IDENTIFICATION AND SOLUBILITY OF IRON SULFIDE IN ANAEROBIC LAKE SEDIMENT*

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ABSTRACT. The dispersed and poorly-crystalline iron sulfide that darkens the color of anaerobic sediment containing high concentrations of dissolved ferrous iron has been tentatively identified as mackinawite (tetragonal FeS) in sediment from Linsley Pond, Connecticut. The mineral was identified by suspending sediment in solutions saturated with H_2S at one atm pressure and determining the equilibrium ion activity product (equilibrium IAP) of the reaction: $FeS = Fe^{++} + S^=$. The IAP was $10^{-17.7}$ compared to published values of $10^{-17.6}$ for synthetic mackinawite. These values can be assumed to approximate the "solubility product" of FeS in environments such as the hypolimnia of Linsley Pond and Lake Mendota. Calculations based on the activity of Fe^{++}, pH, and Eh in Linsley Pond indicate that mackinawite is stable relative to greigite (Fe_3S_4), in agreement with observation. Since greigite has been shown to be stable relative to mackinawite in marine sediment this mineral may be useful in differentiating Fe^{++}-rich and H_2S-rich environments in the fossil record.

ACKNOWLEDGMENTS

INTRODUCTION

Why are anaerobic sediments dark in color? It is commonly observed that the color of a sediment changes as aerobic give way to anaerobic conditions. In a column of sediment the mud is often gray or black at depth and brown, orange, or yellow at the surface, near the zone of oxygenated water. The color does not always change in this direction, however; in situations where a drastic decrease in the amount of oxygen has occurred with time, dark sediment can be found resting on top of lighter sediment. For example, a long core from the Black Sea darkens in the upward direction (Shishkinia, 1961) as does sediment from Lake Mendota (Murray, 1956) and the deep part of Linsley Pond, Connecticut (personal observation). The mud-water interface is dark during the summer and light during the winter in the hypolimnia of lakes such as Esthwaite Water (Mortimer, 1941, 1942) that are deficient in oxygen during summer stratification.

A correlation between platinum electrode (redox) potential and color has been found in lakes that possess alternating layers of light and dark sediment (Kuznetsov and Romanenko, 1963; Semenovich, 1963). The electrochemical basis of redox measurements in the sediment of Linsley Pond is examined elsewhere (Doyle, ms) where it is shown that

the Eh must be less than a maximum value of -80 mv. relative to the normal hydrogen electrode. The purposes of the present paper are, first-ly, to identify the mineral responsible for blackening the sediment in Linsley Pond and, secondly, to establish the relationship between the enviromental Eh and the calculated stability field of the mineral.

Sedimentary iron sulfide minerals.—Treatment with dilute acid re-moves the black color and simultaneously liberates H_2S and ferrous iron from many sediments, including those of Linsley Pond. The common be-lief that ferrous sulfide cause the darkening is based on a reasonable in-terpretation of this observation. The iron sulfide is often called hydro-troilite, $FeS.nH_2O$, although this name has not been accepted by miner-alogists as a valid mineral species (Palache, Berman, and Frondel, 1944). Iron sulfide minerals which have been identified in recent or older sedi-ments and which might be present in the hypolimnia of lakes are listed in table 1. Of these minerals, pyrite is known to occur in Linsley Pond. Vallentyne and Swabey (1955) and Vallentyne (1961) report the occur-rence of pyrite spherules similar to those found in many other sediments (Love, 1962).

Examination of aqueous suspensions of surface sediment from Lin-sley Pond with a hand magnet does not show any ferromagnetism on the part of the authigenic black material, which consists of particles both inside and outside the walls of vascular plant cells, diatom frustules, and other microfossils, as well as a diffuse gray tint on amorphous aggregates of clay and organic detritus. The larger particles could be marcasite, pyrite, or stained or charred organic matter. The absence of strong magnetic susceptibility indicates that they are unlikely to be greigite, smythite (Erd, Evans, and Richter, 1957), or pyrrhotite.

The lack of magnetic susceptibility is less conclusive evidence when it comes to identifying the highly diffuse, acid soluble sulfide that causes the overall dark color of the sediment. This substance is too dilute and poorly crystalline to give an X-ray diffraction pattern in the presence of the detrital material from which it cannot easily be separated. The sul-fide is difficult to concentrate for chemical analysis or X-ray identifica-tion because of the rapidity with which it oxidizes in air. The four minerals listed in table 1 that might be present as disperse acid-soluble sulfides in Linsley Pond are, therefore, smythite, greigite, mackinawite, and amorphous FeS.

Greigite has been described and named by Skinner, Erd, and Grim-aldi (1964) from the beds of Tertiary lakes (probably highly alkaline) in California. Like pyrite, it has been found both as concretions and as particles inside cavities of plant and animal microfossils in recent sedi-ments (Jedwab, 1967) and Tertiary sediments (Polushkina and Sidorenko, 1963). The two minerals are often found together in a sediment and even, according to Polushkina and Sidorenko, in the same microfossil.

