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The Chemistry of the Hydrogen Sulfide and Iron Sulfide Systems in Natural Waters

JOHN W. MORSE, FRANK J. MILLERO, JEFFREY C. CORNWELL and DAVID RICKARD

ABSTRACT

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Reduced sulfur compounds are ubiquitous components of anaerobic sediments and euxinic marine environments. They are primarily produced through a complex net of both chemically and biologically mediated reactions. This results in a wide variety of dissolved and solid inorganic and organic products.

Much of the recent research effort in this area has focused on biogeochemical interactions and modelling sediment diagenesis. Several excellent reviews are available on these specific topics. However, relatively little attention has been paid to more basic inorganic chemistry of this system; the topic of this review.

INTRODUCTION

Authigenic sulfide minerals occur in marine sediments primarily as the result of either biologic processes or submarine hydrothermal activity. The biologic processes leading to sulfide mineral formation are characteristic of anoxic sediments and marine waters where biologic oxidation of organic matter is accomplished through bacterial reduction of sulfate and production of hydrogen sulfide. Subsequent biologically mediated reactions result in the formation of elemental sulfur and numerous reduced sulfur compounds. Under such conditions, iron oxide minerals are also reduced, producing Fe^{2+} ions. These ions can react with the hydrogen sulfide and other sulfur compounds to form a variety of iron sulfide minerals, many of which are thermodynamically metastable. Because iron is the most abundant sulfide-forming metal in most sediments these sulfides are dominantly iron sulfides, with pyrite being by far the most commonly occurring mineral.

Hydrothermally derived sulfide minerals occur in marine sediments in localized deposits, usually associated with active areas of crustal spreading. They often contain a much wider variety of sulfide minerals than those produced through biologic processes. While some of the material presented in this paper is germane to the chemistry of these hydrothermally derived minerals, our primary interest is in the chemistry of iron sulfide minerals characteristic of anoxic marine basins and sediments, and the chemistry of associated dissolved inorganic sulfur compounds. Readers interested in the genesis and chemistry of other sulfide minerals might wish to initially refer to Ribbe (1974) or Vaughan and Craig (1978).

Numerous papers have been written about the sulfur system in natural waters and associated diagenetic reactions in sediments (e.g., Berner, 1970, 1972, 1974, 1980, 1981, 1982; Gardner, 1973, 1974, 1979; Goldhaber and Kaplan, 1974; Goldhaber et al., 1977; Aller, 1980a; Davison, 1980; Jacobs and Emerson, 1982; Jacobs et al., 1985; Boulegue et al., 1982; Emerson et al., 1983; Berner and Westrich, 1985). The literature dealing specifically with the chemistry of hydrogen sulfide and

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David Rickard is a geochemist who obtained his first degree and PhD at Imperial College, London. His thesis topic was the chemical and microbiological formation of iron sulfides. After

his doctorate he moved to Stockholm, Sweden where he was a research fellow with the Swedish Natural Science Research (NERC) Council. After sojourns in the USA as a visiting professor of geochemistry and in Australia as a visiting scientist at the Baas Becking Laboratory, he was ap-

pointed as a research associate professor with NETC in Sweden and founded the Ore Research Group at Stockholm University. He directed that group until he took the Chair in Mining Geology at the Institute of Materials, University College, Newport Road, Cardiff CF2 1TA, U.K.

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related dissolved sulfur compounds, and iron sulfide minerals is widely scattered. Results are often inconsistent or presented in a manner which makes direct comparisons difficult. The primary objective of this article is to present the existing chemical data in a systematic manner. This information will be used as a basis for discussion of the occurrence of iron sulfide minerals and associated metals in common marine sediments and anoxic basins. It is hoped that this paper will not only serve as a useful reference to past work, but also clearly illustrate the many areas where further research is needed.

AN HISTORICAL PERSPECTIVE

Knowledge prior to the 20th century

Claudius Galen (130–200 AD), surgeon to the gladiators, was the author of over 500 medical treatises. His works were first translated into Latin in 1490, and first published in the original Greek in 1525. The editor of the Basle folio (Discori, 1557) of Dioscorides De Materia Medici (c. 50 AD), which dominated science in Europe for 1500 years, was much influenced by the new availability of Galen's works. In an expansive footnote (pp. 473–474) to Dioscorides' description of the mineral pyrite, he quotes Galen as noting the first description of the mineral by Archimedes (c. 287 BC).

The ancients knew pyrite only as a group of minerals that produced sparks when struck, hence the name from πυρ, fire. Theophrastus, however, in the Historia Plantarum (c. 300 BC) had described a mineral which was probably pyrite. The Elder Pliny used this name for pyrite in volume 36 of Historia Naturalis

(80 AD) and noted clearly the mineral's sulfurous nature and its brassy appearance. Dioscorides had previously noted that pyrite could contain copper.

This situation remained through Georgious Agricola's time. In Book 10 of his De Natura Fossilium (1546) he describes pyrite as a generic term for a group of minerals, but was apparently unaware that the mineral contained iron. He notes, however, in De Ortu et Causis Subterraneorum (1546) that pyrite is a mineral from which sulfur could be obtained.

J.G. Wallerius (1747) described pyrite as "sulfur ferro mineralisatum", and distinguished three different varieties including *kies* (pyrite), marcasite and *wasserkies*, a whiter form of marcasite. Marcasite had in earlier times been used as a synonym of pyrite. It derives from the Aramacean term *marquashitha* and was used by Arab scientists of the first millennium. In particular, it was used for pyrite by Jabir (Abu Mussa Djafor al Sofi) in the 8th century. Hatchett (1804) determined that both pyrite and marcasite were FeS_2, and this result was confirmed by Berzelius in 1819. Hauy (1801) had previously commented on "la dimorphie de fer sulfure".

Even at this early stage the relationship between pyrite and organic matter was noted. Bakewell (1815) described an experiment in which mouse droppings accidentally got into a jar of iron(II) sulfate. After standing for some time, in what must have been an interesting laboratory, the droppings were recovered with pyrite crystals. Bischoff (1832) described pyrite in recent mud, associated particularly, with plant stalk. He felt this demonstrated that pyrite formed in the presence of organic matter. Malaguti and Durocher (1852) first described pyrite from

recent marine sediments. They found it in bluish intertidal muds on the beach at Saint-Malo on the Bretagne coast.

Gautier (1893) stated that H_2S was one of the products of the putrefaction of organic matter, and that the pyrite observed replacing fossil bones and shells was precipitated by H_2S produced by decomposing organic matter. In 1895, Beijerink demonstrated the existence of a number of bacteria that were able to reduce sulfate to hydrogen sulfide, and the complex interaction between the diverse disciplines of chemistry, biology, and geology in pyrite formation was established.

Findings during the period 1900–1960

During the next half of the century no great progress was made concerning iron sulfide formation. Doss (1912a) described a mineral 'melnikovite' from the Melnikov Estates, Samara, Russia as a hydrogel from Miocene clays. He suggested that pyrite was formed by a transformation of troilite gel through melnikovite and ultimately pyrite. This work was generally ignored until about 1960, and melnikovite entered the literature as a microscopic description of a fine-grained, black melange of pyrite and an unknown substance from various ore deposits. American research was dominated by the work of Allen et al. (1912) who defined three phases in the sulfur–iron system; pyrite, marcasite, and pyrrhotite.

At the same time a considerable amount of information was being obtained from observation of pyrite and sulfides in the modern natural environment. Daubree (1875) had previously taken great delight in finding pyrite forming in timbers of the British royal yacht, Osborne. In 1875, he described globular pyrite from a Roman pavement situated beneath a conduit for mineral waters at Bourbon-les-Bains. Widespread reports of the globular forms of pyrite in sedimentary environments caused Rust (1931) to coin the name: "framboids" for them from the French framboise or raspberry. In later times it has

become recognized as one of the most common forms of pyrite in sediments.

The ubiquity and importance of pyrite in modern sediments were not recognized until the second half of the 20th century. Sugawara et al. (1953, 1954), were probably the first to comment on the importance of pyrite in sediments. Their work occurred over 50 years after the publication of the report of the Challenger expedition (Murray and Renard, 1891) which had noted the abundance of blue muds in the oceans, and where the surprising decrease of sulfate in the interstitial waters of marine sediments had been remarked upon by Murray and Irving (1895). It was not until the work of Berner in the 1960's that the chemistry, formation and significance of sedimentary iron sulfide formation began to be understood.

THERMODYNAMICS OF H_2S IN AQUEOUS SOLUTIONS

Solubility of H_2S in water and seawater

A critical aspect of understanding the occurrence and behavior of sedimentary iron sulfide minerals is the chemistry of the H_2S system and other inorganic sulfur compounds in dilute solutions and seawater. The chemistry of H_2S in seawater is not dissimilar to that of the carbonic acid system. The primary considerations are the solubility of the gas and the resulting diprotic dissociation.

$$H_2S(g) \rightarrow H_2S(aq) \qquad (1)$$

$$H_2S \rightarrow H^+ + HS^- \qquad (2)$$

$$HS^- \rightarrow H^+ + S^{2-} \qquad (3)$$
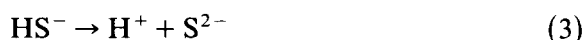
The most extensive measurements of the solubility of H_2S in water and seawater are the work of Douabul and Riley (1979). They made measurements over the temperature range of 2°–30°C and the salinity range of 0–40. Both increasing temperature and salinity were found to decrease the solubility of H_2S. The solubility of a gas in water and seawater can be represented by an equation

of the form used by Weiss (1974):

$$\ln K_0(\text{mol } 1^{-1} \text{ atm}^{-1}) =$$
$$-41.0563 + 66.4005(100/T)$$
$$+15.1060 \ln(T/100)$$
$$+S[-0.60583 + 0.379753(T/100)$$
$$-0.602340(T/100)^2] \tag{4}$$

where S is the salinity and T is the absolute temperature $(T = t°C + 273.15)$. Eq. 4 is valid when the fugacity of H_2S, f_{H_2S}, is at 1 atm. The concentration of H_2S, C^*, at other fugacities can be determined from:

$$C^*(\text{mol } 1^{-1}) = K_0 f_{H_2S} \tag{5}$$

The Henry's law constant $(H_S = 1/K_0)$ for pure water from 25° to 260°C can be estimated (Clarke and Glew, 1971) from:

$$\log H_S(\text{atm-kg } H_2O \text{ mol}^{-1})$$
$$= 102.325 - 4423.11/T$$
$$-36.6296 \log T + 0.13870T \tag{6}$$

The decrease in the solubility of H_2S with the addition of salt or the salting out is similar to other gases and can be represented by the Setchenow equation:

$$\ln(C_0/C) = \ln(\gamma_g) = kS \tag{7}$$

where C_0 and C are the solubilities in water and seawater, γ_g is the activity coefficient of

TABLE I

The salting out and activity coefficients of gases in seawater [1]

Gas	k	γ
H_2S	0.020	1.03
H_4C	0.092	1.16
CO_2	0.095	1.17
Ne	0.101	1.18
O_2	0.121	1.22
Ar	0.121	1.22
Kr	0.128	1.23
CH_4	0.129	1.24
N_2	0.131	1.24
CO	0.134	1.25

[1] Where $n(C_0/C) = \ln \gamma = kI$ (Millero and Schreiber, 1982).

the gas, k is the salting coefficient, and S is the salinity. The value of k at various temperatures can be determined from the salinity-dependent term of eq. 4. A comparison of k and γ_g for H_2S in seawater with other gases (Millero and Schreiber, 1982) is shown in Table I. The values for H_2S are lower than other gases, but similar to other weak acids (e.g., $k = 0.052$ and $\gamma_g = 1.09$ for H_3PO_4 in 0.7 m NaCl; Millero and Schreiber, 1982). Since the activity coefficient of H_2S in seawater is near unity, the interactions between the major sea salts and H_2S are quite small.

Ionization of H_2S in water and seawater

H_2S can dissociate into two other forms in aquatic solutions whose relative abundances are pH-dependent, in a manner similar to a diprotic acid. It is, therefore, important to have reliable constants for the ionization of H_2S in natural waters. The first ionization constant (K_1) has been measured by a number of workers. Almgren et al. (1976) have tabulated the values presented in Table II. They selected the mean value for $pK_1 = 7.01 \pm 0.02$. A problem with these results is that the extrapolations to infinite dilution were not made in a consistent manner.

The value of K_1 is related to observed concentrations and activity coefficients by:

$$K_1 = \gamma_{H^+}[H^+]\gamma_{HS^-}[HS^-]/\gamma_{H_2S}[H_2S]$$
$$= K_1^*(\gamma_{H^+}\gamma_{HS^-}/\gamma_{H_2S}) \tag{8}$$

Where $K_1^* = [H^+][HS^-]/[H_2S]$ is the stoichiometric constant and γ_i is the activity coefficient for species i. Millero [1983a] used the data of Almgren et al. (1976) in NaCl solutions and activity coefficients calculated using Pitzer (1973) equations to estimate a value for $pK_1 = 6.98 \pm 0.02$ at 25°C. This is in excellent agreement with the values obtained by Berner (1967), and Goldhaber and Kaplan (1975). His general conclusion was that the activity coefficient for HS^- is similiar to that of Cl^-.

TABLE II

Values of pK_1 for the ionization of H_2S in water at 25°C (from Almgren et al., 1976)

Value	Reference
7.07	Tumanova et al. (1957)
7.06	Loy and Himmelblau (1961)
7.05	Ringbom (1953)
7.04	Bruner and Zawadki (1909)
	Thiel and Gessner (1914)
7.02	Ellis and Golding (1959)
7.00	Goates et al. (1952)
6.00	Kubli (1946)
	Konopik and Leberl (1949)
	Pohl (1962)
6.98	Khodakovskii et al. (1965)
6.97	Wright and Maass (1932)
	Kapustinskii (1940)
6.96	Latimer (1952)
7.01 ± 0.02 (Mean)	

The experimental values for the ionization constant of HS^- in water(K_2) scatter widely (Goldhaber and Kaplan, 1975; see Table III). The mean value of the results is $pK_2 = 13.78 \pm 0.74$. Because activity coefficients for Na_2S and K_2S are not available, it is difficult to properly extrapolate the results to infinite dilution. If Na_2CO_3 is used as a model, values for pK_2 in pure water as high as 14.6 are estimated. Recent workers (Meyer et al., 1983) have suggested that the $pK_2 = 17.1$ of Gig-

TABLE IV

The speciation of H_2S in various ionic media at 25°C and pH = 8.1 [*1]

Species	H_2O (%)	0.7 m NaCl (%)	Seawater ($S = 35$) (%)
H_2S	7.05	4.00	3.00
HS^-	92.95	96.00	97.00
S^{2-}	$9.3 \cdot 10^{-5}$	$1.9 \cdot 10^{-4}$	$3.8 \cdot 10^{-4}$

[*1] Calculated using $pK_1 = 6.98$, 6.72, 6.60, and $pK_2 = 14.6$, 13.8, 13.8, respectively, in H_2O, NaCl, and seawater.

genbach (1971) may be more reliable than the lower values obtained by others.

Since S^{2-} probably forms strong complexes with divalent ions, pK_2^* in natural waters may be substantially lower than pure water. Fortunately, for most natural waters (pH = 6 to 9) the S^{2-} species is not very abundant. This can be shown from the fraction of various species in water, $0.7m$ NaCl, and $S = 35$ seawater (see Table IV).

