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## SEDIMENTARY PYRITE FORMATION

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**ABSTRACT.** Experimental study indicates that pyrite can be synthesized at neutral pH in concentrated sulfide solution and in natural sediments by the reaction of precipitated FeS with elemental sulfur at 65°C. Similar reaction at sedimentary temperatures is probable but should require several years for completion. Synthetic pyrite formed by this reaction is framboidal.

The major steps in the process of sedimentary pyrite formation are: bacterial sulfate reduction, reaction of  $H_2S$  with iron minerals to form iron monosulfides, and the reaction of iron monosulfides with elemental sulfur to form pyrite. Accordingly the important factors limiting pyrite formation in marine sediments are: the availability of organic matter that can be metabolized by sulfate-reducing bacteria, the diffusion of sulfate into sediments, the total concentration and reactivity of iron minerals, and the production of elemental sulfur.

In sediments from the coastal region of central Connecticut, the main factor limiting pyrite formation is the availability of metabolizable organic matter. Reactive iron and dissolved sulfate are present to excess, and essentially all FeS is transformed by elemental sulfur to pyrite. These sediments are probably typical of many terrigenous marine sediments overlain by aerobic waters. In lower iron sediments, especially carbonates, the principal limiting factor is more likely to be the concentration of reactive iron. In most sediments total iron content and diffusion of sulfate are not limiting.

### INTRODUCTION

The mineral pyrite,  $FeS_2$ , is a common and widespread authigenic constituent of sediments and sedimentary rocks where it is almost always found associated with organic matter. This association is not fortuitous. Thermodynamic calculations (for example, Garrels and Christ, 1965; Berner, 1964d) indicate that pyrite is stable only in the absence of air and in the presence of dissolved sulfide. Such a situation is achieved in modern sediments by the accumulation of organic matter and its metabolism by bacteria which results in the removal of oxygen from associated waters and its replacement by dissolved sulfide. Thus, authigenic pyrite is found with organic matter and is an indicator of anaerobic, sulfidic diagenesis. Although these facts are fairly well known, less is known about the actual process of sedimentary pyrite formation. The present paper is addressed to this problem.

Studies of modern sediments (for example, Ostroumov, 1953; Van Straaten, 1954; Volkov, 1961; Kaplan, Emery, and Rittenberg, 1963) and experimental work (Berner, 1964a; Rickard, 1969) have helped to elucidate some of the fundamental stages in the process of sedimentary pyrite formation. They are: bacterial sulfate reduction, reaction of  $H_2S$  with iron minerals, and transformation of black iron monosulfides to pyrite.

The two principal sources of  $H_2S$  for pyrite formation are the bacterial reduction of dissolved sulfate and the decomposition of organic sulfur compounds. The predominance of the former process in marine sediments is proven by, among much other evidence, the observed content of pyrite. It often exceeds the amount that could form from a hypothetical sediment consisting entirely of organic matter. For example, Kaplan, Emery, and Rittenberg (1963) have shown that marine organic matter averages about 1 percent organic sulfur by dry weight. Marine sediments, on the other hand, often contain more than 1 percent pyrite sulfur (for example, see the data of table 3 in the present paper) but rarely contain more than 10 percent organic matter, even at their uppermost surface. Therefore, in many cases there is far too little organic sulfur contributed to marine sediments to account for the observed pyrite content. The high pyrite content is a consequence of continuous diffusion of dissolved sulfate into sediments where it is reduced to  $H_2S$  and reacted with iron minerals. Simple burial of sea water and reduction of all included sulfate can provide only about 0.3 percent pyrite sulfur; diffusion into the sediment is necessary. The importance of diffusion is indicated by the sulfur isotopic data of Kaplan, Emery, and Rittenberg (1963). They conclude that abundant pyrite in the basins off southern California forms by diffusion of sulfate into the sediments from a reservoir of constant isotopic composition, the overlying sea water.