Mackinawite, described by Evans and others (1964), was first noted in a contemporary sedimentary environment by Berner (1964) who identified

TABLE 1

Sedimentary iron sulfides

Name	Formula and symmetry		Soluble in dilute HCl	Magnetic susceptibility
Pyrite	FeS_2	(cubic)	no	paramagnetic
Marcasite	FeS_2	(orthorhombic)	no	paramagnetic
Greigite	Fe_3S_4	(cubic)	yes	ferromagnetic
Smythite	Fe_3S_4	(rhombohedral)	yes	ferromagnetic
Pyrrhotite	$Fe_{1-x}S$	(hexagonal)	slightly	ferromagnetic
Mackinawite	FeS	(tetragonal)	yes	paramagnetic
"Amorphous"	FeS or $FeS.nH_2O$	(amorphous)	yes	paramagnetic

X-ray data published by Volkov (1961) from ferrous sulfide concretions in the Black Sea. It can be synthesized at room temperature by the action of H_2S on metallic iron, fine-grained goethite, and solutions of $FeSO_4$ (Berner, 1964).

Solubility of iron sulfides.—The various iron sulfides likely to be found in lake sediment have different thermodynamic stabilities and hence different solubilities in water. Depending on the identity of the sulfide, the possible solubility products for the precipitation of the solid phase from solutions containing ferrous and sulfide ions range from about $10^{-16.9}$ to $10^{-18.9}$ (Berner, 1967). This precipitation appears to occur rapidly in nature as it does in the laboratory. Lee (1962) calculates that 80 percent of the iron that enters Lake Mendota every year is precipitated as FeS on the bottom of the lake. Iron sulfide accumulates at the rate of 7.5 x 10^{-3} mg sulfur/cm^2/day in the sediment of the anaerobic hypolimnion of Linsley Pond (Stuiver, 1967). It is clear that either dissolved ferrous iron or hydrogen sulfide can reach high concentrations in lake water but not both together (except at low pH) even under extremely reducing, polluted conditions.

The reaction between ferrous sulfide and its ions may be written:

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

"a" represents the activities of the ions, and IAP the ion activity product. The solid phase precipitates when the IAP exceeds the characteristic equilibrium value; when the IAP is less than this value, the solid dissolves. In practice, of course, this statement is only strictly true if the time element is ignored.

The solubilities (=equilibrium IAP) of synthetic greigite, mackinawite, and amorphous FeS are $10^{-18.2}$, $10^{-17.6}$, and $10^{-16.9}$, respectively (Berner, 1967). The technique introduced here is based on the idea that the equilibrium solubility of the iron sulfide in a lake sediment can be determined by varying the dissolved iron, sulfide, and hydrogen ion

activities in a suspension of the sediment in the laboratory and noting whether solution or precipitation takes place. A comparison of this solubility with the solubility of the synthetic sulfides then suggests the identity of a mineral which is nearly impossible to study by ordinary methods because of its low concentration in the sediment and its rapid disappearance in the presence of oxygen.

<div align="center">PROCEDURE</div>

Collection of sediment.—Sediment containing iron sulfide was collected from Linsley Pond, Connecticut, late in the autumn of 1966 after the breakup of summer stratification. Linsley Pond is a non-calcareous, euthrophic lake in which dissolved iron or (very briefly) H_2S appear in the hypolimnion during summer stratification. The top 15 cm of sediment in the deep part of the lake is nearly jet black during the summer and was also black in the Ekman dredge sample collected during fall overturn (any oxidized sediment which might have been present having been mixed into the sample). A second sample from a depth of 1.5 m below the bottom of the lake was obtained with a Livingston coring apparatus.

The samples were placed in plastic bags and then quick-frozen in an ethanol-dry ice mixture and stored in a freezer. Chips of the brittle, frozen sediment were broken off when required for use in an experiment. While frozen, oxidation of the ferrous sulfide was very slow and limited to an easily removed surface layer.

Sulfide activity.—The activity of sulfide ion was determined by bubbling CP-grade H_2S through a stirred, dilute aqueous suspension of the sediment in distilled water at one atm pressure and measuring pH with a Corning Model 12 pH meter. To avoid streaming potentials the stirring and bubbling were stopped for about one minute before taking each measurement. The activity of sulfide ion in the suspension was calculated from the pH of the reaction:

$$H_2S_{gas} \rightleftharpoons S^= + 2H^+ \tag{2}$$

with the equation, at one atm H_2S,

$$\log a_{S^=} = -21.90 + 2pH \quad \text{(Pourbaix, 1963)} \tag{3}$$

where $a_{S^=}$ is the activity of the sulfide ion. A water bath controlled temperature to 25.0 ± 0.1 deg. Equation 3 was used by Berner in his determination of the solubility of artificial iron sulfides, so any uncertainty in the constant will not affect the validity of the conclusions reached in this paper.