The effect of temperature on the ionization of H_2S in water has been measured by Ellis and Milestone (1967), and Ellis and Giggenbach (1971) to 250°C, and Tsonopoulos et al. (1976) to 150°C, using spectrophotometric methods. The two studies are not in good agreement above 75°C, as shown in Fig. 1. These differences may be due to errors in the

TABLE III

Values of pK_2 obtained by various workers (from Goldhaber and Kaplan, 1975)

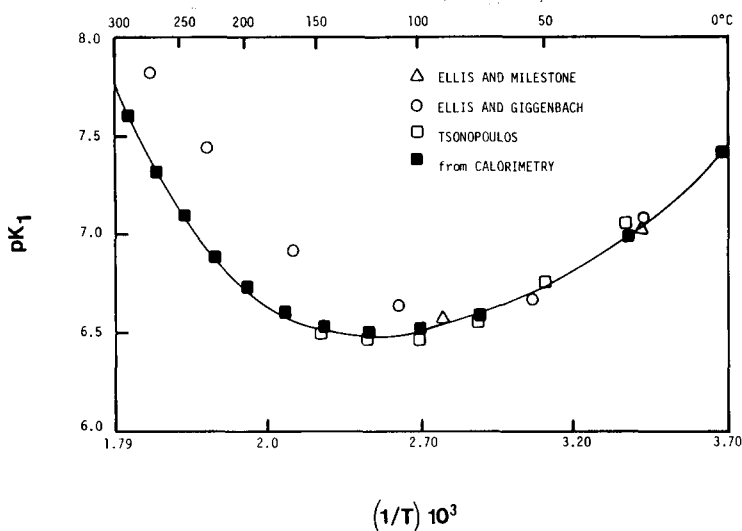| Temperature (°C)	pK_2	Method	Reference
20	12.44	Potentiometric	Kubli (1946)
	13.10	Colorimetric	Konopik and Leberl (1949)
	14.10	Spectrophotometric	Ellis and Golding (1959)
	14.15	Potentiometric	Widmer and Schwarzenbach (1964)
	14.0	Spectrophotometric	Ellis and Milestone (1967)
	17.1	Spectrophotometric	Giggenbach (1971)
25	14.92	Solubility	Knox (1906)
	13.78	Potentiometric	Maronny (1959)
30	13.85	Spectrophotometric	Muhammad and Sundarahm (1961)
	13.78 ± 0.74 (mean)		

Fig. 1. The effect of temperature on the pK$_1^*$ of H$_2$S in water (Ellis and Milestone, 1967; Ellis and Giggenbach, 1971; Tsonopoulos et al., 1976).

assignment of pH values (Barbero et al., 1982). Millero (1986) has estimated that the influence of temperature on pK$_1$ can be described by eq. 9 (solid line in Fig. 1):

$$pK_1 = 32.55 + 1519.44/T$$
$$- 15.672 \log T + 0.02722T \qquad (9)$$

Measurements of the pK$_1$ for H$_2$S in seawater have been made by Goldhaber and Kaplan (1975) and Almgren et al. (1976). The results of Goldhaber and Kaplan (1975) are on the NBS scale; while the results of Almgren et al. (1976) are on the total proton concentration scale (Hansson, 1973). The apparent constants (K') of Goldhaber and Kaplan (1975) are defined by:

$$K_1' = a_{H^+}[HS^-]_T/[H_2S]_T \qquad (10)$$

while the stoichiometric constants (K_1^*) of Almgren et al. (1976) are defined by:

$$K_1^* = [H^+]_T[HS^-]_T/[H_2S]_T \qquad (11)$$

Since the electrode system used by Goldhaber and Kaplan (1975) was not calibrated in seawater, it is not possible to adjust the two studies to a common pH scale.

The effect of salinity on the values of pK$_1^*$ determined by Almgren et al. (1976) at 5 and 25°C are shown in Fig. 2 (also given are the

25°C results of Goldhaber and Kaplan [1975]). The results have been fitted to equations of the form (Millero, 1986):

$$pK_1^* = pK_1 + AS^{1/2} + BS \qquad (12)$$

where the pK$_1$ is given by eq. 9 and A and B are T-dependent coefficients. From the results of Almgren et al. (1976), we obtain ($\sigma = 0.02$):

$$A = -0.2391 + 35.685/T \qquad (13)$$
$$B = 0.0109 - 0.3776/T \qquad (14)$$

From the results of Goldhaber and Kaplan (1975), we obtain ($\sigma = 0.02$):

$$A = -0.2288 + 45.598/T \qquad (15)$$
$$B = 0.0215 - 5.359/T \qquad (16)$$

The effect of temperature on the pK$_1^*$ and pK$_1'$ in seawater are similar to the thermodynamic values.

It should be pointed out that the activity coefficient equations of Pitzer (1973) can predict values of pK$_1^*$, in seawater at 25°C, that agrees to within 0.02 units. It is thus possible to determine reliable values of pK$_1$ in natural waters of known composition (Millero, 1986).

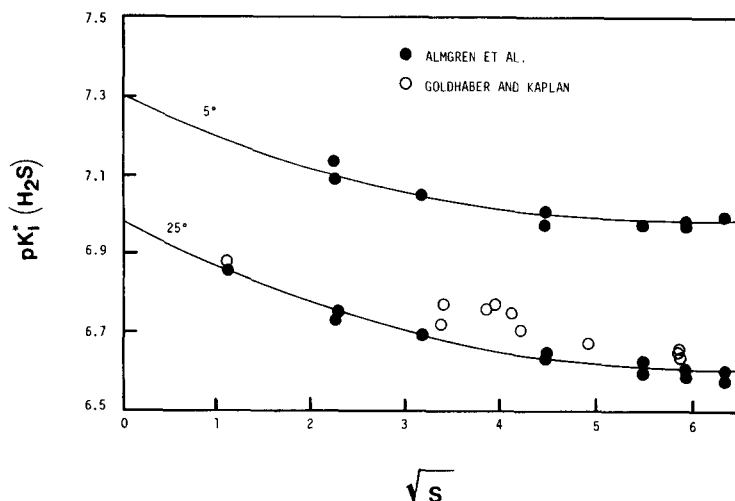The influence of pressure on K$_1$ for the

8

Fig. 2. The effect of salinity on the pK_1^* of H_2S in seawater at 5° and 25°C (Almgren et al., 1976; Goldhaber and Kaplan, 1975).

ionization of H_2S can be estimated from:

$$\ln(K^P/K^0) = -(\Delta V_1/RT)P$$
$$+ 0.5(\Delta K_1/RT)P^2 \qquad (17)$$

where ΔV_1 and $\Delta K_1 = -\partial \Delta V_1/\partial P$ are, respectively, the change in volume and compressibility for the ionization at 1 atm ($P = 0$). For pure water from 25° to 200°C, the values of ΔV_1^0 and ΔK_1^0 are given by (Millero, 1986):

$$-\Delta V_1^0 = 16.33 - 0.05738t + 7.9048 \cdot 10^{-4}t^2$$
$$(18)$$

$$-10^3\Delta K_1^0 = 2.18 - 7.6507 \cdot 10^{-3}t$$
$$+ 1.0540 \cdot 10^{-4}t^2 \qquad (19)$$

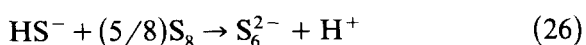For seawater ($S = 35$) the value of ΔV_1^* and ΔK_1^* from 0 to 40°C can be estimated from (Millero, 1986):
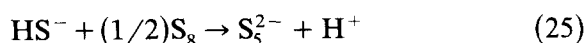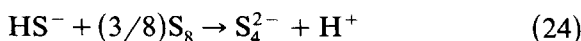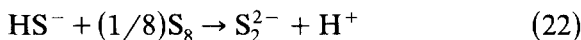
$$-\Delta V_1^* = 11.07 + 0.009t + 0.942 \cdot 10^{-3}t^2$$
$$(20)$$

$$-10^3\Delta K_1^* = 2.89 - 0.054t \qquad (21)$$

Estimates at higher temperatures can be made by assuming that the transfer of the solutes from water to seawater are independent of temperature and equal to the values of 25°C.

Formation of polysulfides

When H_2S is added to oxygen-free water, a clear solution is formed. If the solution contains O_2 and has a pH = 6 to 9, a straw or greenish color develops. The intensity of the color depends upon the initial concentration of elemental sulfur. Upon acidification, a whitish colloidal suspension forms and exhibits an adsorption band at 285 to 290 nm (U.V.). If the solution is diluted to $2 \cdot 10^{-4}$ M, the color disappears completely, but the UV adsorption is still observable. This is related to the formation of polysulfide ions S_n^{2-} through the interaction of S with HS^- (Schwarzenbach and Fisher, 1960; Teder, 1971; Rickard, 1975; Boulegue, 1976; Boulegue and Michard, 1978):

$$HS^- + (1/8)S_8 \rightarrow S_2^{2-} + H^+ \qquad (22)$$

$$HS^- + (1/4)S_8 \rightarrow S_3^{2-} + H^+ \qquad (23)$$

$$HS^- + (3/8)S_8 \rightarrow S_4^{2-} + H^+ \qquad (24)$$

$$HS^- + (1/2)S_8 \rightarrow S_5^{2-} + H^+ \qquad (25)$$

$$HS^- + (5/8)S_8 \rightarrow S_6^{2-} + H^+ \qquad (26)$$

The S_n^{2-} species can react with H^+ to form

TABLE V

Thermodynamic constants for the formation of poly-sulfides in water at 25°C [*1]

Reaction	pK
$(\frac{1}{4})S_8 + HS^- = S_3^{2-} + H^+$	12.5
$(\frac{3}{8})S_8 + HS^- = S_4^{2-} + H^+$	9.52
$(\frac{1}{2})S_8 + HS^- = S_5^{2-} + H^+$	9.41
$(\frac{5}{8})S_8 + HS^- = S_6^{2-} + H^+$	9.62
$HS^{4-} = S_4^{2-} + H^+$	7.0
$HS^{5-} = S_5^{2-} + H^+$	6.1
$H_2S = H^+ + HS^-$	7.0
$HS^- = H^+ + S^{2-}$	13.9

[*1] From Boulegue and Michard (1978) as tabulated by Emerson et al. (1983).

HS_n^- ions. For example:

$$S_4^{2-} + H^+ \rightarrow HS_4^- \qquad (27)$$

$$S_5^{2-} + H^+ \rightarrow HS_5^- \qquad (28)$$

reactions are potentially important (Boulegue and Michard, 1978). At a given pH the total reduced sulfur is given by (Jacobs and Emerson, 1982):

$$S_T = [H_2S] + [HS^-] + [S^{2-}] + [S_4^{2-}]$$
$$+ [HS_4^-] + [S_5^{2-}] + [S_6^{2-}] \qquad (29)$$

however, this may be only an approximation since Gillard (personal communication to Rickard, 1978) has found up to S_{15}^{2-} spectroscopically. Whenever the concentration of sulfur is greater than its saturation value, $\sim 5 \cdot 10^{-6}\ M$ (LaMer and Kenyon, 1947), the sulfur in solution should be great enough to give equilibrium concentrations of all the polysulfides.

The various forms of reduced sulfur as a function of pH can be calculated from this equation and the equilibrium constants for eqs. 22–28. These constants, which have been determined by Boulegue and Michard (1978) and tabulated by Emerson et al. (1983), are given in Table V. Since the constants have not been determined in seawater, it is necessary to make estimates of the activity coefficients of the various reduced ionic species for these solutions (Jacobs and Emerson, 1982).
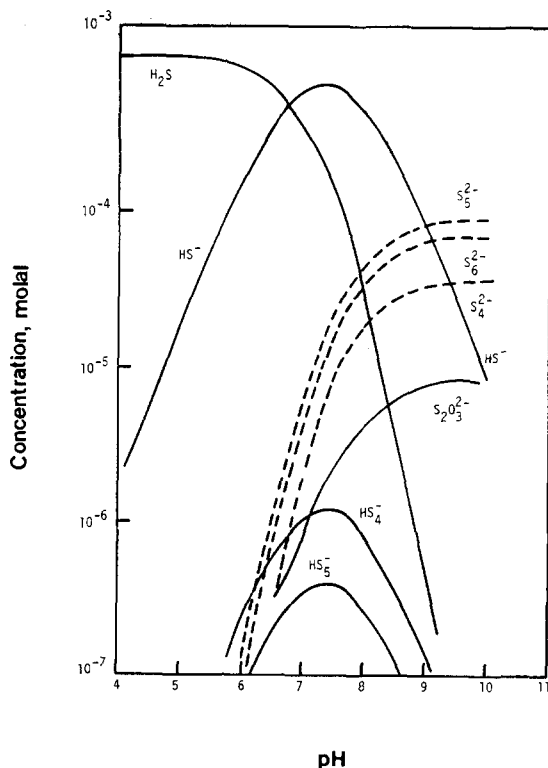
The various forms of reduced sulfur as a

Fig. 3. The various forms of reduced sulfur in water as a function of pH (Boulegue and Michard, 1978).

function of pH have been determined by Boulegue and Michard (1978). These results are shown in Fig. 3. At a pH = 8 the predominant forms are HS^-, S_4^{2-}, S_5^{2-}, S_6^{2-}, and H_2S, respectively, 84%, 8%, 3%, 3% and 2%. Boulegue et al. (1982) have recently determined the various forms of reduced sulfur (HS^-, S_n^{2-}, and $S_2O_3^-$) in pore waters.

It may be interesting to note that not all the bonds in the S_n^{2-} chain are of the same length. The shorter (= high energy) bonds are more susceptible to breakage. This is probably the reason for the increased stability of S_4^{2-}, S_5^{2-} as well as the formation of disulfides (e.g. $Fe^{2+} + {}^-S - S = S - S - S^- \rightarrow FeS_2 + {}^-S - S - S^-$).

Kinetics of oxidation of H₂S in aqueous solution

The oxidation of H_2S in natural waters has been studied by a number of workers (Ostlund and Alexander, 1963; Skopinstev et al., 1964;
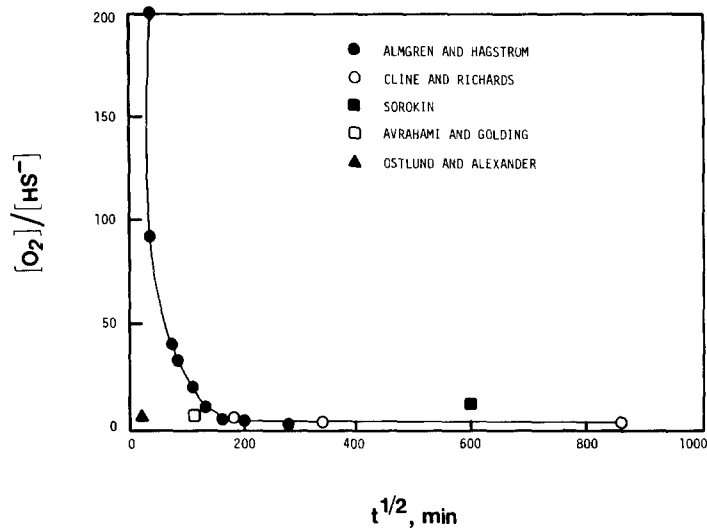
Fig. 4. The half times for the oxidation of H_2S as a function of the $[O_2]/[H_2S]$ ratio (Almgren and Hagstrom, 1974; Cline and Richards, 1969; Sorokin, 1971; Avrahami and Golding, 1968; Ostlund and Alexander, 1963).

