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THERMODYNAMIC STABILITY OF SEDIMENTARY IRON SULFIDES

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ABSTRACT. Solubility equilibrium constants in aqueous solutions saturated with H_2S at 25°C have been determined for synthetic mackinawite (tetragonal FeS), greigite (cubic Fe_3S_4), and freshly precipitated FeS by means of pH measurements combined with analyses for dissolved ferrous iron. Equilibrium with mackinawite and greigite was approached both from undersaturation and supersaturation. Standard free energies of formation at 25°C calculated from the measurements are:

mackinawite	$\Delta F^\circ = -22.3 \pm 0.1$ kcal/mole
greigite	$\Delta F^\circ = -69.4 \pm 0.7$ kcal/mole
precipitated FeS	$\Delta F^\circ = -21.3 \pm 0.2$ kcal/mole

As a check on the measuring technique, determinations were also made of the solubility product of stoichiometric pyrrhotite and the first dissociation constant of H_2S in water. Good agreement for these parameters was found with the results of other studies obtained by different methods.

The results indicate that either mackinawite or greigite can be stable relative to the other in natural sediments and that under earth surface pressures and temperatures both phases are unstable relative to stoichiometric pyrrhotite or stoichiometric pyrrhotite plus pyrite.

INTRODUCTION

Finely divided, black iron sulfide is a common constituent and coloring agent in Recent and Tertiary marine and non-marine sediments. Although the crystallographic and chemical nature of this material has not been established with certainty, recent studies (Polushkina and Sidorenko, 1963; Berner, 1964a, 1967b; Skinner, Erd, and Grimaldi, 1964) suggest that the minerals mackinawite (tetragonal FeS) and greigite[1] (cubic Fe_3S_4) in various degrees of crystallization may be important constituents of the black material. If this is true, then study of the solubility and thermodynamic stability of each of these phases is needed in order to gain greater insight into possible chemical processes operating during the diagenesis of sediments. Knowledge of relative thermodynamic stabilities of sedimentary iron sulfides enables predictions of mineralogic changes over geologic time which otherwise could not be made.

The objective of this study was to determine the solubility product constants and, by derivation, the standard free energies of formation for greigite and mackinawite, and to relate these values to measured values for other iron sulfides including pyrite, stoichiometric pyrrhotite, and freshly precipitated FeS. The solubility of freshly precipitated FeS can be considered as an upper limit for iron sulfide solubility due to its very finely divided, non-crystalline nature; this is analogous to the use of freshly precipitated ferric hydroxide as an upper limit for hydrous ferric oxide solubility.

Besides providing aid in deciphering the processes of diagenesis, a knowledge of solubility is useful in evaluating the role of iron sulfides

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[1] In some Russian literature greigite is referred to as melnikovite.

as controls on the dissolved iron and sulfide concentrations in natural anoxic waters.

METHOD

General procedure.—Equilibrium pH was measured for aqueous suspensions of iron sulfides prepared in various manners (see below) and equilibrated with gaseous H_2S. Temperature was held at 25 ± 0.1°C by means of a water bath. Saturation with H_2S at a pressure of 1 atm was accomplished by constant bubbling of the purified gas through the appropriate solutions. Glass and calomel electrodes were used in conjunction with a Corning Model 12 pH meter and a Varian strip chart recorder to monitor pH during reaction and discern the equilibrium value. Equilibration with greigite and mackinawite was approached from both undersaturation and supersaturation. The apparatus and measuring procedure was identical to that described elsewhere for $CaCO_3$ solubility determinations (Berner, 1965, 1967a). Criteria for equilibrium was a less than 0.01 pH change in 3 hours. Duration of runs ranged from 3 to 6 hours. Buffer calibration with fresh Beckman 4.01 buffer was made at the end of each run, and correction for any non-Nernst response made through the use of two buffers.

In dilute ($<10^{-3}$ molar) solutions stirring rate was found to affect the pH by several hundredths of a unit. Upon reaching equilibrium the magnetic stirrer and H_2S bubbler were turned off for about a minute and then final pH values taken. In such cases calibration was done using unstirred buffer solutions. Good agreement of measured equilibrium constants for H_2S and pyrrhotite in such dilute solutions with values obtained in stirred, more concentrated solutions and with values obtained by others using different techniques provides justification for the procedure adopted.