Once  $H_2S$  is formed it reacts with various iron containing minerals to form iron sulfide. However, the first formed phase is seldom, if ever, pyrite. This was recognized as early as 1911 by Feld.<sup>1</sup> The substances that form by the reaction of iron minerals or dissolved ferrous ion with  $H_2S$  under simulated sedimentary conditions in the laboratory (Berner, 1964a, 1967a; Rickard, 1969) generally are non-crystalline FeS, mackinawite (tetragonal  $Fe_{1+x}S$  with  $x \approx 0.05$ ), and greigite (cubic  $Fe_3S_4$ ). All three are soluble in hot, concentrated HCl whereas pyrite is not. All are very fine grained and black. It is believed that the natural black, finely divided, HCl-soluble iron sulfide found in many modern sediments and commonly referred to as "hydrotroilite" or "FeS" consists of one or more of these phases. This contention is backed by the X-ray identification of mackinawite and greigite in several sedimentary occurrences (for example, Skinner, Erd, and Grimaldi, 1964; Berner, 1964a; Polushkina and Sidorenko, 1963; Jedwab, 1967). None of the three phases is thermodynamically stable under sedimentary conditions. Non-crystalline FeS and the FeS component of mackinawite are unstable relative to stoichiometric pyrrhotite, and greigite is unstable relative to stoichiometric pyrrhotite plus pyrite (Berner, 1967b). Further proof of instability is shown by the transformation of "FeS" to pyrite in modern sediments during early diagenesis and by the rarity of occurrences of mackinawite and greigite in ancient sedimentary rocks. For the purposes of the pres-

<sup>1</sup> On page 102, Feld states "Bei keinem der hier mitgeteilten Versuche konnte die direkte Bildung von Eisenbisulfid festgestellt werden. Es schien stets die Bildung von Monosulfid voranzugehen".

ent paper, the black precursor sulfides are collectively referred to as iron monosulfide or FeS so as to distinguish them from the disulfide, pyrite. Also, in many cases the term pyrite is used generically to refer both to pyrite and its polymorph, marcasite. Factors that govern the crystallization of marcasite rather than pyrite are beyond the scope of the present paper.

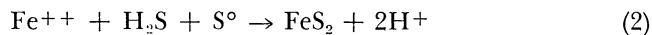
The last important stage in pyrite formation is the transformation of iron monosulfide to pyrite. The rate and mechanisms of this process are not well documented although several suggested schemes have been offered. In the present paper experimental data are presented that are in agreement with the hypothesis of Ostroumov (1953) and others that the overall transformation reaction is:



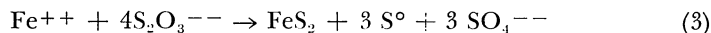
An important problem intimately connected with the origin of sedimentary pyrite is the evaluation of factors limiting the amount of pyrite that can form in a sediment. One factor, diffusion of sulfate, has already been touched upon briefly. Other factors, such as the availability of organic matter and reactive iron, must be evaluated for specific sediments. This has been done in the present study for marine sediments from the Connecticut shore of Long Island Sound. It is hoped that similar studies of other areas will be conducted in order to expand or modify the conclusions presented here with regard to limiting factors and the processes of sedimentary pyrite formation.

#### EXPERIMENTAL PYRITE FORMATION

*Previous studies.*—The synthesis of pyrite from aqueous solution at low temperatures (<100°C) has been known for a long time. Classic studies are those of Feld (1911), Allen and others (1912), and Allen and Crenshaw (1914). In these studies it was shown that FeS<sub>2</sub> forms from aqueous solution only in the presence of elemental sulfur or substances that produce elemental sulfur during decomposition. The simple reaction of dissolved sulfide with ferrous ion does not produce pyrite but instead iron monosulfide. Allen and co-workers synthesized pyrite at low temperatures in two ways: by the reaction of dissolved ferrous ion with H<sub>2</sub>S and elemental sulfur:



and by the reaction of ferrous ion with dissolved thiosulfate:



The stoichiometry of both reactions was verified by chemical analysis of all products. In the case of reaction (3) it is highly probable that pyrite actually forms as a result of the initial thermal breakdown of thiosulfate. Allen and co-workers showed that during prolonged heating dissolved thiosulfate decomposes to H<sub>2</sub>S plus SO<sub>4</sub><sup>--</sup>. In addition, reaction (3) indicates decomposition to elemental sulfur. Once elemental sulfur and H<sub>2</sub>S are present pyrite can then form via reaction (2).