Avrahami and Golding, 1968; Cline and Richards, 1969; Sorokin, 1970, 1971; Chen and Morris, 1972a; Boulegue, 1972; Almgren and Hagstrom, 1974; Gourmelon et al., 1977). The oxidation kinetics are complicated and the results of various workers are not in good agreement. The half times for the pseudo first-order rate equation (k_1 = first-order rate constant, t = time) of total H_2S

$$-d[H_2S]/dt = k_1[H_2S]_T \qquad (30)$$

vary from 0.4 to 65 h (Nriagu and Hem, 1978). This is related to the different conditions used in the various studies and possibly due to the different experimental methods used. This can be demonstrated by plotting the half time versus the initial O_2 to H_2S (or HS^-) ratio in the solutions shown in Fig. 4.

The overall oxidation of the total H_2S can be characterized by the general equation:

$$aH_2S + bO_2 \rightarrow \text{products} \qquad (31)$$
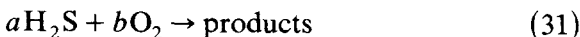
with an overall rate equation given by:

$$-d[H_2S]/dt = k_n[H_2S]^a[O_2]^b \qquad (32)$$

where k_n is the rate constant and $n = a + b$ is the overall order of the reaction. When $[O_2] \gg [H_2S]$, the rate equation has been found to be pseudo first-order in total $[HS^-]$:

$$-d[H_2S]/dt = k_1[H_2S]_T \qquad (33)$$

where $k_1 = k_2[O_2]$ and $t_{1/2} = \ln 2/k_1$.

Chen and Morris (1972a) made the most extensive studies on the effect of pH on the oxidation of H_2S. Below a pH of 6.0 the oxidation rate was very slow. They found induction periods to be 0.2 to 6 h and suggested that the reaction was preceded by a chain mechanism. A summary of the first-order rate constants (they actually suggested a reaction order of 1.34) as a function of pH is shown in Fig. 5. From a pH of 6 to 8.5 the rate equation increases, from 8.5 to 9.0 the rate decreases and increases again to a pH of about 11.0. At pH values above 11.0 the rate equation decreases again. The increase in the reaction rate from pH 6 to 8.5 (the range of most natural waters) is expended due to the ionization of $H_2S = H^+ + HS^-$. The rate constant (k) for the overall oxidation of H_2S (eq. 33) is related to the individual values for $H_2S(k_0)$ and $HS^-(k_1)$ by (Millero, 1986):

$$k[H_2S]_T = k_0[H_2S] + k_1[HS^-] \qquad (34)$$

The data of Chen and Morris (1972b) from pH = 6 to 8 gives $k_0 = 0 \pm 0.01$ M^{-1} h^{-1} and $k_1 = 2.5 \pm 0.1 \cdot 10^7$ M^{-1} h^{-1}. Thus, the oxidation is largely due to the oxidation of HS^- over the pH range of most natural waters. At low levels of sulfide Avrahami and Golding (1968) have suggested the rate de-
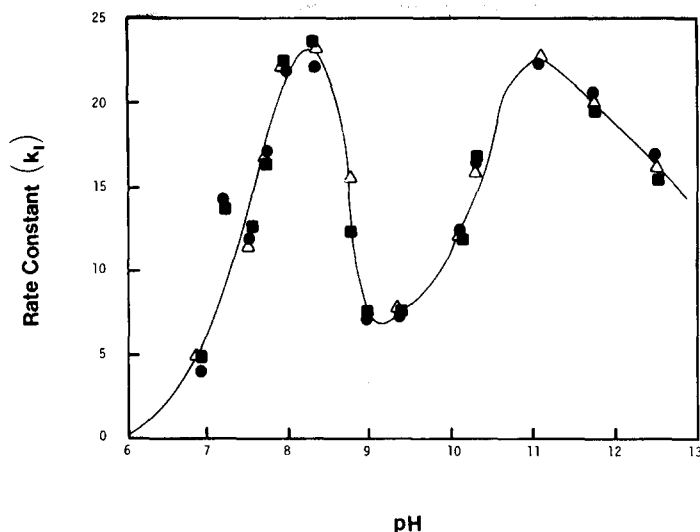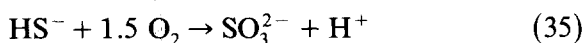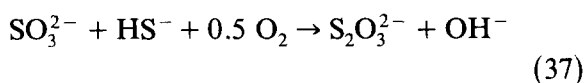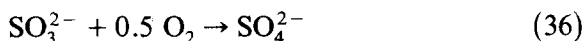
Fig. 5. The pseudo first order rate constant for the oxidation of H_2S in water as a function of pH at $25°C$ (Chen and Morris, 1972a).
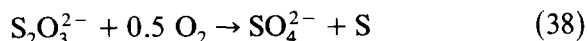
termining step is:

$$HS^- + 1.5\ O_2 \rightarrow SO_3^{2-} + H^+ \tag{35}$$

The SO_3^{2-} is rapidly removed from solution by:

$$SO_3^{2-} + 0.5\ O_2 \rightarrow SO_4^{2-} \tag{36}$$

$$SO_3^{2-} + HS^- + 0.5\ O_2 \rightarrow S_2O_3^{2-} + OH^- \tag{37}$$

The thiosulfate and elemental sulfur are oxidized slowly to SO_4^{2-}:

$$S_2O_3^{2-} + 0.5\ O_2 \rightarrow SO_4^{2-} + S \tag{38}$$

Measurements of HS^-, SO_3^{2-}, $S_2O_3^{2-}$, SO_4^{2-} during the oxidation of H_2S in seawater have been made by Cline and Richards (1969). Their results for a ratio of $[O_2]/[H_2S] = 4.0$ are shown in Fig. 6.
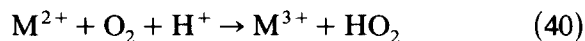
Chen and Morris (1972a) have discussed the effect polysulfides have on the oxidation of H_2S. At a pH = 7.0, the equilibrium calculations (Fig. 3) indicate that polysulfides are a significant fraction of total sulfides and at pH greater than 9 the polysulfides are dominant. Chen and Morris (1972a) suggest that these polysulfides may be responsible for the complex pH behavior above 8.0. Other factors such as dissociation of $HSO_3^- = H^+ + SO_3^{2-}$

(pH = 7.2) may be important. The reaction:

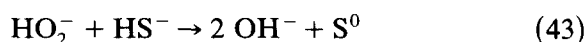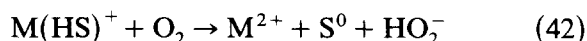$$HSO_3^- + S \rightarrow S_2O_3^{2-} + H^+ \tag{39}$$
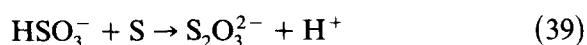
is also shifted to the right at high pH. Since these complications occur at pH's higher than commonly found in natural waters, they do not significantly affect the oxidation of H_2S in these waters.

Catalytic effects of metal ions in water on the oxidation of H_2S have been examined in detail by Chen and Morris (1972b) and Snavely and Blount (1969). The catalytic effects were found to follow the sequence $Ni^{2+} > Co^{2+} > Mn^{2+} > Cu^{2+} > Fe^{2+} > Ca^{2+} = Mg^{2+}$. The oxidation rate is increased 45 to 100 times in the pH range of 7 to 9 and the induction period is reduced (Chen and Morris, 1972b). Two possible mechanisms proposed by Chen and Morris (1972b) involve the formation of a free radical which activates the autooxidation:

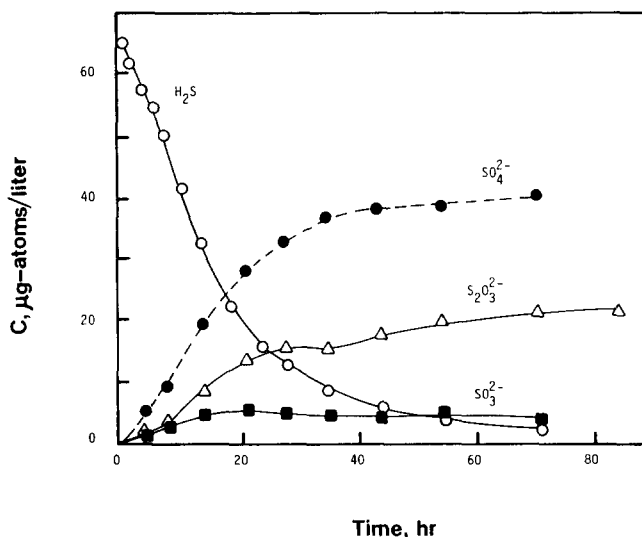$$M^{2+} + O_2 + H^+ \rightarrow M^{3+} + HO_2 \tag{40}$$

$$M^{3+} + HS^- \rightarrow M^{2+} + HS \tag{41}$$

or:

$$M(HS)^+ + O_2 \rightarrow M^{2+} + S^0 + HO_2^- \tag{42}$$

$$HO_2^- + HS^- \rightarrow 2\ OH^- + S^0 \tag{43}$$

Fig. 6. The various forms of sulfur formed during the oxidations of H_2S in seawater (Cline and Richards, 1969).

Organic compounds have also been found to influence the rate of oxidation of H_2S. Phenols, aldehydes, aniline, urea, and vanillin enhance the rate 2 to 20 times. EDTA, NTA, cyanide, citrate, peptone, and glycerol inhibit the oxidation by less than five times (Cline and Richards, 1969; Chen and Morris, 1972b). These studies clearly point out the importance of these catalytic effects in natural waters and may account for the large range of half times found by various workers in seawater. Further experiments are needed in seawater with natural levels or organics to examine these catalytic effects.

The effect of temperature (25–55°C) on the rate of oxidation of HS^- in water has been made by Avrahami and Golding (1968). They found an activation energy (ΔH) equal to 8.0 ± 0.4 kcal. mol^{-1}.

$$d \ln(k)/d(1/T) = -\Delta H/R \qquad (44)$$

For a 25°C increase in temperature the rate will increase by 3.5 ± 0.1 times. The effect of temperature on the oxidation of H_2S in seawater has not been determined.

MAJOR SEDIMENTARY IRON SULFIDE MINERALS

General characteristics

Authigenic iron sulfide minerals are common components of both recent and ancient marine sediments. The major iron sulfide minerals found in sediments are: "amorphous" FeS, which is possibly a mixture of fine-grained greigite and mackinawite (Berner, 1967); mackinawite, sometimes referred to as tetragonal sulfide or kansite, $Fe_{0.995-1.023}S$ (Ward, 1970); greigite, Fe_3S_4; and pyrite, cubic FeS_2. The "amorphous" FeS, mackinawite, and greigite often are transformed during burial diagenesis to pyrite. Rickard (1969) and Sweeney and Kaplan (1973) also have suggested that pyrrhotite ($FeS_{1.1}$) may be a precursor to pyrite formation. However, because of its rarity in marine sediments, it shall not be considered in detail in this paper. "Amorphous" FeS, mackinawite, and greigite have traditionally been considered soluble in hot HCl, while pyrite is not. They are, consequently, often referred to as "acid volatile sulfides" (later we shall critically examine this concept). Here they will be called metastable iron sulfides, since in the

presence of HS^- at concentrations above pyrite saturation (and an oxidizing agent) they transform to pyrite. However, when excess HS^- is not present, they can persist for long periods of time (e.g., Berner, 1974, 1981).

Amorphous FeS

Amorphous iron sulfide is produced by the reaction between hydrogen sulfide and ferrous iron in aqueous solutions at neutral pH. Its exact composition and characteristics have been the source of some disagreement over the years. Berner (1964a) found it to be amorphous by X-ray diffraction and more soluble than mackinawite (Berner, 1967). He suggested that it may be an extremely fine-grained mixture of mackinawite and greigite. Rickard (1969) found X-ray diffraction peaks characteristic of mackinawite and questioned if it was indeed distinct from mackinawite. W.A. Kornicker (pers. commun., 1985) has recently found that amorphous FeS transforms to mackinawite in a stirred aqueous solution with excess H_2S in a few days at room temperature. He has also found that drying can change many of its properties, indicating that it may exist primarily as a hydrate. However, Rickard (1969) found the strongest mackinawate peak in aqueous suspensions sealed in X-ray transparent capillaries after one hour. Sweeney and Kaplan (1973) found the initial precipitate had a narrow range in composition of from $FeS_{0.87}$ to $FeS_{0.92}$, while Berner (1964) and Rickard (1969) found a higher upper sulfur content of $FeS_{1.1}$. They attributed this to adsorption of hydrogen sulfide. It is possible that many of these disagreements may be the result of differences in the methods of preparation, causing different degrees of oxidation. For example, it is thought that Fe_3S_4, the thiospinel, may be produced by oxidation of FeS (Sweeney and Kaplan, 1973) as Fe_3S_4 (smythite) is derived from pyrrhotite oxidation (Taylor, 1970). One of us (Rickard) thinks that deviations from stoichiometry may be due to the incorporation of minor amounts of Fe(III),

S_n^{2-} or even O in the structure. However, the important point is that it is possible to produce under "reasonable" conditions an iron sulfide phase which, while having a similar composition to mackinawite, is extremely fine-grained and can be distinctly more soluble. As such, it is a probable precursor to mackinawite in sediments rich in organic matter and iron where reaction rates are high.

Mackinawite

Mackinawite is a tetragonal sulfur-deficient iron(II) sulfide, FeS_{1-x}. It occurs as both one of the major constituents of black sedimentary iron sulfides and in high temperature sulfide deposits.

Milton and Milton (1958) described the occurrence of a sulfide mineral, apparently valleriite from the Mackinaw Mine, Washington. Kuovo et al. (1963) described a phase with similar properties from Outukupu, Finland. Birks et al. (1959) showed that the Mackinaw material was copper deficient, and that its composition approached FeS. Kuovo et al. (1963) demonstrated that the Outukupu phase was a tetragonal iron sulfide. The phase was defined as mackinawite by Evans et al. (1964). Mackinawite is identical to many previously described synthetic iron(II) sulfide phases. In particular, "kansite" (Meyer et al., 1958) still creeps into the corrosion literature as a synonym for mackinawite. Berner (1962) first identified a synthetic phase as tetragonal iron sulfide and subsequently showed that it was a major constituent of "hydrotroilite", the black iron sulfide of sediments (Berner, 1964).

The mackinawite structure is similar to FeSe space group $p4/nmn$ (Kuovo et al., 1963) having an anti-PbO type structure (Fig. 7). It consists of a distorted cubic close-packed array of sulfur atoms with iron in some of the tetrahedral interstices but vacancies in the larger octahedral spaces. The structure was refined by Taylor and Finger (1971). Each Fe atom is at the center of a slightly distorted tetrahedron which shares edges to form sheets of tetrahedra. The sheets are stacked parallel
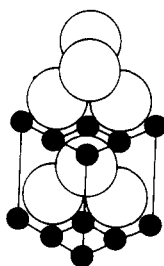
Fig. 7. The crystal structure of mackinawite.

to the c axis, giving a perfect (001) cleavage. The metal–metal distance is 2.602 Å across the shared edge and is close to the metal–metal distance in the body-centered cubic form of iron (2.59 Å). This indicates the importance of metal–metal bonding in mackinawite.

Mossbauer analyses have been presented by Bertaut et al. (1965), Morice et al. (1969), and Vaughan and Ridout (1970). Bertaut et al. (1965) claimed that mackinawite was non-metallic although their analyses revealed no ordered magnetic moment on the iron down to 1.7°K. Hulliger (1968) suggested this was due to an oxyhydroxide film on the particle surfaces. Vaughan and Ridout (1970) confirmed the absence of an internal field and showed that mackinawite contains low-spin Fe^{2+}. They suggested that the d electrons in mackinawite are extensively delocalized in the basal plane forming metallic bonds.