At the termination of each run the contents of each reaction vessel were immediately poured through a 0.45μ Millipore filter, and the filtrate acidified with 2 drops of concentrated HCl. The dissolved H_2S was removed by boiling, and any volume change in the solution noted. Dissolved ferrous iron was subsequently determined by the o-phenanthroline method (Sandell, 1959) using a Beckman Model DU spectrophotometer.

Within minutes of filtering, the Millipore filter containing the black iron sulfide was mounted on a glass slide and subjected to $CuK\alpha$ X-radiation in order to ascertain the nature of the precipitate by means of its X-ray diffraction pattern. Phillips-Norelco or Siemans goniometer units employing pulse-height discrimination were used. Typical diffraction patterns for each phase are shown in figure 1. Synthesis techniques were developed so that solubilities would be measured only for essentially monomineralic phases. X-ray measurements indicated that for all runs, except those in which precipitated FeS was formed, single phases were present within the limits of diffraction resolution.

Preparation of precipitated FeS.—Non-cystalline precipitated FeS was formed by bubbling H_2S through a $FeSO_4$ solution at room temperature. The $FeSO_4$ solution was made by adding grains of $FeSO_4 \cdot 7H_2O$ to distilled water previously deaerated by N_2 bubbling. Precaution against even slight aeration during preparation or solubility determination was necessary to prevent the formation of precipitates of a higher oxidation

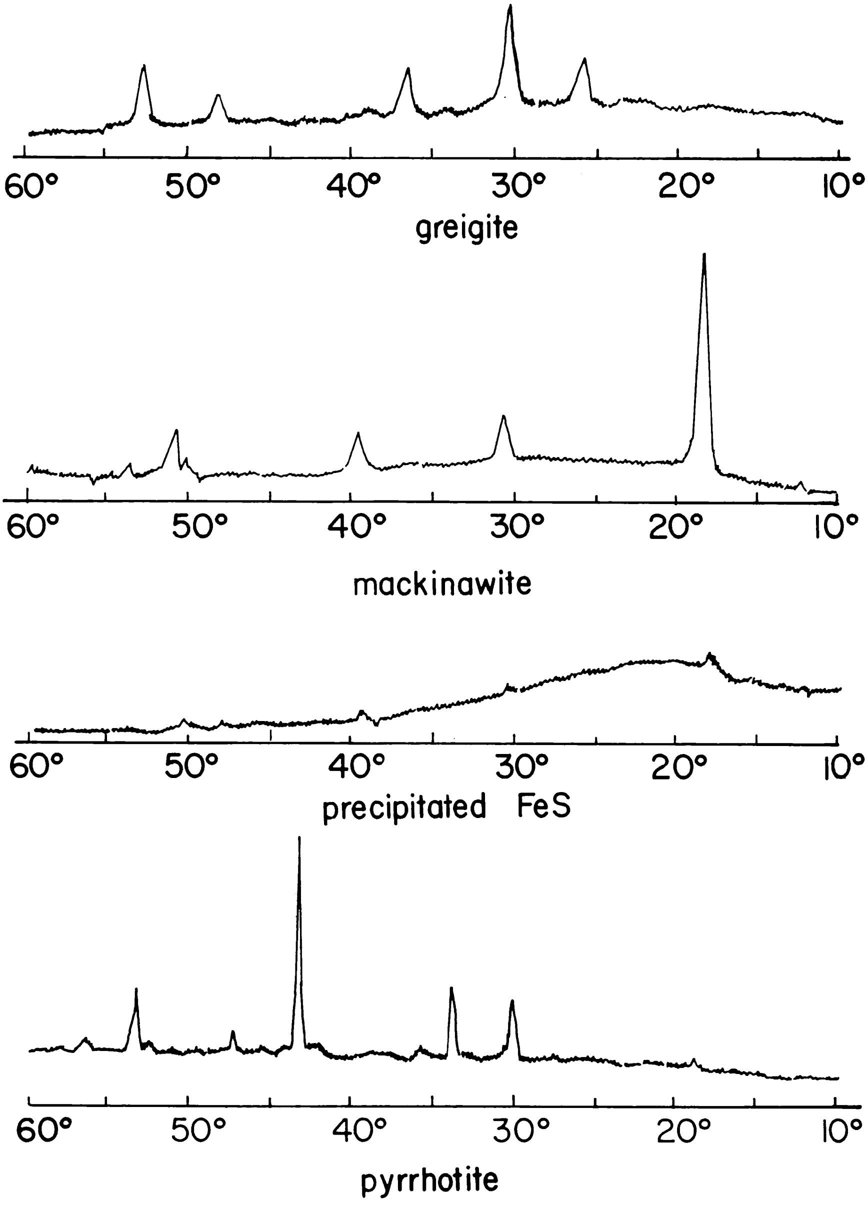

Fig. 1. X-ray diffraction patterns of iron sulfides whose solubility is measured in the study. CuKα radiation with pulse height analysis; abscissae are in degrees 2θ.