Feld also demonstrated reaction (2) and found that it is inhibited as the pH is raised by weak bases such as  $\text{CaCO}_3$  and  $\text{Mg}(\text{OH})_2$ . The dissolved ferrous ion reacts with  $\text{H}_2\text{S}$  to form iron monosulfide, but the unstable FeS does not at pH 7 further react with elemental sulfur to form pyrite at least over a period of weeks at room temperature. Since sedimentary pyrite forms at pH values of about 7 to 8 (Baas-Becking, Kaplan, and Moore, 1960), it must form slowly. It was the purpose of the present experimental study to try to demonstrate the reaction of FeS with elemental sulfur at neutral pH but at elevated temperature in order to enable sufficiently rapid reaction.

*Procedure.*—Allen and others (1912), by aging precipitated FeS with elemental sulfur for 7 days in highly alkaline polysulfide solution, obtained at  $100^\circ\text{C}$  a product that appeared to consist partly of fine grained pyrite. With this in mind the writer also attempted to synthesize pyrite from polysulfide solution but at lower temperature and at more typical sedimentary pH values. The procedure started with the bubbling of  $\text{H}_2\text{S}$  to saturation through NaOH solution at  $65^\circ\text{C}$ . Constant temperature was achieved by means of a thermostated water bath. Concentrations of NaOH used were 0.1 and 1.0 normal which resulted, at  $\text{H}_2\text{S}$  saturation, in measured pH values of 6.9 and 7.9 respectively. After saturation, about 25 ml of the resultant NaHS solution were transferred to each of four 50-ml volumetric flasks to which weighed amounts of dry  $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$  and flowers of sulfur had been added previously. The NaHS solution immediately dissolved and reprecipitated all iron as black FeS whereas the elemental sulfur reacted more slowly to form the polysulfide ions,  $\text{S}_2^{--}$ ,  $\text{S}_3^{--}$ ,  $\text{S}_4^{--}$ , and  $\text{S}_5^{--}$ . Polysulfide formation was evidenced by the acquisition of a yellow or orange color by the NaHS solution. Amounts of sulfur were adjusted so that in two runs it would be completely "dissolved" as polysulfide ions, whereas in two other runs it would be present to excess. After adding the NaHS solution the flasks were bubbled with additional  $\text{H}_2\text{S}$  at  $65^\circ\text{C}$  to insure saturation and then rapidly sealed airtight with glass stoppers coated with epoxy cement. The flasks were then placed in a thermostated drying oven at  $65 \pm 1^\circ\text{C}$  for aging. After the epoxy cement had hardened, the flasks were shaken in order to immerse all floating sulfur grains.

After two weeks the flasks containing the excess elemental sulfur were removed from the oven, cracked open, and the pH immediately measured. Values were found to be the same (6.9 and 7.9) as at the start of the runs. The solids were then filtered, washed free of excess polysulfide solution, and dried. A portion of each sample was mounted in clear Epon 815 plastic, polished, and examined with a Zeiss Neophot Metallograph microscope. The remaining material was leached with acetone to remove all elemental sulfur, and the insoluble residue analyzed by X-ray diffraction. The two samples without excess solid sulfur were removed from the oven after 11 weeks, washed, dried, and also examined by X-ray diffraction.