Taylor and Finger (1971) found crystallographic evidence confirming analytical suggestions that mackinawite was sulfur deficient. It is the first mineral to demonstrate this phenomenon. The considerable amount of metal–metal bonding in the structure, suggested by the very short metal–metal separation, might reduce the strength of the metal–metal bonds, and leave the sulfur unbonded. The unbonded sulfur could be compensated for by the omission of an occasional sulfur atom.

The composition of mackinawite should, therefore, be written FeS_{1-x}, rather than $Fe_{1-x}S$, indicating that it is a sulfur-deficient compound. The composition of pure FeS_{1-x} varies. Rickard (1969) gave a formula for the

synthetic phase of $FeS_{0.9}$. Clark and Clark (1968) found ratios of $FeS_{0.9}$ to $FeS_{0.946}$. Ward (1970) reviewed available data on mackinawite compositions and concluded that the ideal compositions could be represented by a formula near $FeS_{0.94}$. Even so, crystallochemical considerations could support the possibility of a range of compositions.

Synthesis of mackinawite has demonstrated that it is a pure phase in the iron–sulfur system. However, natural mackinawite commonly found in association with sulfide ores shows considerable contents of other transition metals.

Clark (1969) found that mackinawite from the Abessedo Mine, Vinhais, Portugal contained up to 9% chromium. This is the most chromium found in solid solution in any terrestrial sulfide mineral. The mackinawite was associated with native iron. Clark (1969) suggested a complete solid solution between troilite and daubreelite ($FeCr_2S_4$), the only well characterized ternary phase in the Cr–Fe–S system at high temperature. Bruns (1957) found a black ferromagnetic material, kansite, forming during the corrosion of chromium steel by hot H_2S. It had a Cr–Fe atomic ratio of between 0.6 and 1.1 and was associated with daubreelite. Thus it is possible that some sort of solid solution is possible in the Cr–Fe–S system involving mackinawite. However, it now seems probable that the chromium mackinawite formed during hydration of olivine, as proposed by Chamberlain et al. (1965) for the Muskox ultramafic complex.

Mackinawite may also contain significant amounts of Ni, Co, and Cu. In fact, it is now known to be a major ore mineral for Ni in some deposits. Vaughan (1969) found 18.7% Ni in mackinawite from the Vlakfontein nickel pipe in the South African Transvaal. Clark (1970) found more than 18.5% Co in mackinawite from the Kilembe deposit, Uganda. In the same paper, Clark quotes Zoka, Clark and Takeno as finding up to 8.8% copper. Earlier, Clark (1966) had suggested a formula $MS_{0.93} - MS_{0.96}$ (where M is the sum of the

metal cations) for mackinawite.

Vaughan (1970) suggested that mackinawite is able to accommodate cations in additional layers between S–S layers in tetrahedral coordination with sulfur. Such nonstoichiometry would affect the c parameter as observed previously (Vaughan, 1969). Ward (1970) suggested, by comparison with other metal chalcogenides with similar structures, that mackinawite accommodates excess cations in the large octahedral vacancies in the structure. It is apparent that mackinawite can take up a large content of cations with similar atomic radii to iron.

Greigite

Greigite is the thiospinel of iron, Fe_3S_4. It is a major constituent of black sedimentary iron sulfide and is found in younger sedimentary rocks. It was first defined by Skinner et al. (1964) from a Tertiary lacustrine sequence in California. Polushkina and Sidorenko (1963) had previously discovered the thiospinel of iron, but had named it melnikovite, thinking it identical to Doss's (1912a,b) original material. Unfortunately, Doss had used the term to describe a supposed magnetic form of FeS_2, and the name had suffered considerable abuse in the literature in the intervening years. Therefore, the commission on Minerals and Mineral Names of the International Mineralogical Association, approved the name greigite for the mineral. It is still referred to as melnikovite in modern Russian literature.

Greigite is the sulfur analog of magnetite and has a similar inverse spinel structure. The similarity of densities of greigite (4.06 g cm^{-3}) and type smythite (4.07 g cm^{-3}) reflect both the similarity in composition and the similarity of the sulfur packings: greigite has cubic close packing and smythite a mixture of cubic and hexagonal close packing. The unit cell of type greigite has $a_0 = 9.876$ A and consists of eight (Fe_3S_4) groups. Eight Fe atoms occur in tetrahedral sites and sixteen in octahedral sites.

Like the oxyspinel of iron, magnetite, greigite is highly ferrimagnetic (Hulliger, 1968). It also shows semiconducting properties. The Mossbauer spectrum of greigite has been the subject of several investigations (Uda, 1968; Morice et al., 1969; Coey and Spender, 1970; Vaughan and Ridout, 1970). The results show inconsistencies due to temperature and method of separation. The complex room temperature spectrum does not demonstrate the presence of Fe^{3+} ions, although two distinct iron sites are indicated. This apparently confirmed the formulation $Fe_3^{2+}S^0S_3^{2-}$ for greigite suggested by Berner (1967). Vaughan and Ridout (1970) confirmed the room temperature Mossbauer spectrum of Morice et al. (1969), but found that at 4.2°K it resolves into three sets of six-line magnetic hyperfine spectra. These are attributable to high spin Fe^{3+} iron in tetrahedral sites and octahedral sites, and high spin Fe^{2+} in octahedral sites. At higher temperatures the greigite spectrum collapses into a single quadrupole split line, due to the rapid relaxation of atomic spins. Vaughan and Ridout (1970) noted that magnetic reversals due to thermal motion take place in a shorter time than the Mossbauer transition.

The composition of type greigite is $Fe_{3.00}S_{4.00}$ (Skinner et al., 1964). Polushkina and Sidorenko (1963) give the composition of their melnikovite (identical to greigite) as $Fe_{2.83}S_4$ to $Fe_{3.11}S_4$. Black Sea concretions showed melnikovite with a composition of $Fe_{3.15}S_4$, and Doss's original material had a composition of $Fe_{1.84}S_4$. These data would suggest possible significant deviations from the ideal formula for greigite.

A large number of thiospinels are known. Extensive solid solutions exist between end member phases such as Co_3S_4 and Ni_3S_4. Cu may substitute for Co in Co_3S_4 to a marked extent and Ni_3S_4 may take up Fe up to the composition $FeNi_2S_4$, the mineral valleriite (Vokes, 1967). However, only small amounts of nickel (0.22%) have been detected in greigite (Radusinovic, 1966). Vaughan and Ridout (1971) note that low spin Fe^{2+} ions occur in

valleriite which is metallic, but high spin Fe^{2+} ions occur in greigite which is semiconducting. This would explain the lack of solid solution between $FeBi_2S_4$ and Fe_3S_4. Hulliger (1968) states that $CoFe_2S_4$ and $MnFe_2S_4$ are doubtful synthetic spinel phases, although $CuFe_2S_4$ is known. Thus, apart from Ni, Cu might be expected to be found in small quantities in greigite, but not Co and Mn.

Pyrite

The pyrite structure was one of the earliest analyzed by the X-ray diffraction model (Bragg, 1914). Pyrite is an iron(II) polysulfide (Morice et al., 1969). Its structure is cubic (space group Pa3 and Z = 4) with metal atoms at the corners and face centers of the cube and dumbell-shaped polysulfide anions $(S_2)^{2-}$ at the cube center and at the midpoints of the cube edges (Fig. 8). The midpoint of the S_2-group occupies the Cl-sites of an NaCl structure, while the Fe atoms occupy the Na-positions. The S_2^{2-} groups are oriented such that their axes are parallel to four non-intersecting body diagonals of the cubic space lattice.
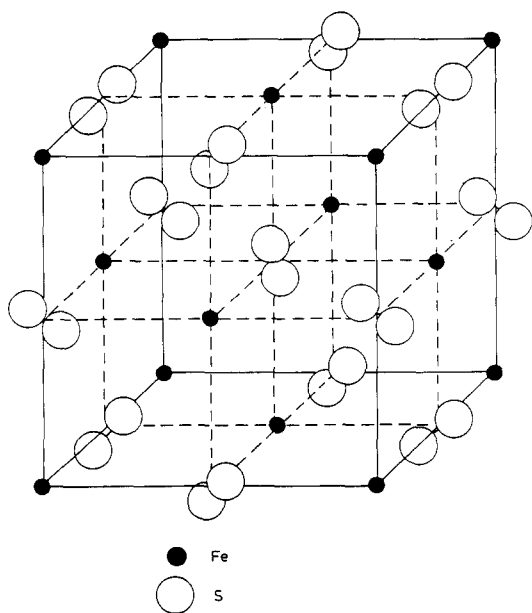

Fig. 8. The crystal structure of pyrite.

The cations are coordinated to six sulfur atoms in a slightly distorted octahedron. The anion octahedra share corners. Each sulfur atom is equidistant from three cations which form a triangular planar group to one side. The other sulfur atom of the pair is on the other side resulting in a distorted tetrahedral coordination for sulfur.

Various correlations of structural parameters with chemical composition have been proposed. Lepp (1956) claimed that lower cell-sizes for pyrite synthesized at lower temperatures were indicative of lower sulfur contents. Studies of the bravoite group (intermediates in the FeS_2-CoS_2-NiS_2 system) have established that cell-size increases with Co and Ni content (Bannister, 1940; Peacock and Smith, 1941; Vaughan, 1968).

Bither et al. (1968) developed a qualitative bonding model for pyrite-type compounds, based on electrical and magnetic properties. Natural pyrite may exhibit p-type or n-type semiconduction (Agaev and Emujazov, 1963) due to minor impurity elements or deviation from stoichiometry (Voitkevitch et al., 1965) and attempts have been made to link this to mode of origin. Synthetic pyrite exhibits n-type semiconduction. Bither et al. (1968) showed that pyrite becomes a metallic conductor if the CoS_2 content is greater than 0.1%.

Hulliger (1968) and Nickel (1968) pointed out the importance of the low spin d^6 configuration in the stability of pyrite-type compounds. The low spin d^6 configuration of pyrite is very stable.

Many pyrite analyses have recorded sulfur iron ratios at variance with the 2.0 of the ideal formula. Kullerud and Yoder (1959) suggested that the composition of pure pyrite is $FeS_{2.00}$, and that variations from this figure are either within experimental error or caused by the presence of impurities.

A large number of sulfides exist, both naturally and synthetically, which are isostructural with pyrite. Thus, pyrite analyses should, and commonly do, record the presence of significant amounts of trace elements, par-

ticularly related transition metals and arsenic. However, it is often difficult to distinguish between matter in true solid solution in the pyrite structure and impurities contained in discrete minerals. Particular confusion may arise from arsenic (possibly present as arsenopyrite), copper (often as chalcopyrite), and gold (usually as the native element).

Considerable data are available for the Co and Ni contents of pyrite. Up to 13.9% Co has been found in pyrite (Fleischer, 1955) but many cobaltian pyrites are zoned. Fleischer (1955) concludes that there is good evidence that sedimentary pyrite generally has Co and Ni.

IRON SULFIDE MINERAL REACTIONS IN AQUEOUS SOLUTIONS

Solubility of iron sulfide minerals

Berner (1967) and Doyle (1968) have performed the only laboratory studies of the solubility of metastable iron sulfides. Berner used synthetic phases, while Doyle used a natural sediment to try to establish which phase was controlling iron sulfide solubility based on Berner's studies. It is not possible from these studies to directly assess the influences of such important natural variables as temperature, pressure, and salinity on the solubility of these phases.

Another problem is that the iron sulfide solubility values are directly dependent on the constants used for hydrogen sulfide solubility and dissociation. Earlier in this paper we pointed out the difficulties in obtaining a precise value for the second dissociation constant of hydrogen sulfide. Based on similar considerations, Goldhaber and Kaplan (1975) suggested it was possible to avoid the problems associated with the second dissociation constant for hydrogen sulfide by considering the solubility controlling reaction to be:
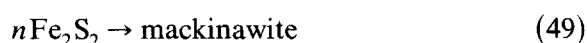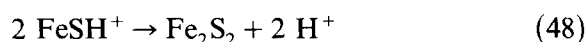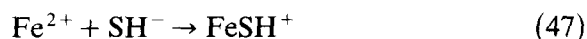
$$H^+ + MS \rightarrow M^{2+} + HS^- \qquad (45)$$

It is then possible to write the solubility prod-

uct as:

$$K_{sp} = [M^{2+}][HS^-]/[H^+] \qquad (46)$$

which avoids use of $K_2(H_2S)$. The recent work of Taylor (1980) on the mechanism of mackinawite formation has added support to this type of approach to solubility. He has suggested that the formation of mackinawite (and probably amorphous iron sulfide) proceeds by the following series of reactions which do not involve H_2S.

$$Fe^{2+} + SH^- \rightarrow FeSH^+ \qquad (47)$$

$$2\,FeSH^+ \rightarrow Fe_2S_2 + 2\,H^+ \qquad (48)$$

$$n\,Fe_2S_2 \rightarrow \text{mackinawite} \qquad (49)$$

Goldhaber and Kaplan (1975) suggested using total ion concentrations rather than calculated activities to express solubility. While we agree that direct analytic data should always be reported in such systems, it is also important to note that use of total concentrations rather than ion activity products precludes the comparison of the relative saturation states of different waters and, in fact, limits the use of the solubility data to waters of nearly the same composition as those in which the solubility measurements were made. The solubility of the iron sulfide minerals are, consequently, presented here as activity products which were calculated based on the data of Berner (1967), the solubility of H_2S of Douabul and Riley (1979), our selected value for $pK_1(H_2S) = (6.98)$, and $\gamma_{Fe^{2+}}$ calculated from the Davies equation. All values are for 25°C and 1 atm pressure.

Amorphous FeS and mackinawite:

$$H^+ + FeS \rightarrow Fe^{2+} + HS^- \qquad (50)$$
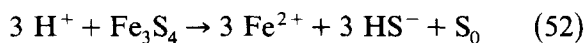
$$K_{sp} = a_{Fe^{2+}} a_{HS^-}/a_{H^+} \qquad (51)$$

$$K_{spA\text{-}FeS} = 1.14(\pm 0.23) \cdot 10^{-3}$$

$$pK_{A\text{-}FeS} = 2.95(\pm 0.09)$$

$$K_{sp\,mack} = 2.86(\pm 0.57) \cdot 10^{-4}$$

$$pK_{mack} = 3.55(\pm 0.09)$$

Greigite:

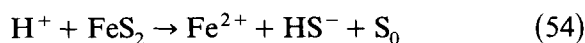$$3\,H^+ + Fe_3S_4 \rightarrow 3\,Fe^{2+} + 3\,HS^- + S_0 \qquad (52)$$

$$K_{sp\,greig} = \left[a_{Fe^{2+}} a_{HS^-}/a_{H^+} \right]^3$$

$$= 1.50(\pm 0.54) \cdot 10^{-13} \qquad (53)$$

$$pK_{greig} = 12.85(\pm 0.15)$$

The solubility product of pyrite has also been calculated using this approach by Emerson et al. (1983):

$$H^+ + FeS_2 \rightarrow Fe^{2+} + HS^- + S_0 \qquad (54)$$

$$K_{sp\,pyrite} = a_{Fe^{2+}} a_{HS^-}/a_{H^+} = 3.98 \cdot 10^{-17} \qquad (55)$$

$$pK_{pyrite} = 16.4$$

In order to apply these thermodynamic activ-

ity products to natural waters it is necessary to know ion activity coefficients in these solutions. Values are presented for seawater of $S = 35$ and a "typical" anoxic sediment pore water in Table VI. It is important to note that major discrepancies exist in the estimates for the Fe^{2+} activity coefficient and that $\gamma_{HS^-} \simeq \gamma_{Cl^-}$.