state. Without such precautions, a gradual negative pH drift and erroneously low values of K_{FeS} can be obtained as a result of slow greigite or pyrite formation. In the absence of any aeration, reproducible values of pH steady for up to 6 hours resulted, and the X-ray patterns (see fig. 1) showed amorphous material with a faint trace of poorly crystallized mackinawite. (Judging by its small peaks relative to the prominent 15°-30° 2θ "amorphous hump", the effect of the mackinawite on solubility should be negligible.)

Preparation of mackinawite.—In most runs mackinawite was synthesized in the manner of Berner (1962) by reacting powdered reagent grade iron with H_2S which was bubbled through distilled water or KCl solution at room temperature. After 2 to 3 hours reaction, the mackinawite was separated anaerobically from the remaining iron and transferred to a solution pre-saturated with H_2S. The mackinawite was then dissolved to saturation in the H_2S solution.

In one run mackinawite was synthesized by precipitation from a $FeSO_4$ solution with aging at 60°C. Elevated temperature was necessary to bring about sufficiently rapid crystallization. The $FeSO_4$ solution was prepared in a strictly anaerobic manner by adding grains of $FeSO_4 \cdot 7H_2O$ to deaerated distilled water while continuously bubbling nitrogen through the solution. After dissolution of the $FeSO_4 \cdot 7H_2O$, the gas inlet tube was immediately switched from N_2 to H_2S, and bubbling was continued as the reaction vessel was heated on a hot plate at 60 ± 5°C for 1 hour. Upon cooling, the reaction vessel, with H_2S still bubbling, was transferred to the 25°C water bath, electrodes were inserted through previously stoppered holes, and the pH monitoring begun. Throughout this procedure great care had to be taken to avoid the formation of greigite by slight aeration.

Greigite preparation.—Greigite was precipitated by bubbling of H_2S through a $FeSO_4$ solution on a hot plate at 80 to 90°C for about 45 minutes. The $FeSO_4$ solutions were made up before each run from *non-deaerated* distilled water and $FeSO_4 \cdot 7H_2O$. The initial dissolved oxygen apparently promoted greigite crystallization rather than mackinawite crystallization. Aeration during heating, however, was carefully avoided to prevent pyrite formation (Berner, 1964a). Upon cooling, the reaction vessel was handled in the same manner as described above for mackinawite.

In two runs greigite equilibrium was approached from undersaturation. After filtering, the greigite plus Millipore filter from a previous precipitation run was re-suspended in a solution pre-saturated with H_2S and the greigite dissolved to saturation.

Stoichiometric pyrrhotite.—Pyrrhotite with nearly stoichiometric composition $Fe_{0.98}S$ was synthesized in vacuo at high temperatures from weighed amounts of elemental iron and sulfur by B. J. Skinner and supplied to the writer in the form of millimeter sized crystals. They were ground slightly immediately prior to use and suspended in solutions pre-saturated with H_2S. Determination of pyrrhotite solubility was used as a check on the measuring precedure, because previous determinations of its stability had been made (see Robie, 1965).

Calculation of K_{FeS}.—For a solution equilibrated with both FeS and H_2S the following equilibria are attained:

$$FeS \rightleftarrows Fe^{++}{}_{aq} + S^{--}{}_{aq}$$

$$K_{FeS} = a_{Fe^{++}}\, a_{S^{--}} \qquad (1)$$

$$H_2S_{gas} \rightleftarrows 2H^{+}{}_{aq} + S^{--}{}_{aq}$$

$$10^{-21.90} = \frac{a_{H^+}{}^2\, a_{S^{--}}}{P_{H_2S}} \qquad (a = \text{activity}) \qquad (2)$$

The value $10^{-21.90}$ is based on the thermodynamic data of Maronny (1959). Substituting (2) in (1) and utilizing the relationship $a = \gamma m$ where γ = activity coefficient and m = molality:

$$K_{FeS} = \frac{\gamma_{Fe^{++}}\, m_{Fe^{++}}\, P_{H_2S}\, 10^{-21.90}}{a_{H^+}{}^2} \qquad (3)$$

In the present study a_{H^+} and $m_{Fe^{++}}$ were measured, P_{H_2S} held constant at one atm, $\gamma_{Fe^{++}}$ estimated (see below), and K_{FeS} calculated by means of equation (3).