Some of the solubility runs lasted for several days and were not considered at equilibrium if the pH drifted 0.002 unit per hour. In experiments run at pH 4 or higher comparatively little dissolution of the sediment took place, and the sediment was suspended in 0.1 N KCl rather than distilled water. The ionic strength was thus maintained at a fairly high level to reduce suspension effects and streaming potentials and also

to keep approximately the same activity coefficient for ferrous iron in all the experiments.

Ferrous iron activity.—The concentration of dissolved cations was measured in samples of the suspension which had been filtered through a 0.45μ membrane filter, acidified, and then boiled briefly to remove dissolved H_2S. Fe^{++} was analyzed colorimetrically with orthophenanthroline (Sandell, 1959). Ca, Mg, K, Mn, and Na were analyzed with a Perkin-Elmer atomic absorption spectrophotometer.

The activity of ferrous iron is related to concentration by the activity coefficient $\gamma_{Fe^{++}}$:

$$a_{Fe^{++}} = \gamma_{Fe^{++}} \, m_{Fe^{++}}$$

where $m_{Fe^{++}}$ is the molar concentration of Fe^{++}.

The individual ion activity coefficient $\gamma_{Fe^{++}}$ was obtained from the ionic strength of the solution using the Debye-Hückel equation (Garrels and Christ, 1965). The cations included in this calculation were Fe^{++}, Ca^{++}, Mn^{++}, and H^+, others being of minor importance. HS^- was assumed to be the only important anion, approximately equal to the total cation concentration in equivalents per liter. As an independent check on this assumption in several experiments the concentration of HS^- was calculated from the pH using the equation (Pourbaix, 1963):

$$\log a_{HS^-} = -7.99 + pH \tag{4}$$
$$\text{(at one atm } H_2S)$$

and the definition:

$$a_{HS^-} = \gamma_{HS^-} \, m_{HS^-}$$

The activity coefficient γ_{HS^-} was calculated from the ionic strength. The concentrations of HS^- resulting from these two calculations differed by less than 15 percent. This was taken to mean that no unexpected ionic species were present in solution, and that the values for the ionic strength are reasonably accurate. In some of the experiments $\gamma_{Fe^{++}}$ fell as low as 0.35.

<center>RESULTS</center>

1. *Supersaturated suspension.*—When approximately 10 ml of the frozen sediment were added to 250 ml of H_2S-saturated KCl solution at pH 4, ferrous iron rapidly came into solution and then slowly precipitated again (fig. 1). The H_2S evidently acted first as an acid, displacing ferrous iron and other cations from exchange sites and dissolving acid soluble minerals such as ferrous carbonate and some iron sulfide. The rise in pH accompanying this solubilization of cations was very rapid. Over the course of the next few hours the pH and iron concentrations both fell somewhat, governed by the precipitation reaction:

$$Fe^{++} + H_2S \longrightarrow FeS + 2H^+. \tag{5}$$
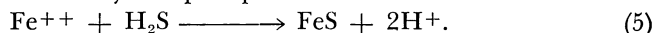
It is emphasized that other cations, for example Mn^{++} (shown in fig. 1) stayed in solution.

The ion activity product of Fe^{++} and $S^=$ is plotted as the upper curve in figure 1. The IAP stabilized at about $10^{-17.65}$ in this experiment,

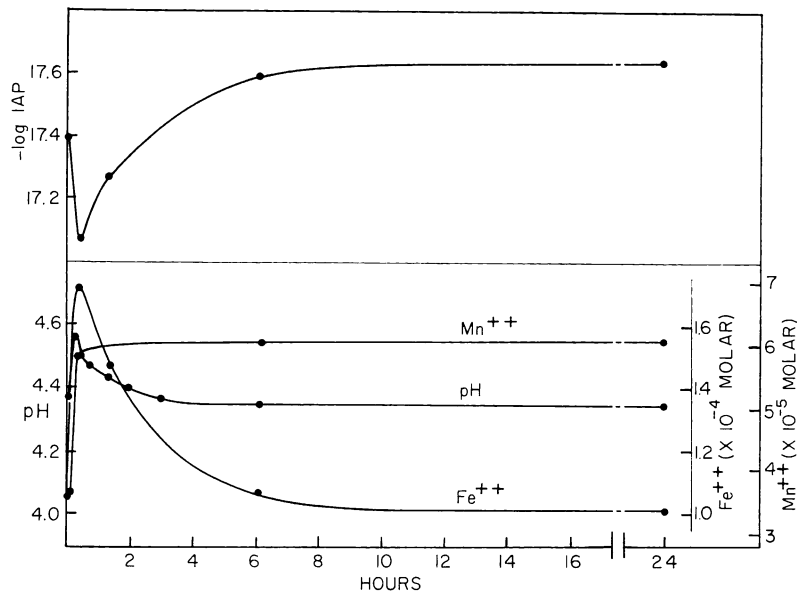Fig. 1. Chemical changes in a suspension of 10 ml of Linsley Pond sediment in 240 ml 0.1 N KCl saturated with H$_2$S at 1 atm pressure.

