polysulphides, or more oxidised sulphur species, were not available for reaction.

Smythite indicates low temperature conditions at the time of its formation. Its occurrence also implies that, at some stage, siderite was present in the system, either as a distinct mineral or as a transitory phase in the replacement of another rhombohedral carbonate.

The dependence of greigite formation on the prior presence of mackinawite, can be used to indicate that the environmental conditions before greigite formation were favourable for the production of mackinawite. However, since greigite can form from mackinawite at an acid pH at low temperatures or at higher pH values at slightly higher temperatures, its use as an environmental indicator is limited.

The formation of marcasite instead of pyrite demonstrates that the system must have contained a pre-existing iron sulphide, and that sulphur was available. It is probable that more acid conditions prevailed in the environment of marcasite formation since this would encourage the formation and preservation of sulphur. However, since sulphur can exist metastably under a variety of pH conditions, the presence of marcasite is inconclusive proof of the prevalence of acid conditions.

Pyrite and pyrrhotite form under such a variety of physico-chemical conditions, that little information can be gained from their presence apart from the obvious conclusion that the conditions were not suitable for the formation or preservation of the four other iron sulphide minerals.

Non-stoichiometry is common in the iron-sulphur system. Pyrite, marcasite, pyrrhotite and mackinawite are known to normally possess formulae diverging from simple whole number ratios of elements. The smythite and greigite formulae are also likely to vary from the ideal, although there are no published data to support this contention. However, there is no evidence as yet to suggest that the apparently metastable sulphides, mackinawite, greigite, smythite and marcasite, are not pure phases in the iron-sulphur system.

#### REFERENCES

- ALLEN, E. T., CRENSHAW, J. S. and JOHNSON, J., 1912. The mineral sulphides of iron. — *Am. Jour. Sci.*, vol. 33, pp. 169-235.

- BAAS BECKING, L. G. M., 1956. Biological processes in the estuarine environment. VI. The state of iron in the estuarine mud samples. — *Kon. Nederl. Akad. Wetensch. Amsterdam*, vol. 59, pp. 185-189.
- BERNER, R. A., 1962a. Tetragonal iron sulphide. — *Science*, vol. 137, p. 669.
- , 1962b. Experimental studies of the formation of sedimentary iron sulfides. — In (M. L. JENSEN, ed.). *Biogeochemistry of sulfur isotopes*. Yale Univ. Press.
- , 1964. Iron sulfides formed from aqueous solutions at low temperatures and pressures. — *J. Geol.*, vol. 72, pp. 293-306.
- , 1967. Thermodynamic stability of sedimentary iron sulfides. — *Am. Jour. Sci.*, vol. 265, pp. 773-785.
- BIRKS, L. C., BROOKS, E. J., ADLER, I. and MILTON, C., 1959. Electron probe analyses of minute inclusions of a copper-iron mineral. — *Am. Mineral.*, vol. 44, pp. 974-978.
- BOBROVNIK, D. D., 1967. (The sooty sulphide of iron). — *Miner. Sborn. Lvov. Univ.*, vol. 21, pp. 282-283. (In Russ., Eng. summ.).
- BURKIN, A. R. and RICKARD, D. T., 1969a. Preparation and properties of ferric sulfide. — *J. Chem. Soc. London* (in press).
- , 1969b. Kinetics and mechanism of the sulphidation of goethite. — *J. Chem. Soc. London* (in press).
- CHUKROV, F. V., GENKIN, A. D., SOBOLEVA, S. V. and UROOVA, G. V., 1965. Smythite from the iron ore deposits of the Kerch Peninsular. — *Geochem. Int.*, vol. 2, pp. 372-381.
- CLARK, A. H., 1966. Some comments on the composition and stability relations of mackinawite. — *N. Jb. Miner. Mh.*, vol. 10, pp. 300-304.
- ERD, R. C., EVANS, H. T. and RICHTER, D. H., 1957. Smythite, a new iron sulfide and associated pyrrhotite from Indiana. — *Am. Mineral.*, vol. 42, pp. 309-333.
- EVANS, H. T., MILTON, C., CHAO, E. C. T., ADLER, I., MEAD, C., INGRAM, B. and BERNER, R. A., 1964. Valleriite and the new iron sulfide, mackinawite. — *Art. 133, U. S. G. S. Prof. Paper*, 475-D, pp. 64-69.
- GRENVOLD, F. and HARALDSON, H., 1952. On the phase relations of synthetic and natural pyrrhotites ( $Fe_{1-x}S$ ). — *Acta Chem. Scand.*, vol. 6, pp. 1452-1469.
- JEDWAB, J., 1967. Minéralisation en greigite de débris végétaux d'une vase récente (Grote Geul). — *Bull. Soc. Belge. Geol.*, vol. 76.
- KOROLEV, D. F. and KOZERENKO, S. V., 1965. Experimental study of the formation of iron sulfides from solution. — *Doklady Akad. Nauk. SSSR.*, vol. 165, pp. 194-196.
- KOUYO, O., VUORELAJENEN, Y. and LONG, J. V. P., 1963. A tetragonal iron sulfide. — *Am. Mineral.*, vol. 48, pp. 511-524.
- KRAMN, T. P. and SUKHITSKAYA, N. Ya., 1965. (Melnikovite from the Kimmerian sediments of the Kerch Peninsular). — *Min. Sborn. Lvov. Univ.*, vol. 19, pp. 520-523. (In Russ., Eng. summ.).
- KULLERUD, G., 1967. Sulfide studies. — In (F. H. ABELSON, ed.). *Researches in Geochemistry*, vol. 2, pp. 286-321, Wiley, New York.
- LUNDQVIST, D., 1947. X-ray studies on sulfides of nickel and iron obtained by precipitation from water solutions. — *Arkiv. f. Kemi, Mineral. o. Geol.*, vol. 244, no. 23, pp. 1-7.
- MEYER, S. H., RIGGS, O. L., MCGLASSON, R. L. and SUDBURY, J. D., 1958, Cor-

- rosion products of mild steel in hydrogen sulphide environments. - Corrosion, vol. 14, pp. 69-75.
- MILTON, C. and MILTON, D. J., 1958. Nickel-gold ore of the Mackinan Mine, Snohomish County, Washington. - Econ. Geol., vol. 53, pp. 426-447.
- MORICE, J. A., REES, L. V. C. and RICKARD, D. T., 1969. Mossbauer analyses of the iron sulphides. - J. Inorg. and Nucl. Chem. (In press).
- RICKARD, D. T., 1968. Synthesis of smythite—rhombohedral  $Fe_3S_4$ . - Nature, vol. 218, p. 356.
- , 1969. The microbiological formation of iron sulphides. - Stockholm Contr. in Geol. (In press).
- SKINNER, B. S., ERD, R. C. and GRIMALDI, F. S., 1964. Greigite, the thiospinel of iron; a new mineral. - Am. Mineral., vol. 49, pp. 543-555.
- TAKENO, S., 1965. Thermal studies on mackinawite. - J. Sci. Hiroshima Univ., Series C, vol. 4, pp. 455-478.
- TAYLOR, L. A., 1968. A new occurrence of smythite,  $Fe_3S_4$ . - Geol. Soc. America, 1968 Annual Meeting, Mexico City. Program, with abstracts, p. 294.
- UDA, M., 1965. On the synthesis of greigite. - Am. Mineral., vol. 50, pp. 1487-1489.
- VOLKOV, I. I. and OSTROUMOV, E. A., 1957. The forms of sulphur compounds in the interstitial waters of the Black Sea sediments. - Geochem. Int., vol. 4, pp. 397-406.

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