The activity coefficient $\gamma_{Fe^{++}}$ was derived from the ionic strength by means of tabulations of the Debye-Huckel equation (Klotz, 1950, p. 332). Corrections for ion pairing between Fe^{++} and other possible ions were not necessary due to the absence of strong interactions at the ionic strengths employed (Sillén and Martell, 1964).

Ionic strengths were calculated from ionic concentrations derived in the following manner: For pure H_2S-FeS solutions the electro-neutrality relation was:

$$m_{H^+} + 2m_{Fe^{++}} = m_{HS^-} \qquad (4)$$

The value of $m_{Fe^{++}}$ was measured, m_{H^+} was calculated from pH and a close approximation to γ_{H^+}, and m_{HS^-} was calculated from the other two via equation (4). A check on the validity of equation (4) is provided by independent calculation of m_{HS^-} from equations (10) and (11) (see below), the measured pH, and an approximate value of γ_{HS^-}. This validity was demonstrated for all runs where no additional Fe^{++} other than that from FeS solution was present (mackinawite and pyrrhotite runs in distilled water). For $FeSO_4$ solutions the electroneutrality condition was:

$$m_{H^+} + 2m_{Fe^{++}} = 2m_{SO_4^{--}} \qquad (5)$$

Because the solutions of $FeSO_4$ used were relatively concentrated and the pH was always less than 4 but greater than 2.9, the concentrations of HS^- and HSO_4^- could be safely neglected. The value of $m_{SO_4^{--}}$ was calculated via equation (5) from the measured $m_{Fe^{++}}$ and pH.[2]

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[2] Sulfate ion is thermodynamically metastable in saturated H_2S solutions, but due to its well known inert behavior at room temperature, no reduction or reaction with H_2S would be expected.

Determination of greigite solubility.—Measurement of Eh (oxidation potential) for several greigite solubility runs using a platinum electrode indicated a close correspondence with the half cell:

$$H_2S_{aq} \rightleftarrows 2H^+_{aq} + S^\circ_{rhombic} + 2e$$

This is demonstrated in table 5. Although rhombic sulfur was not unequivocally recognized in X-ray patterns of greigite, the assumption was made that all greigite solubility runs were close to equilibrium with rhombic sulfur as indicated by the Eh measurements. Justification of this assumption was provided by one greigite run where the purposeful addition of excess rhombic sulfur resulted in no change in Eh. Also, the addition of sulfur to a Fe-free saturated H_2S solution resulted in change of the Eh value to that predicted by the above half cell, indicating the feasibility of the half cell as an electrode controlling mechanism. The assumption of sulfur saturation enables simplification of the equilibrium reaction to:

$$Fe_3S_{4\,greigite} \rightleftarrows 3Fe^{++}_{aq} + 3S^{--}_{aq} + S^\circ_{rhombic}$$

$$K_{Fe_3S_4} = a_{Fe^{++}}{}^3\, a_{S^{--}}{}^3 = K_{FeS}{}^3 \qquad (6)$$

Thus, K for greigite could be calculated in the same manner as that for FeS.

Calculations of standard free energies of formation.—The standard Gibbs free energy of formation from the elements at 25°C, ΔF°, was calculated as follows:

For FeS:

$$\Delta F^\circ_{FeS} = \Delta F^\circ_{Fe^{++}} + \Delta F^\circ_{S^{--}} + 1.364 \log K_{FeS} \qquad (7)$$

For Fe_3S_4:

$$\Delta F^\circ_{Fe_3S_4} = 3\Delta F^\circ_{Fe^{++}} + 3\Delta F^\circ_{S^{--}} + 1.364 \log K_{Fe_3S_4} \qquad (8)$$

Values of $\Delta F^\circ_{Fe^{++}}$ and $\Delta F^\circ_{S^{--}}$ were taken from Garrels and Christ (1965).