which is close to the equilibrium IAP for mackinawite and considerably lower than the equilibrium IAP obtained when H$_2$S is bubbled for a few hours through pure solutions of ferrous sulfate causing the precipitation of amorphous FeS (Berner, 1967). It is likely that mackinawite already present in the sediment nucleated the precipitation of tetragonal rather than amorphous FeS.

2. *Undersaturated suspension.*—An experiment in which the same sample of mud was suspended twice in H$_2$S-saturated KCl showed that the solubility of FeS in the suspension was not that predicted for a rapidly reversible equilibrium with a single phase. The lower curve in figure 2, showing the change in pH when a chip of frozen sediment was dropped into H$_2$S-saturated KCl, is analogous to the pH curve of figure 1. The final IAP was 10$^{-17.65}$. Thirty-three hours later the suspension was filtered, rinsed with distilled water, and resuspended in fresh H$_2$S-saturated KCl solution. This time no ferrous iron went into solution to reprecipitate as ferrous sulfide, so the second curve in figure 2 represents approach to equilibrium from undersaturation rather than supersaturation. The final IAP for approach from undersaturation was 10$^{-18.06}$. The highly undersaturated suspension dissolved rapidly at first and had not reached equilibrium after 48 hours.

3. *Attempt to prevent precipitation of FeS during solubility determination.*—A third experiment was devised to measure the solubility of the ferrous sulfide without precipitating the exchangeable and dis-
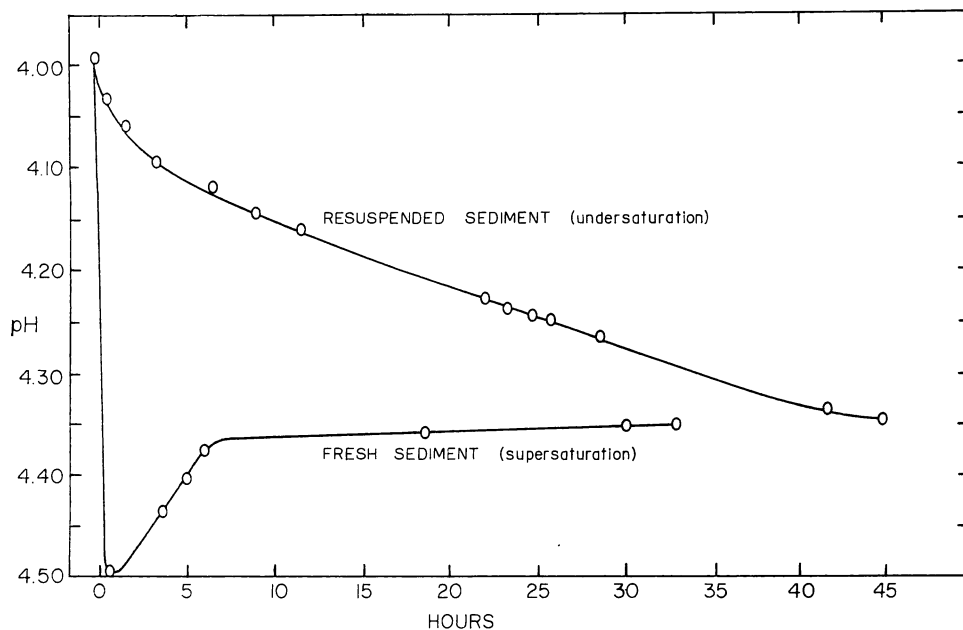
Fig. 2. Change in pH with time as equilibrium in a suspension of 10 ml of Linsley Pond sediment in 240 ml 0.1 N KCl is approached both from undersaturation and supersaturation. Lower curve, frozen sediment. Upper curve, second equilibration with the same sediment after filtering.