Davison (1980) has used the $Fe^{2+} - HS^-$ solubility approach to critically evaluate the observed compositions of a number of anoxic waters in terms of ferrous sulfide solubility. His calculated activity products for the different waters along with their saturation state relative to the different metastable iron sulfides, based on the values calculated here, are presented in Table VII. A wide range of

TABLE VI

The activities of ions in seawater and a "typical" anoxic pore water

Component	M	γ	a	M	γ	a	Δγ	a_{pw}/a_{sw}
Na^+	0.486	0.69	0.34	0.486	0.70	0.34	0.00	1.0
K^+	0.0186	0.62	0.012	0.0186	0.63	0.012	0.00	1.0
H^+	$\sim 10^{-8}$	0.70	$\sim 7 \cdot 10^{-9}$	$\sim 10^{-7}$	0.95	$\sim 10^{-7}$	0.25	14
NH_4^+	~ 0	0.61	~ 0	~ 0.0005	0.62	0.00031	0.01	∞
Mg^{2+}	0.0547	0.25	0.014	0.0547	0.26	0.014	0.01	1.0
Ca^{2+}	0.0107	0.22	0.0024	0.0107	0.24	0.0026	0.02	1.1
Sr^{2+}	0.00009	0.22	$2 \cdot 10^{-5}$	?	0.23	–	0.01	–
Ba^{2+}	–	0.19	–	–	0.20	–	0.01	–
Fe^{2+}	~ 0	0.17	~ 0	$5 \cdot 10^{-6}$	0.17	$8.5 \cdot 10^{-7}$	0.00	∞
Cl^-	0.566	0.63	0.36	0.566	0.63	0.36	0.00	1.0
F^-	0.00007	0.34	$2 \cdot 10^{-5}$	0.00007	0.33	$2 \cdot 10^{-5}$	-0.01	1.0
Br^-	0.00087	0.65	0.00057	0.00087	0.65	0.00057	0.00	1.0
HCO_3^-	0.00193	0.54	0.0010	~ 0.056	0.53	0.030	-0.01	30
I^-	–	0.69	–	?	0.69	–	0.00	–
OH^-	$\sim 10^{-6}$	0.24	$\sim 2 \cdot 10^{-7}$	$\sim 10^{-7}$	0.23	$\sim 2 \cdot 10^{-8}$	-0.01	0.1
$B(OH)_4^-$	0.00009	0.47	$4 \cdot 10^{-5}$	0.00009	0.46	$4 \cdot 10^{-5}$	-0.01	1.0
$H_2PO_4^-$	–	0.40	–	–	0.39	–	-0.01	–
SO_4^{2-}	0.0297	0.085	0.0025	~ 0	0.084	~ 0	-0.001	0
CO_3^{2-}	0.0020	0.029	$5.8 \cdot 10^{-5}$	–	0.028	–	-0.001	–
HPO_4^{2-}	$\sim 10^{-7}$	0.051	$\sim 5 \cdot 10^{-9}$	~ 0.0005	0.049	$2.45 \cdot 10^{-5}$	-0.001	4900
PO_4^{3-}	–	$4.4 \cdot 10^{-6}$	–	–	$4.1 \cdot 10^{-5}$	–	$3.7 \cdot 10^{-5}$	–

Legend
$\Delta\gamma = \gamma_{pw} - \gamma_{sw}$
Bicarbonate based on charge balance.
All γ's except Fe^{2+} based on Millero and Schreiber (1982).
γ for Fe^{2+} is based on Davison (1979). It is not reliable in pore waters due to unknown interactions with polysulfides, organics etc. In addition, major disagreements exist about appropriate values for the hydroxy complex (e.g. also see Morel and Morgan, 1972; Kester et al., 1975; Baes and Mesmer, 1976).

TABLE VII

Fe^{2+}-HS$^-$ activity products and saturation states (Ω) relative to different metastable iron sulfides in anoxic waters

Site	$a_{Fe^{2+}} a_{HS^-}^{*1}$ ($\times 10^4$)	$\Omega_{amorph.}$	$\Omega_{mack.}$	$\Omega_{greig.}$
Skejennungen	87.1	7.64	30.5	$4.4 \cdot 10^6$
Esthwaite	25.7	2.25	8.98	$1.1 \cdot 10^5$
Abereiddy	11.5	1.01	4.01	$1.0 \cdot 10^4$
Clear Lake	5.62	0.49	1.97	1200
Black Sea	1.41	0.12	0.49	18.7
Cariaco Trench	0.37	0.03	0.13	0.34
Lake Nitinat	0.16	0.01	0.06	0.03

*1 See Davison (1980) for detailed discussion.

saturation states is observed, from waters that are over 7 times supersaturated with respect to mackinawite to waters which are only 3% of saturation relative to greigite. Clearly, it is not possible to make any sweeping generalizations about what iron sulfide phase controls the Fe^{2+} − HS$^-$ activity product in anoxic waters.

A number of studies have been conducted in order to try to establish which iron sulfide phase controls pore water chemistry in anoxic sediments. Doyle (1968) used sediments from Linsely Pond, Connecticut, in which mackinawite was the dominant phase, in laboratory experiments. He obtained indirect results in good agreement with the solubility of mackinawite predicted from Berner's (1967) data. Doyle suggested that mackinawite should be stable relative to greigite in freshwater sediments. However, this cannot be an absolute generalization since both greigite and pyrite have been observed forming in freshwater and non-marine sediments (e.g., Dell, 1972, 1975; Browne and Wood, 1974). Boulegue et al. (1982) found that for pore waters of the Great Salt marsh of Delaware the Fe^{2+} concentrations in the depth range of 50–54 cm were close to those predicted for equilibrium with amorphous iron sulfide. At shallower depths (10–14 cm), they were close to the value predicted for greigite equilibrium. This is consistent with the less reducing conditions

found at the shallower depths. Jacobs and Emerson (1982) have also found evidence for pore water equilibrium with greigite in sediments from Saanich Inlet. It is important to keep in mind that frequently several iron sulfide phases can be present in close association in reducing sediments and that the concept of pore waters being in equilibrium with a given phase should be used with caution.

Iron sulfide reaction pathways and kinetics

The previous discussions have alluded to the fact that formation of the sedimentary iron sulfide minerals involves a complex set of chemical reactions in which kinetics plays an important role. Berner (1970) was among the first to succinctly summarize the major processes involved in the formation of sedimentary iron sulfides, for typical anoxic marine sediments overlain by oxic waters. His three major steps in the formation of pyrite were: (1) reduction of sulfate to hydrogen sulfide by bacteria; (2) reaction of the hydrogen sulfide with iron minerals to form iron monosulfides; (3) reaction of the iron monosulfides with sulfur to form pyrite. Berner considered the most important factors influencing this set of reactions to be the availability of metabolizable organic matter for bacterial reduction of the sulfate, diffusion of sulfate into the sediment, the concentration and reactivity of iron minerals, and the production of elemental sulfur. His experimental work confirmed the earlier hypothesis of Ostroumov (1953) that the net reaction for formation of pyrite is:

$$FeS + S^0 \rightarrow FeS_2 \tag{56}$$

Since Berner (1970) outlined these basic processes considerable additional work has been done on the details of the reactions involved and what circumstances may result in different reaction paths being followed (see Fig. 9 for general summaries). Rickard (1974) and Pyzik and Sommer (1981) have investigated the interaction of hydrogen sulfide with goethite, which is believed to be the most
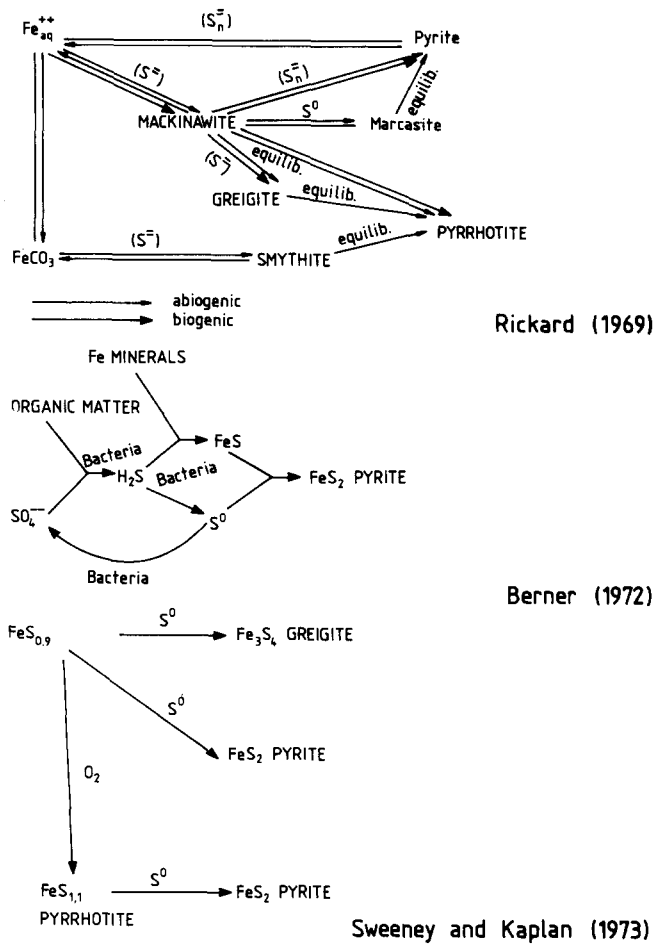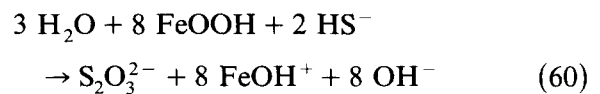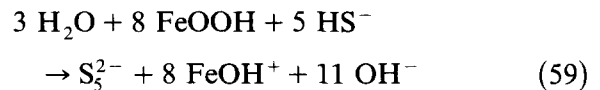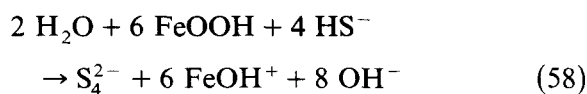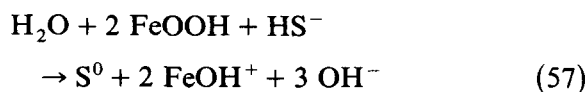
Fig. 9. The proposed reaction paths for pyrite formation in anoxic sediments of Rickard (1969), Berner (1972), and Sweeney and Kaplan (1973).

important sedimentary source for the iron involved in the formation of iron sulfides. Here we will concentrate on the more recent study of Pyzik and Sommer (1981) which incorporated many of Rickard's (1974) findings into a more mechanistic model. Their results and model are applicable to the interaction of hydrogen sulfide with goethite over the pH range of 7 to 8.5. They pointed out that there are at least four possible reactions which could be important:

$$H_2O + 2\ FeOOH + HS^-$$

$$\rightarrow S^0 + 2\ FeOH^+ + 3\ OH^- \tag{57}$$

$$2\ H_2O + 6\ FeOOH + 4\ HS^-$$

$$\rightarrow S_4^{2-} + 6\ FeOH^+ + 8\ OH^- \tag{58}$$

$$3\ H_2O + 8\ FeOOH + 5\ HS^-$$

$$\rightarrow S_5^{2-} + 8\ FeOH^+ + 11\ OH^- \tag{59}$$

$$3\ H_2O + 8\ FeOOH + 2\ HS^-$$

$$\rightarrow S_2O_3^{2-} + 8\ FeOH^+ + 8\ OH^- \tag{60}$$

Tetra- and pentasulfides, the only stable polysulfides under the reaction conditions (Giggenbach, 1972), form by reaction of the elemental sulfur with dissolved hydrogen sulfide (Teder, 1971).

$$(x - 1)S^0 + HS^- \rightarrow S_x^{2-} + H^+ \tag{61}$$
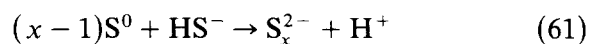
where $x = 2$, 3, 4, or 5.

Iron reduction was found by Pyzik and Sommer (1981) to occur in two phases: an initial rapid phase which was truly dependent

on a surface reduction process and a dissolution phase from which most of the ferrous iron is produced. The second phase reaction follows the rate equation:

$$d(\text{reduction Fe})/dt = kA_{\text{FeOOH}}S_T^{0.5}a_H^{+0.5} \quad (62)$$

where k is the rate constant, A is the specific surface area of goethite, S_T is the total molar sulfide concentration, and (H^+) is the hydrogen ion activity.

As part of their study, Pyzik and Sommer (1981) also measured the rate of FeS formation. The rate equation they found for their data was:

$$d(\text{FeS})/dt = kS_Ta_{H^+}A_{\text{FeOOH}} \quad (63)$$

They hypothesized that the FeS formed first as dissolved hydrate ($\text{FeS.H}_2\text{O}$) which then precipitated by a dehydration reaction. Their overall reaction sequence is summarized in Fig. 10.

It was previously mentioned that Taylor (1980) envisions a different reaction path for the formation of FeS. In his model, aqueous FeSH^+ complexes react to produce Fe_2S_2 dimers and H^+. These dimers then polymerize to make solid FeS. Ivarson and Hallberg (1976) have also suggested that an oxidation-reduction cycle driven by bacteria, which involves the mineral jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$), may be important for the formation of FeS in the dynamic upper sediment zone near the oxic–anoxic boundary.

Since mackinawite is often a probable precursor to greigite and/or pyrite formation and may be dissolved if iron or hydrogen sulfide concentrations become sufficiently low, it is important to understand its dissolution kinetics. Pankow and Morgan (1979) have carried out a detailed study of mackinawite dissolution under anoxic conditions. At pH values less than 4.3, the dissolution rate was found to be first-order with respect to H^+ ion concentration. The equation that they arrived at for the rate of mackinawite dissolution under these conditions is:

$$d[S_T]/dt = k_1(A/V)a_{H^+} \quad (64)$$
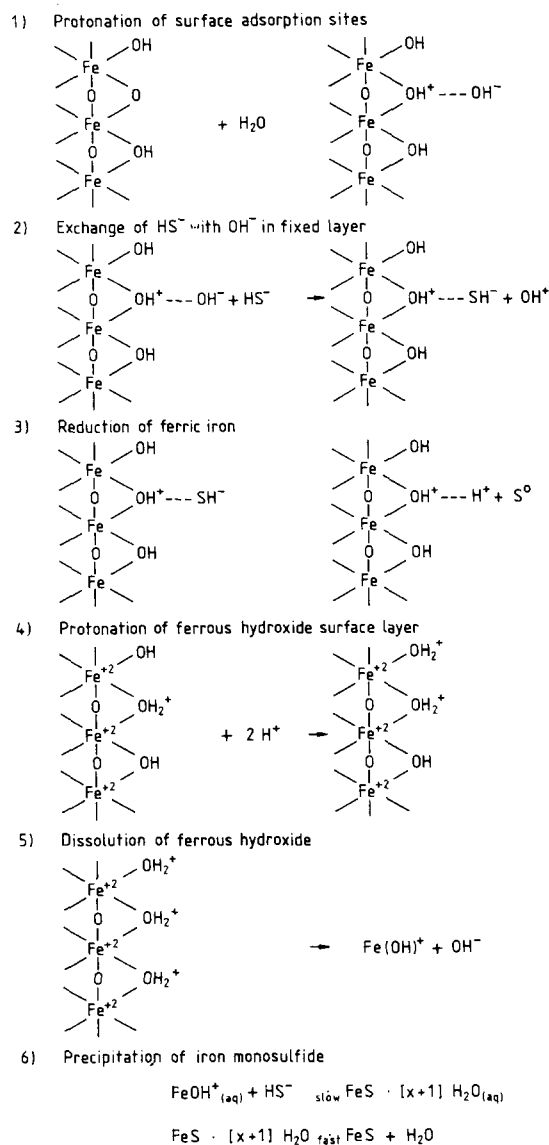
Fig. 10. The postulated overall reaction mechanism for formation of ferrous monosulfide (from Pyzik and Sommer, 1981).

where S_T is the total reduced sulfur evoked, K_1 is the rate constant, A is approximate surface area of mackinawite, and V is the solution volume. The reaction was found to be close to independent of ionic strength and to have an activation energy of 6.8 ($\pm$1.2) kcal. mol^{-1}. At pH values greater than 5 the dissolution rate of the mackinawite was found to be pH-independent and a second rate constant was added (k_2).

$$d[S_T]/dt = (A/V)(k_1a_{H^+} + k_2) \quad (65)$$

The activation energy in the higher pH regime was 7.3 ($\pm$1.0) kcal. mol^{-1}. Pankow and Morgan (1979) suggested that since the rate of dissolution was pH-independent above a pH of 5, some mechanism other than hydrogen ion attack on mackinawite surfaces must be important for dissolution. They also found that copper at low concentrations could significantly slow the dissolution rate of mackinawite, perhaps by replacing surficial iron and forming a CuS coating on the mackinawite.