Determination of K_1 of H_2S.—As a calibration check on the use of electrodes for solubility measurements in sulfide-rich solutions, the first dissociation constant of H_2S, K_1, was also determined. H_2S was bubbled through distilled water, 0.01 molar KCl, and 0.1 molar KCl, and the equilibrium pH measured for the reaction:

$$H_2S_{aq} \rightleftarrows H^+_{aq} + HS^-_{aq}$$

At the low pH involved the electroneutrality relation is simply:

$$m_{H^+} = m_{HS^-} \qquad (9)$$

or:

$$\frac{a_{H^+}}{\gamma_{H^+}} = \frac{a_{HS^-}}{\gamma_{HS^-}}$$

The equilibrium relation for the above reaction is:

$$K_1 = \frac{a_{H^+}\, a_{HS^-}}{a_{H_2S}} \qquad (10)$$

TABLE 1

Determination of the first dissociation constant, K_1 of H_2S in aqueous solution. $P_{H_2S} = P_{total} = 1$ atm, T = 25°C.

Solution	pH	$-\log K_1$
Distilled H_2O	3.98	6.97
0.01 m KCl	3.98	6.98
0.10 m KCl	3.99	7.01

If P_{H_2S} is known, a_{H_2S} can be calculated from National Bureau of Standards Thermodynamic data for H_2S_{gas} and H_2S_{aq} cited in Garrels and Christ (1965, p. 424). For 25°C and $P_{H_2S} = 1$ atm:

$$a_{H_2S} = 10^{-0.99} \qquad (11)$$

Substituting (9) and (11) in (10):

$$K_1 = \frac{a_{H^+}^{2}\,\gamma_{HS^-}}{10^{-0.99}\,\gamma_{H^+}} \qquad (12)$$

From a knowledge of the ionic strength, activity coefficients can be calculated from Debye-Huckel theory and combined with pH measurements to determine K_1.

RESULTS

Experimental results are summarized in tables 1 to 5. Best values for standard free energies of formation at 25°C for phases measured in the present study and for other iron sulfides are listed in table 6.

Discussion.—Values of K_1 for H_2S and K_{FeS} for pyrrhotite are listed in tables 1 to 3. In table 3 comparison is made with the results of other studies, and, as can be seen, there is reasonably good agreement between values of K_1 for H_2S obtained by different methods. This helps to justify the electrometric method used in the present study. Further credence is given to the method by the good agreement for the solubility constant of

TABLE 2

Determinations of stability of freshly precipitated ferrous sulfide and of pyrrhotite, $Fe_{0.98}S$, $P_{H_2S} = P_{total} = 1$ atm, T = 25°C. Duration of runs 3 to 6 hours.

Method	pH	$m_{Fe^{++}}$	$-\log K$	$\Delta F°_{FeS}$
Precipitation from $FeSO_4$ solution	3.65	1.2×10^{-2}	16.85	−21.32
Precipitation from $FeSO_4$ solution	3.60	1.5×10^{-2}	16.86	−21.34
Precipitation from $FeSO_4$ solution	3.70	5.5×10^{-3}	16.99	−21.51
Precipitation from $FeSO_4$ solution	3.93	2.7×10^{-3}*	16.79	−21.24
Solution of pyrrhotite in distilled H_2O	3.99	1.2×10^{-5}	18.88	−24.15

*—Value calculated from known $m_{SO_4^{--}}$ by electroneutrality equation (5).

TABLE 3

Comparison of measured equilibrium constants with results of other studies. $P_{total} = 1$ atm, $T = 25°C$, FeS_{po} refers to pyrrhotite composition $Fe_{0.98}S$ to FeS.

Method	$-\log K_{1_{H_2S}}$	$-\log K_{FeS_{po}}$	Reference
Electrometric pH	6.99 ± 0.02	18.88	This study
Spectrophotometric	7.02	———	Ellis and Golding (1959)
Conductimetric	7.06	———	Loy and Himmelblau (1961)
Survey of methods	6.96	———	Latimer (1952)
Free energy calculation based on high temperature solid gas equilibria	——	18.9	Robie (1965)

pyrrhotite of composition $Fe_{0.98}S$ determined in the present study and the K value for FeS calculated from the thermodynamic data of Robie (1965). (The slight deviation from FeS stoichiometry would cause only minor differences, within the experimental error of both studies.)