solved ferrous iron in the sediment. Approximately 10 ml of sediment were placed in 240 ml of H_2S-saturated KCl as in the preceding experiments. As soon as the pH began to level off after its initial rise (indicating incipient precipitation of FeS), 50 ml of suspension was removed, and 50 ml of H_2S-saturated KCl solution was added to the flask. This fresh solvent lowered the pH (simultaneously lowering $a_{S^=}$) and diluted the suspension to 80 percent of its former concentration so that the iron sulfide continued to dissolve. This procedure was then repeated a number of times; after each dilution the pH rose somewhat and then leveled off indicating that Fe^{++} had stopped coming into solution. By the end of the experiment about 95 percent of the sediment had been removed from the flask by dilution. Part of the 50 ml removed before each addition of fresh solvent was analyzed for Fe^{++} and other cations. The IAP was calculated for each value of $a_{S^=}$ and $a_{Fe^{++}}$. If C_n = the concentration of Fe^{++} (in μmoles/ml) in the sample taken when the pH had leveled off after the nth dilution, then the total iron dissolved from the sediment during the experiment up to and including the nth dilution equals:

$$\sum Fe^{++} = 250\ C_n + 50\ (C_0 + C_1 + \ldots C_{n-1}). \tag{6}$$

In figure 3 each successive IAP is plotted against the total iron which had gone into solution up to that point.
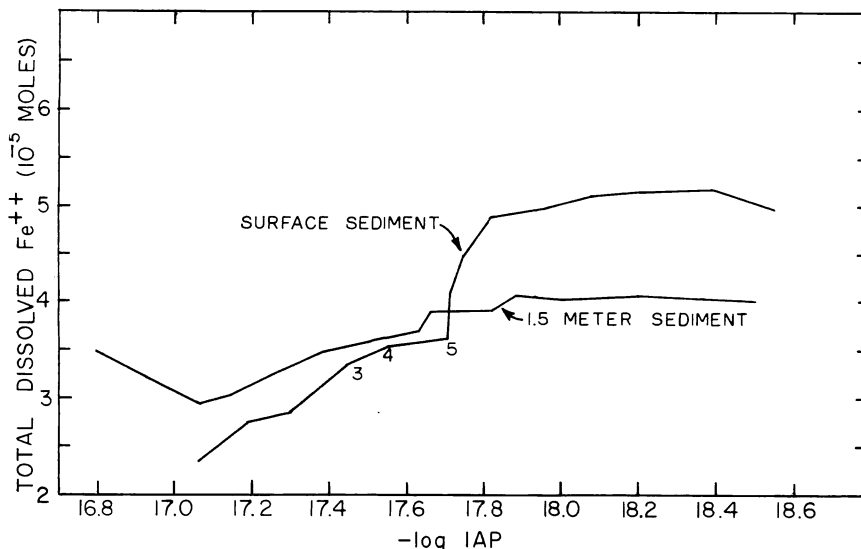
Fig. 3 Progressive leaching of iron from suspension of sediment as sulfide activity and pH are lowered by successive dilutions. Numbers on curve refer to the number of dilutions.

Considering the curve for surface sediment in figure 3, we see that at IAP $= 10^{-17.1}$, 24 μmoles of ferrous iron were in solution. This was exchangeable iron, iron in the interstitial water, and possibly some iron sulfide with an equilibrium IAP greater than $10^{-17.1}$. Over the next five dilutions the pH, $a_{S^=}$, and $a_{Fe^{++}}$ declined step-wise as iron was leached away from the sediment.

After the fifth dilution a less-soluble iron sulfide, which above $10^{-17.7}$ had been supersaturated, suddenly began to dissolve. During the next several dilutions enough ferrous sulfide dissolved to bring the ion activity product back to approximately $10^{-17.7}$ at which point there was no further drift of pH. The time-course of the glass electrode in reaching equilibrium after the third, fourth, and fifth dilutions is shown in figure 4; a remarkable difference in behavior when a mineral with an equilibrium IAP of about $10^{-17.7}$ started to dissolve is evident.

Quite abruptly the reservoir of material dissolving near this IAP was exhausted, and further lowering of $a_{S^=}$ by dilution did not dissolve any more iron although the sediment still appeared black.

A similar experiment performed on the sediment from 1.5 m below the mud-water interface is also shown in figure 3. Although some iron dissolved as the activity of sulfide was lowered by dilution, there was no material with an equilibrium IAP well enough defined to show up on this graph. The sediment was a chocolate-brown color before being treated with H_2S and appeared, compared with the jet-black surface sediment, relatively free from acid-soluble iron sulfide. Nevertheless, it turned black in the H_2S-KCl solution, showing that reactive iron (Fe++,
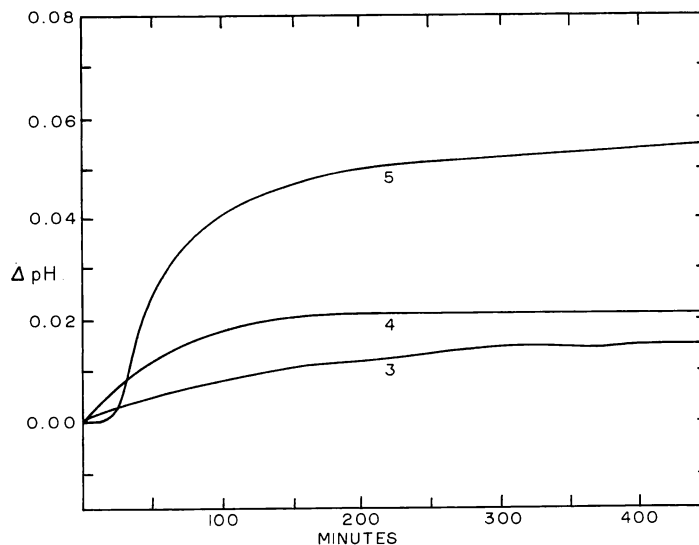
Fig. 4. Change in pH with time after dilutions numbered 3, 4, and 5 on figure 3. The pH reference point is the pH immediately before making the dilution.