While greigite can be an important component of sediment iron sulfides and is widely accepted as the necessary precursor for the formation of framboidal pyrite (e.g., Berner, 1969, 1970; Sweeney and Kaplan, 1973), less is known about its mechanism and kinetics of formation than mackinawite or pyrite. Considerable controversy has existed over whether air (O_2) is necessary for the conversion of mackinawite to greigite (see previous discussion) and Hallberg (1972) has suggested that mackinawite may not be necessary as a precursor to greigite. Taylor et al. (1979) have found that only a very short exposure of mackinawite to air results in the probable formation of a magnetite and elemental sulfur surface which can then drive formation of greigite through a series of oxidative reactions. In over 200 experiments performed over a temperature range of 35°–160°C, no greigite was ever observed when air was strictly excluded. They also note that, based on topotaxial relations found between mackinawite and greigite by Horiuchi et al. (1970) and Horiuchi (1971), conversion of mackinawite to greigite could occur by growth of a sulfur sublattice on the mackinawite (101) plane and outward diffusion and redistribution of iron atoms to produce a greigite (222) plane.

The mechanisms involved in the formation of sedimentary pyrite have received extensive investigation and speculation. Some early workers suggested that sedimentary pyrite was formed by the reaction of ferrous iron with thiosulfate (e.g., Allen et al., 1912; Volkov and Ostroumov, 1957), or polysulfides (Roberts et al., 1969). Others have favored sedimentary pyrite formation by precursor iron sulfide such as mackinawite or greigite interacting with excess H_2S and elemental sulfur (e.g., Berner, 1969, 1970; Rickard, 1969; Skripchenko, 1969; Feld, 1977). Also, Sweeney and Kaplan (1973) demonstrated that spherical greigite reacting with oxygen was a likely precursor to framboidal pyrite formation, while Goldhaber and Kaplan (1974) found evidence that euhedral pyrite could be formed by mackinawite interaction with elemental sulfur.

Rickard (1975) carried out an extensive review of earlier investigations of the kinetics and probable mechanisms involved in the formation of pyrite from aqueous solutions. His experiments produced euhedral pyrite. Its rate of formation could be described by the equation:

$$\text{Rate} = k_1(\text{FeS})_2(\text{S})P_{\text{H}_2\text{S}} \tag{66}$$

or,

$$\text{Rate} = k_2(\text{FeS})_2(\text{S})\{\text{SS}^{2-}\}a_{\text{H}^+} \tag{67}$$

where k_1 and k_2 are rate constants, (FeS) is the iron sulfide surface area, (S) is the surface area of elemental sulfur, $P_{\text{H}_2\text{S}}$ is the partial pressure of hydrogen sulfide, and $\{\text{SS}^{2-}\}$ is the sum of the dissolved sulfide activities. Rickard (1975) determined the activation energy of the reaction to be 17 kcal. mol^{-1}. This model demands that both FeS and elemental sulfur must undergo dissolution reactions. The final pyrite producing reaction is believed to be a direct precipitation reaction between ferrous iron, hydrogen sulfide, and polysulfide derived from the elemental sulfur.

$$\text{Fe}^{2+} + \text{S}_5^{2-} + \text{HS}^- \rightarrow \text{FeS}_2 + \text{S}_4^{2-} + \text{H}^+ \tag{68}$$
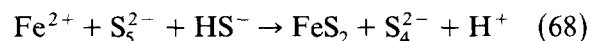
Berner et al. (1979) have stressed that for the conversion of mackinawite and greigite to pyrite excess H_2S must be present, and that for sediments overlain by waters low in sulfate, which is the primary source of the H_2S, these metastable phases may persist for extensive periods of time. The validity of his hypothesis was reinforced by the general ob-

servation of a correlation of the ratio of FeS_2 to "acid volatile" FeS with salinity, though this hypothesis has since been questioned (Davison et al., 1985).

Recently, considerable interest has been focused on the findings of Howarth and his associates that euhedral pyrite can form directly and rapidly from solution without precursor iron sulfide phases (Howarth, 1978; Howarth and Teal, 1979; Luther et al., 1982; Giblin and Howarth, 1984). The primary environment for this type of pyrite formation is salt marsh sediments with high organic content, rapid sulfate reduction, and low pH. Howarth (1979) and Berner et al. (1979) both emphasize the importance of low pH in keeping the solution undersaturated with respect to monosulfides but supersaturated with respect to pyrite. Luther et al. (1982) found framboidal and euhedral pyrite coexisting in marsh sediments from Great Sippewissett, Sapelo Island and Hackensack Meadows, and from Newark Bay sediments. They suggested, based on earlier studies, that the framboidal pyrite was formed by a slow process from greigite, and that single crystal pyrite forms rapidly by direct precipitation.

The interpretation of processes occurring in these sediments is largely based on ^{35}S-derived data. Jorgensen et al. (1984) have found major problems with the ^{35}S technique as currently used. Their results indicate that current methods can grossly overestimate the rate and proportion of pyrite formation. This has thrown many of the previously discussed results into considerable question. Also, the observations that crystalline greigite is not dissolved by normal "acid volatile" sulfide methods (Berner, personal communication quoted by Westrich, 1983) and that commonly used methods may cause oxidation of FeS-derived S to S^0 make questionable much of the currently available data on the distribution and proportions of "acid volatile" sulfides and pyrite (see later discussion of this problem).

Raiswell (1982) has invoked a reasoning similar to that of Howarth's to explain his observations of the distribution of different forms of pyrite in a pyritiferous carbonate concretion and the surrounding sediment. The sediment surrounding the concretion contained framboidal pyrite which he speculated formed from highly supersaturated waters and monosulfide precursors. He believed that the euhedral pyrite within the iron-poor concretion may not have formed rapidly, but precipitated from waters undersaturated with respect to the iron monosulfides yet supersaturated with respect to pyrite. Sulfur isotope measurements of the pyrites were in substantial agreement with this model.

The microbiological formation of iron sulfides

The main source of sulfide in sediments for iron sulfide formation is from dissimilatory sulfate reduction by bacteria of the genera *Desulfovibrio* and *Desulfotomaculum*. The fact that laboratory cultivation of these bacteria results in precipitation of metal sulfides has been known since Beijerinck first cultivated them in 1895. It is, in fact, used as a qualitative diagnostic check on bacterial growth in batch culture studies. The medium first blackens as bacterial H_2S reacts with small amounts of iron in the medium and then clears as the iron sulfide settles and the bacterial growth rate lessens. Issatchenko (1912) first reported a specific mineral sulfide being formed through this process when he identified pyrite in cultures of sulfate reducers. Miller (1950) prepared a variety of metal sulfides by this method, including sulfides of antimony, bismuth, cobalt, cadmium, iron, nickel, lead, and tin. He failed to produce copper sulfide, and did not identify any of the metal sulfides produced. Baas Becking and Moore (1961) synthesized sulfides of copper, lead, zinc, and silver in biologic systems including covellite, digenite, galena, sphalerite, and "argentite" (acanthite, according to McDiarmid, 1966).

However, a major question still remained unanswered: are bacterially produced metal sulfides any different from inorganically produced metal sulfides? The question is of more

than academic importance because (a) sedimentary iron sulfides are bacterially produced, and (b) an extremely close spatial association exists between the iron sulfides and the bacteria themselves in laboratory cultures. Observations show that, probably as a result of unfavorable conditions, viable, motile, sulfate-reducing bacteria may become coated with iron sulfides during laboratory cultivation. The iron sulfide is precipitated on the cell wall, within the capsule or slime layer surrounding the cell itself. In such an environment it would be possible for the organism itself to exert some influence on the iron sulfide formed.

Rickard (1968, 1969) made a detailed study of the iron sulfides formed through the reaction between iron bacterium *Desulfovibrio desulfuricans* in batch culture. Mackinawite, greigite, pyrrhotite, marcasite, and pyrite were formed. No differences were found between the compositions and structures of these biogenic iron sulfides and those produced by purely inorganic processes. Furthermore, the biogenic and abiogenic iron sulfides were formed under the same conditions (Rickard, 1969). Rickard (1969) concluded that the bacteria produce only sulfide species (not polysulfides nor intermediate sulfur oxyacids) and that biogenic and abiogenic iron sulfides could not be distinguished.

Hallberg (1972) reported a similar investigation but used a continuous culture system with more closely defined experimental conditions than is possible with batch culture techniques. Hallberg reported the synthesis of pyrite, greigite, and mackinawite, but suggested that a primary hexagonal phase was a new iron sulfide possibly resulting from bacterial activity. However, subsequent studies of this material have cast a shadow of doubt over this observation, especially with regard to the presence of sulfide in this material.

Issatchenko (1912) reported that pyrite was formed within the bacterial cells themselves. His 1912 paper contains beautiful hand-painted watercolors of this phenomenon.

More recently, H.E. Jones (personal communication to Rickard) has identified probable iron sulfide particles of unknown identity and composition within the cells of sulfate-reducing bacteria. Freke and Tate (1961) found "magnetic Fe_4S_5" produced by semi-continuous cultures of sulfate-reducing bacteria. At that time Postgate (1965), in one of his periodic reviews of all things connected with sulfate-reducing bacteria, thought that this was a "remarkable observation". Subsequently Rickard (1969) showed that Freke and Tate's material was a mixture of greigite and hematite, and was formed under conditions which would be expected from the inorganic experiments of Berner (1964) and Rickard (1969).

Although the possibility that the iron sulfides formed through bacterial activities may include unusual varieties cannot be dismissed, present evidence indicates that they are no different from inorganically-produced varieties. Valleriite-type sulfides may contain a variety of materials between the sulfide layers and it is not outside the bounds of possibility that, in the presence of bacteria, organic substances might be included. A detailed reinvestigation of Hallberg's material might be worthwhile in this respect. Furthermore, the presence of organic-iron sulfide complexes such as ferrodoxins within the bacteria might be considered to encourage the development of methods for investigating the actual nature of H.E. Jones' intracellular iron sulfide inclusions.

Overall, however, the major pathways of iron sulfide formation are identical in the presence and absence of bacteria.

Oxidative dissolution of iron sulfides

Although the primary concern with respect to the iron sulfide minerals has been with their formation and relative stability, it is important to realize that they can also be attacked by oxidative processes in natural waters. Oxidative processes are especially important near interfaces between oxic and

anoxic water masses, and in the upper portion of anoxic sediments where the boundary between oxic and anoxic oxidations is highly dynamic (e.g., see Berner, 1980). In this region diffusion, bioturbation, bioirrigation, and transport of oxygen by plant roots can all contribute to non-steady state micro- and mini-environments. Recently Luther et al. (1980) and Giblin and Howarth (1984) have placed special emphasis on the seasonality of oxygen transport by plant roots in salt marshes and its potential importance to the net iron budget of such environments.

Little is known about the mechanism or kinetics of oxidative dissolution of mackinawite. There is some indication that it may involve direct attack on the mackinawite by molecular oxygen (see Pankow and Morgan, 1980, for discussion). We have also been unable to find any studies of the oxidative dissolution of greigite. However, an extensive literature exists on the aqueous oxidation of pyrite by molecular oxygen. Lowson (1982) has compiled an excellent review of this literature and, consequently, we will only briefly summarize the most salient points for natural systems here.

Lowson's review of the oxidative dissolution indicates that there is general agreement on the overall stoichiometry of the reaction being:

$$2\ FeS_2 + 7\ O_2 + 2\ H_2O \rightarrow 2\ FeSO_4$$
$$+\ 2\ H_2SO_4 \qquad (69)$$
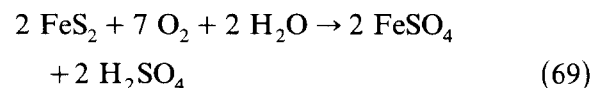
However, there is little agreement on the order of the reaction with respect to oxygen, the influence of pH and pyrite surface area, the activation energy of the reaction, or the mechanisms involved. Among the most attractive models are those in which dissolved oxygen is adsorbed to form surface atomic oxygen:

$$O_{2(aq)} \rightarrow 2\ O_{(ads)} \qquad (70)$$

followed by a slow reaction in which the pyrite sulfur is oxidized to adsorbed thiosulfate:

$$3\ O_{(ads)} \cdot FeS \rightarrow Fe_2O_{3(as)} \qquad (71)$$
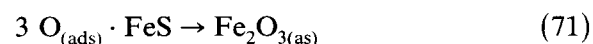
The thiosulfate is then desorbed and can disproportionate to sulfite and elemental sulfur:

$$Fe_2O_{3(ads)} \rightarrow FeS_2O_{3(aq)} \qquad (72)$$

$$FeS_2O_3 + 2\ H^+ \rightarrow Fe^{2+} + H_2SO_3 + S^0 \qquad (73)$$
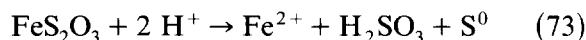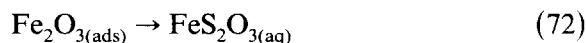
Sulfite is then further oxidized to sulfate:

$$H_2O_3 + (1/2)O_2 \rightarrow HSO_4^- + H^+ \qquad (74)$$

The dissolved ferrous iron produced by this reaction can also be subsequently oxidized. This may lead to the precipitation of iron oxides or jarosite.