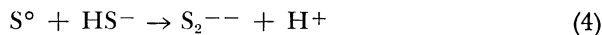
TABLE 1  
Pyrite synthesis from polysulfide solution at  $65 \pm 1^\circ\text{C}$

S <sup>0</sup> content	pH	Color of sulfide	Solubility in HCl	X-ray pattern
Excess solid	7.9	gray	none	pyrite
Polysulfide only	7.9	black	complete	no pyrite
Excess solid	6.9	gray	none	pyrite
Polysulfide only	6.9	black	complete	no pyrite

*Results.*—Results are summarized in table 1. Note that during aging the color of the precipitate in the runs that contained elemental sulfur changed from jet black to a medium gray, whereas in the runs without excess sulfur the color remained black. This color change was due to the formation of pyrite. X-ray diffraction patterns of the gray material matched that expected for weakly crystallized pyrite (four broadened principal peaks). The black samples, by contrast, contained no pyrite. They were completely soluble in hot HCl (pyrite and marcasite are insoluble) and showed none of the principal peaks for either pyrite or marcasite on X-ray diffractograms. Thus, pyrite does form at neutral pH and temperatures as low as  $65^\circ\text{C}$  by the reaction:



but only in the presence of excess solid elemental sulfur. This rules out, at least on the time scale of the experiments, the possible two step mechanism for pyrite formation:



which overall is equivalent to reaction (1). The nucleation properties of the surface of orthorhombic sulfur apparently promote pyrite crystallization by some yet unexplained mechanism.

Crystallization of pyrite on the surface of solid sulfur was proven by microscopic observation. The synthetic pyrite occurred only as aggregates of crystals embedded in the surface of orthorhombic sulfur grains. At very high magnification minute microspheres averaging about  $1 \mu$  in diameter were seen. The surface texture of the spheres indicated that they were comprised of aggregates of even smaller pyrite crystals. This textural form of pyrite is very similar to that exhibited by occurrences in natural sediments to which the term framboidal has been applied (Berner, 1969).

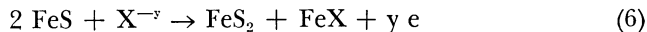
In order further to demonstrate reaction (1) an additional experiment was conducted. Samples of natural sediment rich in black iron monosulfide (IB-2 of table 3) were placed in each of four 50-ml volumetric flasks along with deaerated sea water. To two flasks were also added

weighed amounts of flowers of sulfur. The flasks were then sealed airtight, and two (one with sulfur, one without) aged at 65°C in an oven, and the other two at room temperature. After a few weeks the color of the sample containing elemental sulfur at 65°C changed from black to gray, while the others remained black. After one month the 65° samples were removed from their flasks and analyzed for monosulfide sulfur, pyrite sulfur, and HCl-soluble iron by the methods described later in this paper. Results are shown in table 2. Note that in the presence of elemental sulfur pyrite increased, while acid soluble iron and FeS sulfur decreased. This suggests that FeS was converted to pyrite. On the other hand, the elemental sulfur-free "blank" showed no evidence for pyrite formation. Neither of the two samples at room temperature has changed color after more than 7 months aging. This suggests that a relatively long time is needed at sedimentary temperatures for the complete transformation of FeS to FeS<sub>2</sub>, a conclusion in agreement with that of Feld (1911).

TABLE 2  
Pyritization of natural sediment at 65°C (sample IB-2)

Sample	Wt % Sulfur			Color
	FeS	Pyrite	Fe <sub>HCl</sub>	
Original sediment	0.29	0.79	3.65	Black
Sediment, 28 days, 65°C	0.38	0.80	3.51	Black
Sediment and S <sup>o</sup> , 28 days, 65°C	0.00	1.21	2.98	Gray

*Mechanism of transformation of FeS to FeS<sub>2</sub> in sediments.*—Possible mechanisms for the transformation of iron monosulfide to pyrite can be divided into two categories: those that involve the subtraction of iron and those that involve the addition of sulfur. Since the transformation is an oxidation, the two general types can be written as the half reactions:

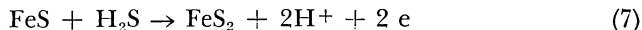


where:



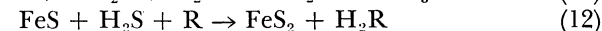
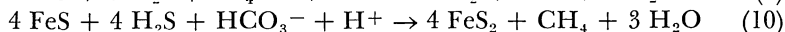
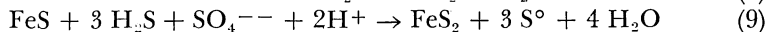
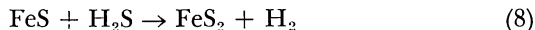
e = electron

and:

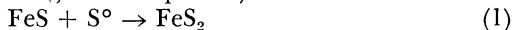


In marine sediments the latter type reaction must predominate. This is because at the H<sub>2</sub>S concentrations found in most pyritic sediments the only stable iron mineral is pyrite (Berner, 1964d), and other non-sulfides should not form during diagenesis. Only when there is a limited amount of H<sub>2</sub>S formation, as found in some lake sediments, should reactions of type 1, which conserve sulfide, be important.

Some thermodynamically possible overall complete reactions of type 7 are:



(R = an organic compound)



Oxidizing agents for each reaction are, respectively,  $\text{H}_2\text{S}$ ,  $\text{SO}_4^{--}$ ,  $\text{HCO}_3^-$ ,  $\text{N}_2$ , organic matter, and elemental sulfur. The writer can think of no other possible oxidizing agents that are sufficiently abundant in natural sulfidic sediments and that can bring about the transformation of FeS to  $\text{FeS}_2$  with a net negative change in free energy. As pointed out earlier no experimental evidence exists for the formation of pyrite at low temperatures by inorganic oxidizing agents other than elemental sulfur or sulfur producing species such as  $\text{S}_2\text{O}_3^{--}$ . This observation suggests that all the potential inorganic oxidizing agents listed above, except elemental sulfur, are not effective in bringing about pyrite formation. The first two reactions have never been observed by the writer during several years of experimentation. Reactions involving organic matter, however, have not been investigated. It is possible that natural organic substances act to bring about transformation of FeS to  $\text{FeS}_2$ , either directly or via microbiological catalysis, but there exists no evidence to support this contention. The common presence of organic matter within natural pyrite framboids (Love, 1957) does not necessitate an organic origin because framboids can be synthesized in the absence of organic matter (Berner, 1969). It is also conceivable that bacteria, heretofore undiscovered, are capable of catalyzing any of the other inorganic reactions cited above, but again, such an hypothesis is purely speculative.

Formation of pyrite by reaction (1), by comparison, is not purely speculative. The experimental results of the present section show that pyrite can be formed in a few weeks by this reaction in the presence of  $\text{H}_2\text{S}$  at neutral pH and  $65^\circ\text{C}$ . It is quite probable that the reaction also occurs at sedimentary temperatures. Also, pyrite formed in the laboratory by this reaction bears a striking resemblance to natural framboidal pyrite in sediments and sedimentary rocks. This conclusion is in agreement with the earlier conclusions of Feld (1911), Ostroumov (1953), and Volkov (1961) that sedimentary pyrite forms by the reaction of FeS with elemental sulfur. If other mechanisms do not operate simultaneously, a contention that needs to be proven, then pyrite may form only by the suggested reaction, and, thus, elemental sulfur may exert an important control on the amount of FeS transformed to pyrite.