Standard free energy values for mackinawite are based on an assumed stoichiometric composition of FeS. From earlier work (Berner, 1962; 1964a) it is possible that the mackinawite is actually enriched in iron by a few percent over the 1:1 composition so that the effect of this small compositional variation on $\Delta F°$ has not been considered. It is noteworthy, however, that the K_{FeS} values obtained for mackinawite formed from iron corrosion (highly reducing conditions with H_2 gas formation) and mackinawite formed by precipitation from $FeSO_4$ solution (less reducing conditions) show little or no differences; no obvious compositional trend is apparent.

As can be seen from figure 1 there is a definite broadening of the X-ray diffraction peaks for greigite and mackinawite as compared to pyrrhotite. This broadening can be attributed to a finer crystallite size for the greigite and mackinawite or compositional variation within each

TABLE 4

Determinations of stability of mackinawite in aqueous solution at $P_{H_2S} = P_{total} = 1$ atm, $T = 25°C$. Duration of runs 3 to 6 hours. Method of preparation discussed in text.

Method	pH	MFe^{++}	$-\log K_{FeS}$	$\Delta F°$ FeS
Solution in distilled H_2O	4.26	6.4×10^{-5}	17.60	−22.35
Solution in distilled H_2O	4.27	7.7×10^{-5}	17.51	−22.22
Solution in distilled H_2O	4.25	8.0×10^{-5}	17.54	−22.26
Solution in 0.01 m KCl	3.96	4.6×10^{-4}	17.50	−22.21
Solution in 0.01 m KCl	3.98	3.9×10^{-4}	17.53	−22.25
Precipitation from $FeSO_4$ solution at 60°C.	3.30	9.7×10^{-3}	17.62	−22.37

TABLE 5

Determinations of stability of greigite in aqueous solution at $P_{H_2S} = P_{total} = 1$ atm, T = 25°C. Duration of runs 3 to 6 hours. Calculated Eh is based on the half cell, $H_2S \rightleftarrows 2H^+ + S^\circ + 2e$. Method of preparation discussed in text. NM = not measured.

Method	pH	$m_{Fe^{++}}$	Measured Eh (v)	Calc Eh (v)	$-\log K_{FeS}$	$\Delta F^\circ_{Fe_3S_4}$
Precipitation from $FeSO_4$ solution at 80-90°C	2.93	1.3×10^{-2}	0.000	0.000	18.22	−69.6
"	2.92	1.1×10^{-2}	−0.003	0.000	18.32	−70.0
"	2.97	1.2×10^{-2}	−0.004	−0.003	18.16	−69.3
"	2.93	1.2×10^{-2}	NM	—	18.25	−69.7
"	2.99	9.5×10^{-3}	NM	—	18.23	−69.6
"	2.95	9.6×10^{-3}	NM	—	18.31	−69.9
"	2.92	1.1×10^{-2}	NM	—	18.32	−70.0
Re-solution of precipitated Fe_3S_4 in distilled H_2O	4.01	8.3×10^{-5}	−0.071	−0.064	18.00	−68.7
"	4.04	7.3×10^{-5}	NM	—	18.00	−68.7

phase. If the former effect predominates, then fine crystal size might give rise to supersolubility due to excess surface free energy. In order to check this possibility, widths of peaks that fall near $2\theta = 30^\circ$ (Cu radiation) were compared to the 30° peak of coarsely crystalline pyrrhotite and approximate crystallite sizes derived using the procedures outlined by Klug and Alexander (1954). The average size obtained, which is characteristic of essentially all samples studied, was 250 ± 50 Å. Using this size, reasonable values for specific surface free energy from Nielsen (1964), and the assumption of cube-like crystals, one obtains a maximum value of 0.2 ± 0.1 kcal/mole of FeS for the excess surface free energy of both phases. The value is a maximum because it is assumed that the entire

TABLE 6

Standard free energies of formation from the elements at 25°C for sedimentary iron sulfides. Error limits are the total range of reproducibility only.

Mineral	Composition	ΔF° kcal/mole	Reference
"Precipitated FeS"	FeS	−21.3 ± 0.2	This study
Mackinawite	FeS	−22.3 ± 0.1	This study
Greigite	Fe_3S_4	−69.4 ± 0.7	This study
Pyrrhotite (stoichiometric, "troilite")	FeS	−24.2	Robie (1965) and this study
Pyrite	FeS_2	−38.3	Robie (1966)
Marcasite	FeS_2	No data	—
Smythite	Fe_3S_4	No data	—
Pyrrhotite (monoclinic)	Fe_7S_8	No data	—

surface of every 250 Å crystal is exposed to the solution and that the line broadening is due solely to fine crystallinity. Since 0.2 kcal/mole is almost within experimental reproducibility, because both greigite and mackinawite are affected equally, and because stabilities relative to pyrrhotite and pyrite are not appreciably changed, no corrections for crystal size have been made. In fact it is quite possible that the size of the synthetic materials studied in the present work may more closely approximate natural greigite and mackinawite than idealized coarse crystals.