Trace metal–sulfide association

Most trace metals of environment interest form highly insoluble sulfides, with pK_{sp} values ranging from 25.2 for ZnS to 53.2 for HgS (Framson and Leckie, 1978, based on S^{2-} instead of HS^-). From early measurements of hydrogen sulfide concentrations for typical shallow water fine-grained. sediments, concentrations for trace metals in equilibrium with their sulfide minerals were calculated. (Based on our present knowledge of ion complex formation the activity coefficients which were used were much too large.) The calculated equilibrium concentrations were very low. When actual measurements of dissolved metals in anoxic pore waters were made, the observed concentrations were several orders of magnitude higher than predicted (e.g., Brooks et al., 1968; Presley et al., 1972). Since that time considerable controversy has persisted over the relative importance of sulfide-type complexes versus organic matter in maintaining trace metals at their relatively high concentrations in anoxic pore waters (see for example, Duchart et al., 1973; Rashid and Leonard, 1973; Saxby, 1973; Gardner, 1974; Boulegue, 1977; Krom and Sholkovitz, 1978; Mantoura et al., 1978; Lyons et al., 1979; Boulegue et al., 1982). Based on this literature it appears that the relative importance of organic complexes may vary substantially at different locations, but that in general polysulfide complexes are probably more important. An example of the significance of
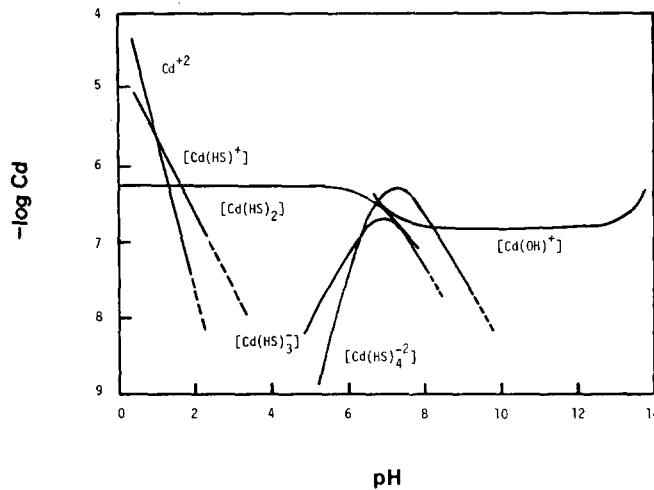
Fig. 11. Cd speciation as a function of pH in a solution with hydrogen sulfide [after Ste-Marie et al., 1964].

these types of complexes is presented in Fig. 11 for Cd speciation (Ste-Marie et al., 1964). When these types of interactions have been considered, close to equilibrium metal concentrations can be calculated in a variety of sediments for several metal sulfide phases (e.g., Boulegue et al., 1982; Jacobs and Emerson, 1982; also see Emerson et al., 1983 for an excellent summary review).

The study of trace metal behavior in sediments and anoxic waters has primarily divided itself into three interrelated areas: (1) the composition of the sulfide fraction of suspended matter and sediments; (2) coprecipitation reactions versus the formation of discrete phases; and (3) adsorption of "scavenging" reactions. The first area is largely descriptive. It is important for identifying the trace metals which are most strongly associated with sulfide phases.

Korolov (1958) was among the first to note the strong association of Mo with sedimentary sulfides. He found that 70 to 96% of the Mo found in anoxic environments could be coprecipitated with iron sulfides, but that much of it was released during the transformation of FeS to pyrite. Bertine (1972) also found a strong association of Mo with iron sulfides. Her data indicated that in anoxic waters approximately 70% of the Mo is combined with iron sulfides. She also pointed out

the probable importance of sorption reactions and suggested that MoS_3 may form as a discrete phase. Philipchuk and Volkov (1974) have found a strong correlation in Black Sea waters between increasing HS^- concentrations and decreasing concentrations of Mo. Mo is strongly correlated with the sulfidic fraction in the underlying sediments. Malcolm (1985) has also recently made a detailed study of Mo behavior in anoxic sediments. He found it was very mobile in the upper portion of these sediments, but was fixed in a sulfide phase at depth.

Zinc is also strongly associated with sulfides in many anoxic waters and sediments (e.g., Spencer et al., 1972; McArthur, 1978; Kitano et al., 1980; Luther et al., 1980). Elderfield et al. (1979) found that Zn behavior was similar to that of Mo in being excluded during transformation reactions from iron sulfide to pyrite. The importance of Pb interaction with suspended sulfides has been demonstrated in the Cariaco Trench where ^{210}Pb is scavenged from the water column on iron sulfides (Bacon et al., 1980). Other trace metals which have been found to be frequently associated with the sulfide fraction of suspended matter and sediments in anaerobic environments include: Cu, Co, Ni, Cd, As, Sb, Hg, and occasionally Mn (e.g., see preceding references and Volkov and Fomina, 1974; Boulegue, 1977; Suess,

1979; Kitano and Fujiyoshi, 1980; Oakley et al., 1980; Boulegue et al., 1982; Jacobs and Emerson, 1982; Jacobs et al., 1985; Davies-Colley et al., 1985). It is important to note that the relative association of the different trace metals varies in different environments. For example, Nissenbaum and Swaine (1976) found Ni and Co strongly associated with sulfides, while Zn and Mo were more strongly bound by organic matter.

Interest has also focused on the questions of whether trace metals found associated with the sulfide fraction of suspended matter and sediments are presented as discrete phases or as coprecipitates with the more common abundant iron sulfides. In spite of the importance of this question, little solid observational or experimental data is available. Cd has received the most attention. Framson and Leckie (1978) point out that geometric restrictions and the fact that CdS is highly ionic while FeS is highly covalent, make Cd substitution in FeS difficult. They measured a distribution coefficient for Cd in FeS of $3.5 \cdot 10^{-4}$. Based on these results it was hypothesized that Cd should form a separate sulfide phase. The observations of Jacobs and Emerson (1982) for Saanich Inlet sediments are consistent with this concept, while those of Boulegue (1977) for groundwaters from En-ghien-les-Bains, France suggest the coprecipitation of Cd with FeS.

Suess (1979) has identified γ-MnS in marine sediments, but again there is a question of how general the formation of MnS as a distinct phase is, since Jacobs and Emerson (1982) and Boulegue (1977) have found evidence for the coprecipitation of Mn with FeS. The possible formation of CuS as a separate phase in marine sediments has also been suggested as a possibility, based on calculations which indicate some sediments are close to equilibrium with either covellite or chalcocite (Jacobs and Emerson, 1982; Boulegue et al., 1982). However, Boulegue et al. (1982) pointed out that the large uncertainty in calculating Cu activity coefficients in solutions rich in polysulfides and organic matter make such conclusions highly speculative.
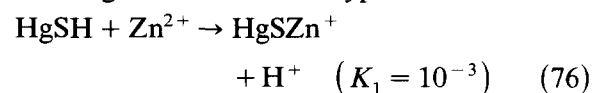
The most comprehensive study of trace metal geochemistry in anoxic waters is the recently completed dissertation of Jacobs (1984). Metal profiles were measured in the anoxic waters of Saanich Inlet, Lake Nitinat, Framvaren Fjord, and the Cariaco Trench. The most important observation is that in most cases dissolved metal concentrations in sulfidic waters are not controlled by equilibrium with pure metal sulfides. This can be interpreted as strong evidence that adsorption or coprecipitation reactions play an important role in controlling trace metal concentrations in anoxic waters. This hypothesis is further reinforced by the previously mentioned observation of Bacon et al. (1980) that ^{210}Pb is being removed from anoxic waters in the Cariaco Trench by incorporation into metal sulfides.
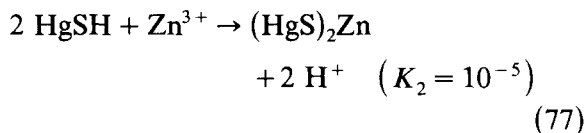
Surprisingly little work has been done on the surface chemistry of metal sulfides in general and iron sulfides as clearly defined phases in particular. Early work on solid surfaces such as CdS was aimed at establishing their potential for metal chromatography (e.g., Phillips and Kraus, 1963, 1965). They proposed surface exchange reactions of the form:

$$M_{2/m}S^+(2/n)N^{+n} \rightarrow (2/m)M^{+m} + N_{2/n}S$$

$$(75)$$
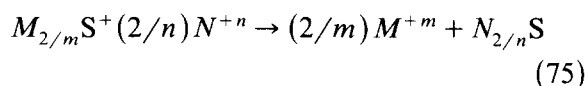
Wu and Yang (1976) used Cu(II)S as an adsorbate for a variety of radiotracers. They established the general relation that the adsorption affinity of metals on sulfides is inversely related to the metal sulfide solubility. A similar general relationship has recently been found by Oakley et al. (1980) for metal "doped" synthetic sediments.

James and McNaughton (1977) have studied the sorption of Zn(II) on HgS at Zn concentrations below that of its sulfide solubility. They found a strong pH-dependence for the sorption reaction. Two major types of exchange reactions were hypothesized:

$$\text{HgSH} + \text{Zn}^{2+} \rightarrow \text{HgSZn}^+$$

$$+ \text{H}^+ \quad (K_1 = 10^{-3}) \quad (76)$$

$$2 \, HgSH + Zn^{3+} \rightarrow (HgS)_2 Zn$$
$$+ 2 \, H^+ \quad \left(K_2 = 10^{-5} \right)$$
$$(77)$$

Under low conditions, reaction 76 is dominant while at higher pH values, reaction 77 is most important.

Few studies have been done in which the surface chemistry of a specific iron sulfide was investigated. Nelson et al. (1977) measured the sorption of silver on mackinawite. The experiments were done at pH of 9 and ionic strength of 0.1. They found rapid and nearly complete removal of the silver from solution (greater than 99% in less than 5 min). It was suggested that the silver may diffuse into the mackinawite crystal lattice and displace Fe. Conway et al. (1980) used cyclic voltametry to study the surface reactivity of FeS and FeS_2. At low pH values the FeS_2 surface processes were almost completely reversible, while FeS surface processes were more complex and less reversible. Under alkaline pH conditions the FeS_2 surface reactions also became less reversible and possibly involved a surface region 20 times thicker than under the low pH conditions.

In recent years there have been significant advances in surface analytic techniques. One technique which has proven especially useful in the study of metal sulfides is ESCA (electron microscopy for chemical analysis), now more often referred to as XPS (X-ray photoelectron spectroscopy). It has proven particularly useful for quantitative analysis and determination of metal ion valence states. Studies in which this approach has been used to characterize sulfides include: Brown et al. (1979) who studied Hg^{2+} and Hg^0 sorption on pyrite and pyrrhotite; Gopalakrishnan et al. (1979) who found that CuS was unique in having both Cu^{2+} and Cu^+ present with an average valence of $+1.33$; Folmer and Jellinek (1980) who found $+1$ Cu in a number of sulfides and selenides; and Van Bruggen (1982) who found Cu in all sulfide binary and ternary compounds to be monovalent, even when formed from $Cu(II)$ solutions.

DISTRIBUTIONS OF HYDROGEN SULFIDE AND IRON SULFIDE MINERALS IN MARINE ENVIRONMENTS

Hydrogen sulfides and related compound

Analytic methods

The concentrations of H_2S ($SH_2S = H_2S + HS^- + S^{2-}$) have been determined in natural environments using a variety of techniques. A modified methylene blue method (Cline, 1969) is most commonly used, with a detection limit of approximately 1 μmol l^{-1}. Silver sulfide ion selective electrodes have been successfully used in sediment and water (Berner, 1963; Orion Research, 1977; Vivit et al., 1984). Davison and Heaney (1980) have utilized polarographic techniques for sulfide determination, Goldhaber and Kaplan (1980) used AgS gravimetry for porewater analysis, iodometric methods have been used (American Public Health Association, 1980), and others use a gas chromatographic head-space technique (Hawke et al., 1985).

Sulfate reduction products other than H_2S (e.g., S_n^{2-}, $S_2O_3^{2-}$, SO_3^{2-}, polythionates) have been measured infrequently. Polysulfides have been determined colorimetrically (Giggenbach, 1972; Pyzik and Sommer, 1981), using a potentiometric titration (Boulegue et al., 1982) and by polarographic techniques (Luther et al., 1985a). Thiosulfate and sulfite have been analyzed by colorimetric (Jacobs, 1984), Hg titration (Boulegue et al., 1984), ion chromatographic (Moses et al., 1984), and polarographic techniques (Luther et al., 1985b), with the latter two techniques useful for polythionates. Very low levels of these sulfur redox intermediates are found in most anoxic environments, but refinement of techniques and their application to more sulfidic environments may change our perception of their role in S cycling. Indeed, recent investigations of salt marsh porewater by Luther et al. (1985) have revealed high concentrations of organic and inorganic S intermediates.

Elemental sulfur determination in sediments involves its extraction into an organic

solvent followed by chemical analysis. Organic solvents have included acetone (Berner, 1970; Zhabina and Volkov, 1978; Jacobs, 1984), hexane (Heim et al., 1984), and carbon disulfide (Fliermans and Brock, 1973; Troelson and Jorgensen, 1982). Chemical analysis techniques for elemental sulfur include colorimetric determination as a ferric thiocyanate (Fliermans and Brock, 1973), conversion of S^0 to H_2S followed by H_2S titration (Zhabina and Volkov, 1978) and gas chromatography (Heim et al., 1984). Concentrations in marine sediments generally are much less than 10 μmol per gram dry sediment.

Environmental distributions

Hydrogen sulfide in the marine environment has been studied both in the water column of anoxic basins and in sediment pore waters. Water column anoxia occurs when

physical constraints on vertical mixing and horizontal advection result in dissolved oxygen inputs lower than those required for the oxidation of labile organic matter (Richards, 1965; Deuser, 1975). When the oxygen is depleted, other electron acceptors (NO_3^-, Mn(IV), Fe(III), SO_4^{2-}) are used for the microbial organic matter oxidation (Stumm and Morgan, 1981; Froelich et al., 1979). In anoxic marine waters, low concentrations of energetically more favored electron acceptors results in the predominance of sulfate reduction relative to other microbial processes.

Characteristic O_2 and H_2S distributions in three anoxic basins are presented in Fig. 12. Maximum H_2S concentrations range from approximately 40 μmol l^{-1} in the permanently anoxic Cariaco Basin (Bacon et al., 1980) and seasonally anoxic Saanich Inlet
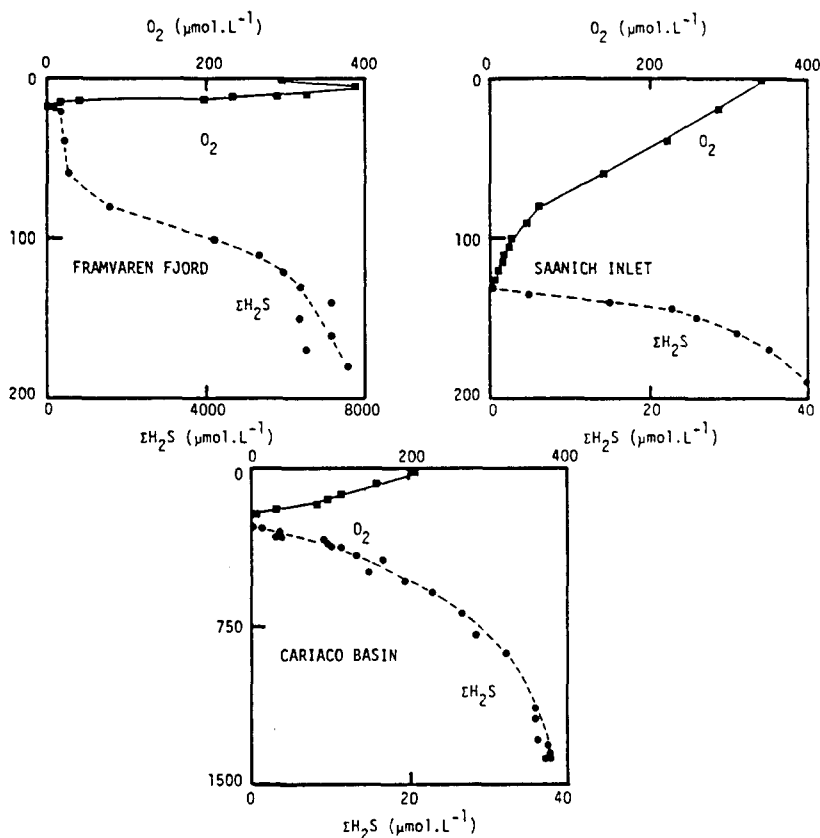