FeCO$_3$) was present. The difference in the iron sulfide composition of the surface and 1.5 m sediment probably reflects a change in the conditions of deposition within the lake, a phenomenon similar to that seen in Lake Mendota (Murray, 1956). It may conceivably be a diagenetic phenomenon such as pyrite formation from FeS, however.

These experiments indicated that the iron sulfide in the surface sediment was soluble over a range of IAP from at least $10^{-17.1}$ to approximately 10^{-18}, much of the material having an IAP close to $10^{-17.7}$. This is close to the equilibrium IAP of mackinawite (Berner, 1967); there is no change in slope of the upper curve of figure 3 in the neighborhood of IAP $= 10^{-18.2}$, which might have indicated the presence of greigite plus free sulfur.

Although this experiment was designed to prevent the precipitation of ferrous sulfide, it was noted that the 1.5 m sediment turned black, or at least gray, when dispersed in the H$_2$S-saturated KCl. Some FeS must have precipitated as the pH rose during the first stages of the experiment. Although it seems unlikely that the large amounts of FeS dissolving with an IAP of $10^{-17.7}$ in the surface sediment could be an artifact produced in this way, this possibility was checked experimentally.

4. *Direct measurement of iron sulfide in sediment at low pH.*—The solubility of the iron sulfide increases rapidly as the pH is reduced. Figure 5 shows the results of a series of experiments in which various amounts of sediment were suspended in H$_2$S-saturated distilled water maintained at pH 3 with HCl. Each point on this graph represents a different quantity of sediment (from 1 ml to 30 ml) made up to 50 ml with
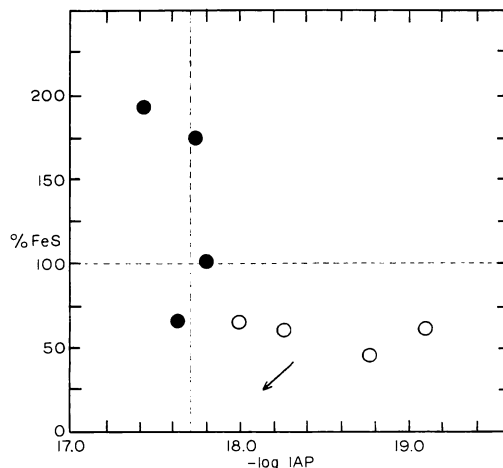
Fig. 5. Solution of FeS in Linsley Pond sediment at a pH of approximately 3. Each circle represent a suspension containing a different amount of sediment. Open circles: experiment terminated after 72 hrs while pH was increasing faster than 0.002 units/hr. (Closed circles, pH constant or drifting less than 0.002 pH units/hr).
Ordinate:

$$\frac{\text{FeS in sediment after leaching with } H_2S}{\text{FeS in untreated sediment}} \times 100 \text{ percent}$$

H_2S-saturated distilled water. The tendency for the pH to rise as iron sulfide dissolved was countered by addition of dilute HCl. It was necessary to add acid quite rapidly during the first few hours, then more and more slowly. Finally, the pH was allowed to drift to a final value between pH 3.0 and 3.1 (about 1.3 pH unit lower than in the previous experiments).

At the end of each experiment part of the suspension was filtered rough a 0.45μ membrane filter, and the residue rinsed with distilled er. The filter residue was then transferred to a vacuum flask and boiled briefly with 6N HCl. H_2S released from the acid soluble sulfide was trapped in a solution of ammoniacal zinc acetate and measured by iodometric titration (Kolthoff and Sandell, 1952). The boiled residue was filtered again and weighed. In figure 5 results are expressed as a ratio of the sulfide remaining after leaching under H_2S + HCl to the amount present in the fresh sediment.

When large quantities of sediment were put into suspension, precipitation of FeS in the sediment took place even at pH 3. These suspensions gained sulfide and so lie above the 100 percent line in figure 5. The more dilute suspensions, on the other hand, showed a net loss of FeS, eliminating the possibility that the IAP is that of FeS formed during the experiment. It appears from the data of figure 5 that the IAP of material precipitated and some of the material dissolved both lie in the neighborhood of $10^{-17.7}$, again suggesting that nucleation of mackinawite occurred when FeS precipitated.