Detailed comparison of results of this paper with "FeS" solubility results of earlier studies (Bruner and Zawadski, 1909; Moser and Behr, 1924; Kolthoff and Griffith, 1938; Treadwell and Gubeli, 1941) is difficult because these studies include no identification of the crystal form of the sulfide, no correction for ionic strength and activity coefficients, and no details pertaining to the possible aeration of the original Fe^{++} solutions or FeS prior to equilibration with H_2S. In general, values obtained in these earlier studies for "FeS" dissolved or precipitated at 25°C and aged from 1 hour to several days give calculated values of K_{FeS} that fall roughly in the range 10^{-17} to 10^{-18}, in general agreement with the findings of the present study. In one study (Kolthoff and Griffith, 1938) a precipitation experiment was continued, with constant H_2S bubbling, for one week, and ferrous sulfide was synthesized at 80°C and used in dissolution runs. It is instructive to note that solubilities were obtained that, when corrected for ionic strength, gave calculated values of K_{FeS} of approximately $10^{-18.1}$. It is quite possible that in these runs K_{FeS} for greigite was being measured, and, if so, there is agreement with results of the present study (see table 5).

From the free energy data of table 6 the direction and free energy change of several solid-solid reactions at 25°C, 1 atm total pressure can be obtained. They are:

$$FeS_{\text{precipitated}} \rightarrow FeS_{\text{mackinawite}} \qquad \Delta F^\circ_{\text{reaction}} = -1.0 \text{ kcal/mole}$$

$$FeS_{\text{mackinawite}} \rightarrow FeS_{\text{pyrrhotite}} \qquad \Delta F^\circ_{\text{reaction}} = -1.9 \text{ kcal/mole}$$

(strictly speaking these reactions are not stoichiometric)

$$3FeS_{\text{mackinawite}} + S^\circ_{\text{rhombic}} \rightarrow Fe_3S_{4\,\text{greigite}} \qquad \Delta F^\circ_{\text{reaction}} = -2.5 \text{ kcal/mole}$$

$$Fe_3S_{4\,\text{greigite}} \rightarrow 2FeS_{\text{mackinawite}} + FeS_{2\,\text{pyrite}} \qquad \Delta F^\circ_{\text{reaction}} = -13.5 \text{ kcal/mole}$$

$$FeS_{\text{mackinawite}} + S^\circ_{\text{rhombic}} \rightarrow FeS_{2\,\text{pyrite}} \qquad \Delta F^\circ_{\text{reaction}} = -16.0 \text{ kcal/mole}$$

$$Fe_3S_{4\,\text{greigite}} + 2S^\circ_{\text{rhombic}} \rightarrow 3FeS_{2\,\text{pyrite}} \qquad \Delta F^\circ_{\text{reaction}} = -45.5 \text{ kcal/mole}$$

As can be seen from the above, at 25°C mackinawite and greigite are unstable phases relative to stoichiometric pyrrhotite or stoichiometric pyrrhotite plus pyrite. It is also quite probable that iron-rich mackinawite is unstable relative to metallic iron plus pyrrhotite.

A metastable equilibrium diagram for mackinawite and greigite of the type discussed earlier (Berner, 1964b) is shown in figure 2. The boundary curve is a plot of the half cell reaction:

$$3FeS_{\text{mackinawite}} + S^{--}_{aq} \rightleftarrows Fe_3S_{4\,\text{greigite}} + 2e$$

$$Eh = -0.530 + 0.0296pS^{--} \qquad (pS^{--} \equiv -\log_{10}a_{S^{--}}) \qquad (13)$$

It should be noted that ordered monoclinic pyrrhotite, Fe_7S_8, and smythite, Fe_3S_4, for which there are no thermodynamic data are not included in the above calculations so that nothing can be said concerning their stability relative to mackinawite and greigite. Due to the highly negative ΔF° of formation for pyrite, it is probable that both smythite and Fe_7S_8 are unstable relative to stoichiometric FeS pyrrhotite plus pyrite.