Fig. 12. Hydrogen sulfide and oxygen distributions in three anoxic basins. The data from Framvaren Fjord, Saanich Inlet and Cariaco Basin are from Skie (1983), Emerson et al. (1979) and Bacon et al. (1980), respectively. Note the 200 times increase of ΣH_2S in Framvaren Fjord relative to the other two basins.
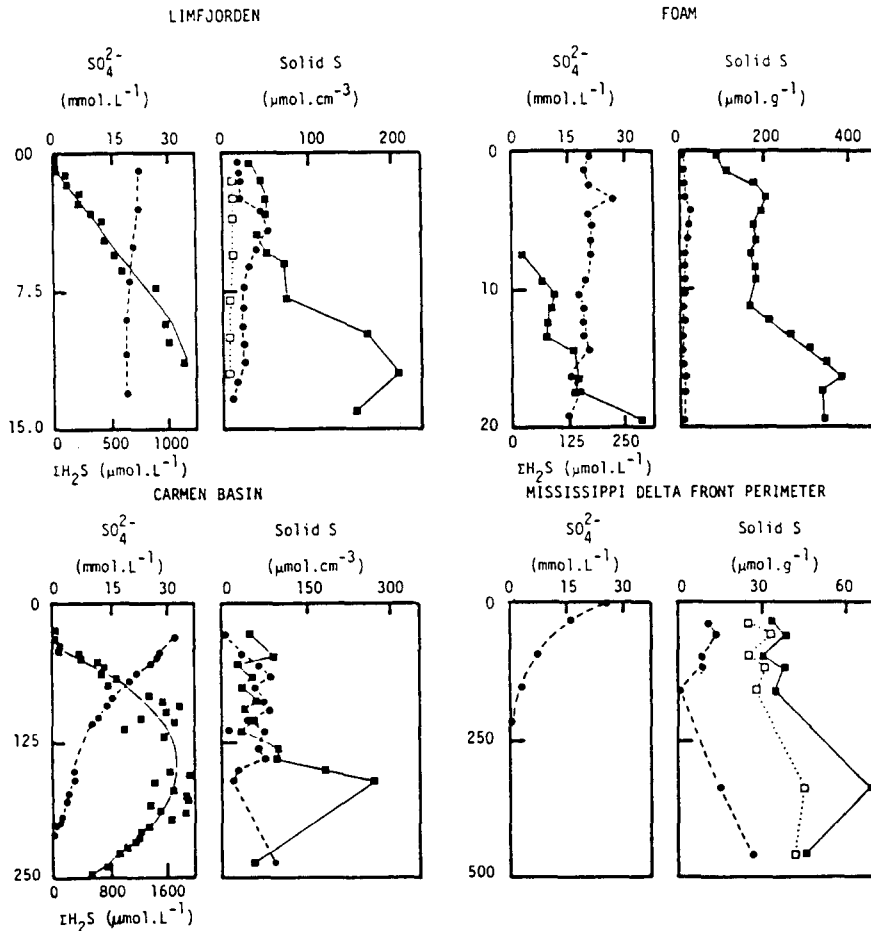
LIMFJORDEN

FOAM

Fig. 13. Pore water and solid phase S distributions in anoxic sediments for Limfjorden (Howarth and Jorgensen, 1984), the FOAM site (Goldhaber et al., 1977), the Carmen Basin (Goldhaber, 1980) and a piston core from 509 m depth off the Mississippi delta (Cornwell, unpublished data). For the dissolved data, ΣH_2S and SO_4^{2-} are presented. Concentrations of acid volatile-S and pyrite-S vary greatly within cores and between sites. The Mississippi delta samples were analyzed with cold 6 N HCl + $SnCl_2$ (AVS1), hot 6 N HCl + $SnCl_2$(AVS2) and total reduced sulfur (ΣS) via Cr reduction.

(Emerson et al., 1979) to almost 8000 μmol l^{-1} in Framvaren Fjord (Skei, 1983). A survey of anoxic basins (Deuser, 1975) indicates that most anoxic marine basin SH_2S concentrations are less than Framvaren Fjord, with a median value of 350 μmol g^{-1}. The world's largest anoxic basin, the Black Sea, has SH_2S values up to 400 μmol l^{-1}.

The distribution of other reduced sulfur species has only recently been carried out by Jacobs [1984]. She found that the sulfur redox intermediates were detectable only near the O_2-SH_2S interface, with S^0 exceeding 7 μmol l^{-1} on one occasion in Saanich Inlet and

$S_2O_3^{2-}$ values of 12 μmol l^{-1} in Lake Nitinat, an order of magnitude lower than SH_2S values. Iron concentrations in these basins appear to generally conform to mackinawite-greigite solubility limits.

Sediment distributions of SH_2S are also quite variable, ranging from undetectable to several thousand μmoles per liter (Fig. 13). These distributions are probably not good indicators of sulfate reduction rates because of the variable availability of labile Fe within sediments. There is little information on the distribution of sulfur redox intermediates in marine sediments except for elemental S,

which generally makes up only a small part of total sediment S. As in anoxic basins, sulfur redox intermediates should occur most readily where upwardly diffusing H_2S reacts with oxygen. Sediment bioturbation may also produce these other S redox species by mixing reduced acid volatile sulfide minerals and pyrite into oxic horizons.

Iron sulfides in sediments

Analytic methods

The determination of the forms of solid phase iron sulfides in sediments has been attempted using several different kinds of techniques. Direct observation of sediments using SEM and microprobe techniques (Suess, 1979) are useful for crystalline phases, but is not especially useful for identifying iron monosulfide phases, nor are they very quantitative. X-ray diffraction is not a good alternative because of the low levels of iron sulfide (generally less than several percent of sediment) commonly found.

The most common methods for iron sulfide determination in aquatic sediments are based on the rapid dissolution of iron monosulfide minerals in acid and the absence of significant pyrite dissociation under equivalent con-

ditions. These techniques create two categories of iron sulfide minerals: acid volatile sulfides (amorphous FeS, mackinawite, and possibly greigite) and pyrite. It is not possible to distinguish individual monosulfide minerals in this analysis scheme. The general procedure involves the addition of acid to a closed reaction vessel, the stripping and trapping of the H_2S produced, and the analysis of sulfide by gravimetry or iodometric titration.

A wide variety of extraction conditions has been used to determine acid volatile sulfide (AVS) content (Table IX). Hot and cold digestion, using 1 to 12 N HCl, have been most commonly used. An artifact of these digestions is the underestimation of AVS because of the reaction of liberated ferric iron with sulfide to produce elemental sulfur (Pruden and Bloomfield, 1968). Stannous chloride has commonly been added to reduce ferric iron to ferrous iron to prevent sulfide oxidation (Berner et al., 1979; Pruden and Bloomfield, 1968). Titanium(III) has also been used to reduce this interference (Albert, 1984; D. Albert, personal communication 1985).

Several observations by investigators have indicated that caution should be exercised when interpreting AVS data. Berner (personal communication cited in Westrich, 1983) has

TABLE VIII

Extraction methods for iron sulfide digestion

(A) Acid volatile sulfide (H_2S emanation)	
(1) Cold HCl (1–12 N)	Aller (1980b), Jorgensen (1977), Goldhaber et al. (1977)
(2) Hot HCl (6–12 N)	Berner (1974), Zhabina and Volkov (1978)
(3) Cold HCl (6 N) + SnCl$_2$	Westrich (1983)
(4) Hot HCl (6 N) + SnCl$_2$	Westrich (1983), Berner et al. (1979)
(5) Cold H$_2$SO$_4$ (1 N) + TiCl$_3$	Albert (1984)
(B) Total reduced S (H_2S emanation)	
(1) Cr^{2+} reduction	Zhabina and Volkov (1978), Westrich (1983)
(C) Total S	
(1) Aqua-regia digestion	Goldhaber et al. (1977)
(2) Combustion	Berner (1974)
(D) Pyrite—via Fe content	
(1) HNO$_3$ digestion after removal of iron oxide and silicates	Lord (1982)

TABLE IX

Comparison of iron sulfide digestion results for four sediments from the Gulf of Mexico region [1]

Digesting solution	Port Aransas	Gulf Shelf	Orca Basin	Delta Front
1 N HCl	6.9 ± 0.3	–	51.8 ± 0.3	7.9 ± 0.5
6 N HCl	6.1 ± 0.1	0.1	54.3 ± 4.5	8.1 ± 2.1
6 N HCl + SnCl$_2$	7.7 ± 0.1	0.1	70.5 ± 0.1	8.2 ± 0.3
Hot 6 N HCl	5.1 ± 0.2	0.1	53.9 ± 0.7	5.5 ± 0.1
Hot 6 N HCl + SnCl$_2$	18.3 ± 1.2	8.1 ± 1.5	103.4 ± 1.3	24.9 ± 0.9
1 N H$_2$SO$_4$ + TiCl$_3$	–	–	68.0 ± 1.0	8.4 ± 0.2
HCl + Cr^{2+}	40.2 ± 0.9	84.7 ± 4.2	114.5 ± 0.7	30.2 ± 1.6
Pyrite-S(1)	32.5 ± 0.9	84.6 ± 4.2	44.0 ± 0.7	22.0 ± 1.6
Pyrite-S(2)	21.9 ± 1.5	76.6 ± 4.6	11.1 ± 1.5	5.3 ± 1.8

[1] The Port Aransas sample is from a shallow salt marsh creek, the Shelf sample is from 30 to 35 cm deep in a core (water depth = 161 m), the Orca Basin sample is from 372 to 377 cm in a core, and the Delta Front Perimeter sample is from a sulfate-depleted core (97 to 99 cm interval) taken from 509 m water depth. All values are μmol g^{-1} dry sediment. Pyrite-S(1) is the pyrite estimate from the difference of the cold 6 N HCl + SnCl$_2$ and chromium results; pyrite-S(2) is the difference between the hot 6 N HCl + SnCl$_2$ and chromium digestions.

suggested that hot acid conditions are required for rapid dissolution of greigite. Chanton (1983), however, has indicated that such hot acid digestions with stannous chloride can dissolve significant quantities of pyrite. Our own results (Cornwell and Morse, 1986) show that synthetic greigite dissolution is incomplete without heating and that stannous chloride enhances greigite recovery. We have also found a slow dissolution of crystalline pyrite and are investigating the dissolution of poorly crystalline synthetic pyrite with a hot 6 N HCl and stannous chloride mixture.

Comparisons of different AVS extraction techniques have not been published. Table X shows data from four sediment samples using different extractants. The extraction efficiency of 1 and 6 N HCl are quite similar, with hot HCl showing a somewhat lower value in two cases, probably because of enhanced Fe(III) dissolution. As expected, the addition of stannous chloride in the 6 N HCl digestion yields somewhat larger values because of the elimination of the Fe(III) interference. The much higher values obtained from the hot HCl + SnCl$_2$ digestion are somewhat surpris-

ing and, at this time, we cannot explain the differences. Recovery of elemental sulfur with the hot HCl + stannous chloride digestion cannot account for all of the difference because of low concentrations of elemental S in these sediments. The 1 N H$_2$SO$_4$ + TiCl$_3$ technique yields values similar to the 6 N HCl + SnCl$_2$ technique.

Pyrite sulfur has been estimated in several ways. Zhabina and Volkov (1978) and Westrich (1983) have used an HCl–Cr(II) reduction technique for the determination of total reduced sulfur (e.g., H$_2$S + S^0 + AVS + FeS$_2$). The concentration of pyrite in sediments low in elemental S is estimated as the difference between AVS and total reduced S. Estimates of pyrite S for our four Gulf of Mexico sediments are strongly influenced by the AVS method used, with the pyrite concentration varying up to a factor of four for the Orca Basin and Delta Front Perimeter samples (Table X). The question remains as to whether the hot 6 N HCl + stannous chloride overestimates non-pyritic iron sulfides, or whether cold conditions underestimate it.

Berner (1970) and others have used total

digestions to characterize sediment S content. This technique measures the same components as the chromium reduction technique as well as organic S. Organic S makes up a negligible portion of total S (Berner, 1970) and, in most reducing marine sediments, an organic S correction is unnecessary for pyrite determination.

Another means of estimation of pyrite content is via the determination of pyrite-Fe. Lord (1982) has developed a technique in which iron oxides and iron silicates are decomposed with reducing and hydrofluoric acid solutions, leaving pyrite-Fe to be digested with nitric acid. Comparison of this method with chromium reduction-AVS techniques yields excellent agreement (Canfield et al., unpublished manuscript).

Sediment distributions

Much of our understanding of the distribution of iron sulfides in marine sediments has come from relatively few investigators and few sites. Berner and many co-workers (Berner, 1970; Goldhaber et al., 1977; Aller, 1980a,b; Westrich, 1983) have provided detailed sulfur distributions and understanding of biogeochemical processes for sediments from coastal Connecticut and Long Island Sound. Studies in coastal sediments from Denmark by Jorgensen and co-workers (Jorgensen, 1977; Troelson and Jorgensen, 1982; Howarth and Jorgensen, 1984) have emphasized sulfate reduction rates and the fate of reduced sulfur. Other important sulfide study sites (emphasizing sediment sulfides) include the Gulf of California (Goldhaber and Kaplan, 1980), numerous studies in salt marshes (Howarth, 1979; Lord and Church, 1983; King et al., 1985), and investigations of hydrothermal sediments (Zhabina and Sokolov, 1982).

The distribution of iron sulfides in four different sedimentary environments is shown in Fig. 13. The short cores from Limfjorden and the FOAM site indicate that the formation of AVS and pyrite occurs very near the sediment–water interface, with pyrite being the most important S burial phase. The Carmen Basin site shows similar quantities of AVS and pyrite to depths exceeding 1 m. The Mississippi Delta core presents results from cold $6\ N + SnCl_2$ digestions, hot $6\ N + SnCl_2$ digestions, and Cr^{2+} reduction digestions for total reduced S. Pyrite concentrations in this core are the difference between total reduced S and AVS, the latter changing dramatically with AVS reaction conditions. The strong correlation between Cr^{2+} and hot AVS digestions ($r^2 = 0.80$, $df = 5$, $P < 0.01$) suggest that hot AVS digests $76 \pm 7\%$ of pyrite-S (defined as total reduced S-cold AVS). Part of this amount could be greigite S or poorly crystalline pyrite. Further investigations will help to clarify this point (Cornwell and Morse, 1986).

The quantity and distribution of AVS and pyrite-S in marine sediments depends upon a large number of variables including carbon input rate, sediment burial rate, sulfate diffusion, bioturbation, iron input and reactivity, and sediment temperature (Berner and Westrich, 1985; Goldhaber and Kaplan, 1980; Berner, 1984). A sediment with a water content of 50% can have a maximum reduced S content of 30 μmol g^{-1} if the only S source is buried pore water SO_4^{2-}. Examination of Fig. 13 shows a much higher S content in these sediments, a result of enhanced SO_4^{2-} input from diffusion, mixing, and bioirrigation.

Although there has been much progress in the area of sediment S biogeochemistry, the mechanisms which result in different forms of reduced iron sulfide in sediments are not well understood. The role of reduction rate, iron availability, and S redox species such as polysulfides in determining the form of iron sulfide produced in marine sediments is not well known at this time. Progress can best be made by further detailed lab studies on sulfide mineral genesis, improvement of techniques for identifying sedimentary sulfides, and examining a broader spectrum of sulfide deposition sites.

ACKNOWLEDGEMENTS

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