Only about 40 percent of the total acid-soluble sulfide could be made to dissolve in a reasonable length of time (3 days) at pH 3. However, the final values for those open circles in figure 5, which lie to the right of $10^{-17.7}$ and show loss of sulfide, do not represent true solution equilibrium. After three days in H_2S solution the pH of these runs was still drifting very slowly upward at a constant rate. On figure 5 this would be slow drift downward and to the left, as indicated by the arrow.
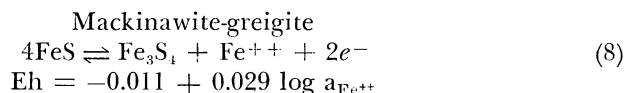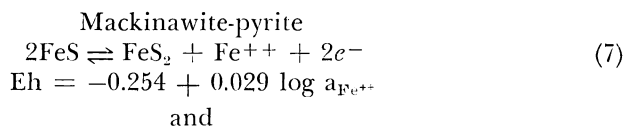
DISCUSSION

It is necessary to distinguish between the equilibrium IAP of a substance and the rapidity with which it dissolves. The equilibrium IAP is a thermodynamic property which can be calculated from the free energies of the solid phase and the solvated ions; the rate at which a solid actually dissolves is a kinetic phenomenon depending on such phenomena as concentration gradients and catalysis. Both the equilibrium IAP and the kinetics of dissolution of a mineral are affected by crystal size if the crystals are extremely small. Berner (1967) concluded that the effect of excess surface energy on his values for the free energy of formation of mackinawite and greigite is negligible, despite the finely divided state of the minerals in his experiments. The crystal size of FeS in Linsley Pond sediment is, of course, not known but is also likely to be very small.

An iron sulfide with an equilibrium IAP nearly identical to that of the mineral mackinawite was found in the sediment of Linsley Pond, but it only constituted about 40 percent of the total iron sulfide which could be dissolved in boiling hydrochloric acid. The 40 percent solubility at pH 3 was a limit set by the kinetics of the system and does not imply that only this much sedimentary ferrous sulfide has an equilibrium IAP of $10^{-17.7}$. The slow rate of solution and slight discrepancy between the equilibrium IAP of the artificial and sedimentary FeS suggest that the crystallite size of the mineral in the sediment is somewhat larger than the 250 Å calculated by Berner for his artificial minerals. The difference in IAP is small, however, and may also reasonably be attributed to compositional differences or experimental error.

It is possible that some of the iron sulfide in the sediment of Linsley Pond is more soluble than mackinawite. Berner (1967) found a maximum IAP of about $10^{-16.9}$ for freshly precipitated amorphous FeS (at 25°C), a figure consistent with the largest values listed by Sillén and Martel (1964). The presence of a small amount of this material, presumably metastable with respect to mackinawite, would not have been detected by the techniques used here. Although it is conceivable that other, as yet undescribed, polymorphs of ferrous sulfide may have solubilities close enough to that of mackinawite to confuse the identification, the existence of minerals such as $Fe(SH)_2$ is entirely hypothetical at present.

*Iron sulfide precipitation in anaerobic water and sediments.—*As oxygen disappears from a body of water such as the hypolimnion of Linsley Pond, ferrous iron or hydrogen sulfide frequently appear in solution. The concentrations of dissolved sulfide and ferrous iron are interconnected through the precipitation of the black iron sulfide minerals which are often found in oxygen-poor environments. The precipitation reaction has been shown to be fairly reversible in the laboratory and probably also in nature—something approaching true equilibrium may obtain quite frequently in both ferrous iron dominated and hydrogen sulfide dominated waters. Precipitation and solution characteristically take place in the reduced microzone at the sediment surface and perhaps also in the stagnant overlying water of lakes and reservoirs. As a results of the experiments reported here it is suggested that the equilibrium IAP (the "solubility product") of ferrous sulfide precipitation in nature lies between $10^{-16.9}$ and $10^{-17.7}$, that is, Fe^{++} and $S^{=}$ are in equilibrium with amorphous or tetragonal FeS.

*Iron sulfide stability diagram.—*Fields of stability for pyrite, mackinawite, and greigite at 25°C are plotted in figure 6. The equilibrium reactions are:

Mackinawite-pyrite
$$2FeS \rightleftharpoons FeS_2 + Fe^{++} + 2e^- \tag{7}$$
$$Eh = -0.254 + 0.029 \log a_{Fe^{++}}$$

and

Mackinawite-greigite
$$4FeS \rightleftharpoons Fe_3S_4 + Fe^{++} + 2e^- \tag{8}$$
$$Eh = -0.011 + 0.029 \log a_{Fe^{++}}$$

where $a_{Fe^{++}}$ is the activity of ferrous ion. The method of calculating such fields has been described by Garrels and Christ (1965). The free energy of formation of greigite and mackinawite have been taken from Berner (1967), the other necessary thermodynamic data from Garrels and Christ. The boundary between mackinawite and greigite is metastable, since greigite is unstable with respect to pyrite at all Eh values shown on figure 6.