Although the above calculations are strictly valid only at 25°C, it is quite probable, from the known thermodynamic behavior of solids over short temperature ranges, that the reactions will proceed in the same directions at temperatures within 10 to 20° of 25°C.

SEDIMENTOLOGICAL APPLICATIONS

If the black iron sulfide found in most recent sediments is, in fact, poorly crystallized mackinawite, greigite, or a mixture of both, then the solubility of the natural materials would be expected to fall between that of freshly precipitated FeS ($pK = 16.9$) and greigite ($pK = 18.2$). Verification of this is provided by studies currently in progress by R. Doyle of Yale University (personal communication) who, by the use of selected leaching techniques and solubility determinations of iron sulfide in lake and estuarine sediments has been able to demonstrate the presence of different materials with solubilities falling in this range. Use of the solubility data of the present study, thus, can be used as a general guide to the nature of FeS in sediments and its role in controlling the concentration of dissolved iron and sulfide in pore water.

From the discussion in the previous section it is clear that greigite and mackinawite are unstable with respect to pyrite and stoichiometric pyrrhotite. Although transformation rates and the factors controlling them are unknown at present, it is probable that neither greigite nor mackinawite will persist long in the geologic record. At present no sedimentary occurrences older than the Tertiary have been reported for either mineral.

Figure 2 is applicable to recent sediments in which pyrite or pyrrhotite has not yet completely formed at the expense of mackinawite or greigite. Since many natural Eh and pS^{--} measurements for H_2S-rich marine sediments fall in the greigite field but near the greigite-mackinawite boundary (for example, see Berner, 1963) either phase or both may persist in any given environment providing pyrite (the most stable phase) doesn't form instead.[3] It is possible that during diagenesis in many occurrences originally precipitated FeS may be oxidized first to greigite before being further oxidized to pyrite. This step-wise oxidation can

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[3] Unpublished results of R. Doyle (personal communication) for lake sediments containing black FeS definitely fall in the mackinawite stability field.

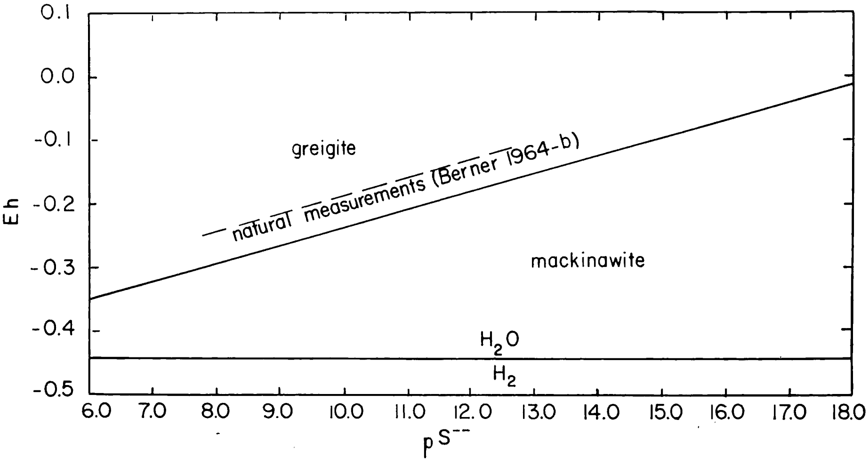

Fig. 2. Eh-pS^{--} diagram for mackinawite and greigite at 25°C, 1 atm total pressure (pS $= -\log a_{S^{--}}$). Lower curve marked H_2O/H_2 is the stability field boundary for water at $P_{H_2} = 1$ atm, pH $= 7.5$.

actually be demonstrated in the laboratory at elevated temperatures by the admission of small amounts of air to H_2S-saturated $FeSO_4$ solutions.

Volkov (1961) has ascribed the non-disappearance of black iron sulfide with depth in sediments of the Black Sea to a lack of sufficient oxidizing agent (elemental sulfur) to transform all the black material to pyrite. If this is true, one might expect to find an "arrested" oxidation with the partial formation of greigite instead of pyrite from the original FeS. In fact this is what has been found in iron sulfide-rich concretions taken from several meters depth in the sediments. From Volkov's X-ray data it can be shown (Berner, 1964a) that the concretions consist of a mixture of greigite with a lesser amount of mackinawite.

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