*The greigite-mackinawite boundary.—*The redox potential in the interstitial water of Linsley Pond is known to be more negative than the Eh of the ferrous-ferric equilibrium defined by the equation (Doyle, ms):

$$Fe^{++} + 2H_2O = \gamma\text{-}FeOOH + 3H^+ + e^- \tag{9}$$
$$Eh = 0.965 - 0.177 \text{ pH} - 0.059 \log a_{Fe^{++}}$$
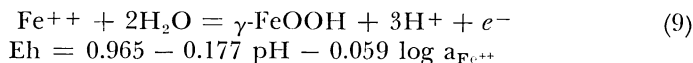
In the autumn of 1966 the pH and $a_{Fe^{++}}$ were 6.95 and 0.00082 respectively in the interstitial water of the sediment. The above equation using this value of pH is plotted as line A on figure 6 with a vertical dropped at $\log a_{Fe^{++}} = -3.09$ (line C). The Eh of the sediment as measured at that time falls somewhere on line C, within the stability field of mackinawite. The stability calculations therefore agree with the experimental
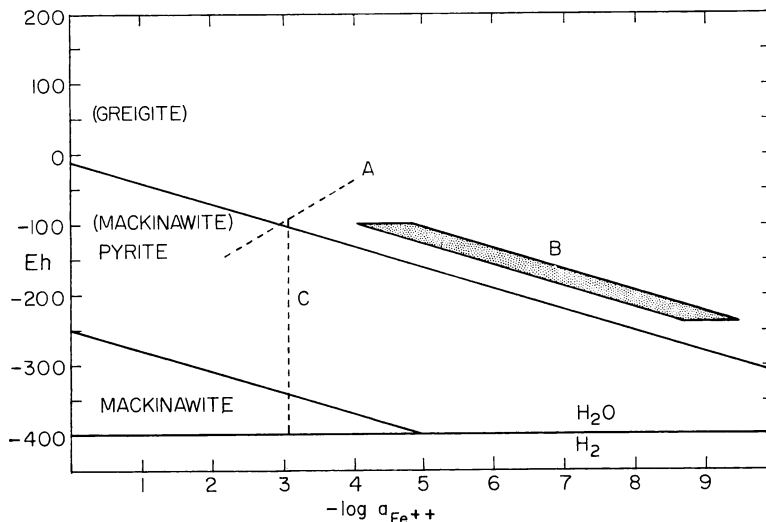
Fig. 6. Pyrite-mackinawite-greigite stability fields. A. equation 9 at pH 7 (see text); B. calculated position of marine (H_2S-rich) sediment; C. Linsley Pond sediment somewhere on this line. The lower and upper diagonals represent eqs 7 and 8, respectively (see text).

results of this paper. Eh and $a_{Fe^{++}}$ vary both in space and time in the hypolimnion of Linsley Pond, but sporadic measurements made over three years suggest that the variation in these properties is small a few centimeters below the surface in the region of the lake from which the mackinawite-containing sediment was collected.

It is interesting to compare the sediment of Linsley Pond with the very different conditions that obtain in anaerobic marine sediments. High concentrations of H_2S and HS^- characterize anaerobic marine environments in which sulfate is the principal inorganic hydrogen acceptor while the concentration of Fe^{++} is generally too low to be detectable by colorimetry or atomic absorption spectrophotometry. By making use of the equilibrium IAP for ferrous sulfide, the relationship between Fe^{++} and Eh of Fe^{++}-rich and sulfide-rich sediments can be shown together in figure 6. Data for the environments containing H_2S have been recalculated from redox potential and sulfide measurements published by Berner (1963) for coastal and intertidal marine sediments. A range of values for $a_{Fe^{++}}$ corresponding to an equilibrium IAP range of $10^{-16.9}$ to $10^{-17.7}$ is shown at each Eh.

It is clear that Linsley Pond and the marine sediments fall on opposite sides of the mackinawite-greigite boundary. Berner (1967) has noted that anaerobic marine sediment lies in the field of greigite, and this may also be true of non-marine environments which contain appreciable H_2S. Greigite and mackinawite have been found together in marine sediment, both being metastable with respect to pyrite. It appears

that the presence of greigite may be a useful distinguishing feature of sediment laid down under sulfide-rich rather than Fe^{++}-rich conditions.

CONCLUSIONS

At least 40 percent of the acid-soluble sulfide that stains the anaerobic sediment of Linsley Pond a jet black color has an equilibrium IAP of $10^{-17.7}$ in solutions saturated with H_2S at one atm pressure, nearly identical to that of tetragonal FeS (mackinawite). Calculations based on Eh and the activities of Fe^{++} and H^+ confirm that mackinawite is the stable phase in this environment.

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