#### PYRITE FORMATION IN CONNECTICUT COASTAL SEDIMENTS

*Area of study.*—In order to gain a clearer idea of limiting factors and processes of pyrite formation, measurements of modern pyritic sedi-

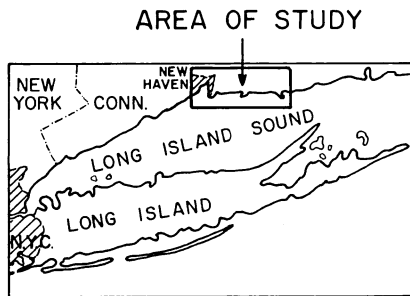
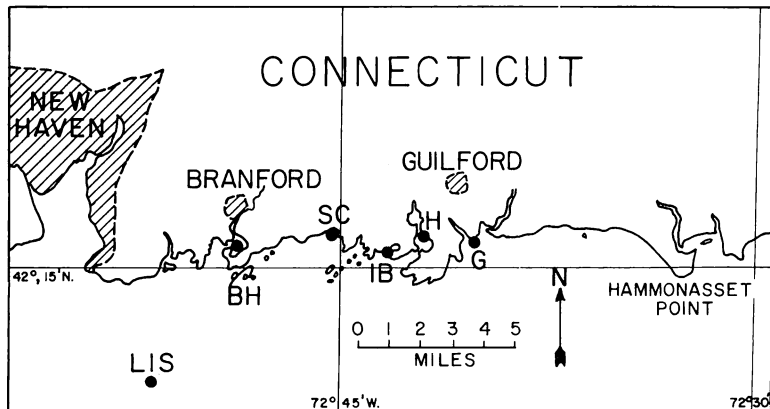


Fig. 1. Location map of sediment samples.

ments from the Connecticut coast of Long Island Sound were conducted. The area chosen for study is near Yale University where chemical analyses were performed. This enabled analysis soon after sampling. Chemical species affected by aeration or spurious bacterial activity were determined within a few hours of removal from the anaerobic sediments. The sediments studied were all dark sulfidic muds located either on tidal flats or in deeper water slightly off shore. Some samples contained considerable sand (G-1, G-2). Locations of sampling sites are shown in figure 1. Samples were collected in tenite coring tubes either by hand insertion into tidal flats or by lowering a winch operated gravity corer containing the tubes into offshore sediments from a boat. Upon removal the tubes were sealed, and samples retained within them until analysis. In several tidal flats where only the top few centimeters were sampled, the tubes were inserted horizontally.

*Analytical techniques.*—All samples were analyzed for organic carbon, pyrite sulfur, and HCl-soluble iron. In addition some samples were analyzed for elemental sulfur and acid soluble FeS sulfide. Samples analyzed for sulfide were first checked for dissolved sulfide by the direct



insertion of glass and silver sulfide electrodes into each mud sample. The dissolved sulfide in all analyses reported in this paper was present in much lower concentrations than the acid soluble sulfide so that it can be neglected. This was a consequence of choosing for sulfide analysis only highly blackened sediments. Acid soluble sulfide was determined using CdS standards by the iodine titration method described in an earlier paper (Berner, 1964b). After acid extraction the samples were dried and analyzed for elemental sulfur by the acetone-copper method (Berner, 1964b). Use of flowers of sulfur standards indicated greater than 95 percent recovery. However, results should be considered with caution because of problems inherent in the determination of elemental sulfur in sulfidic sediments (Berner, 1964b; Nriagu, 1968).

Iron soluble in HCl was removed by boiling each sample in 12 N HCl for one minute on a hot plate. This treatment was adopted because it extracts the most reactive (toward  $H_2S$ ) iron compounds and is reproducible. Dissolved iron was determined by the O-phenanthroline colorimetric method (Sandell, 1959) using a Beckman Model DU-2 spectrophotometer. After washing and drying, several samples were again subjected to the one minute hot acid treatment, and little additional iron (less than 5 percent of the iron removed during the first leaching) was extracted. Thus, the treatment removes essentially all acid extractable iron during one minute of boiling and is reproducible. An idea of the types of minerals included in the extraction is provided by the experimental observation that iron in fine grained reagent hematite, limonitic goethite, and chlorite is completely dissolved by similar acid treatment, whereas no iron is removed from finely ground pyrite. Variable but relatively small proportions of iron are removed from sand- and silt-sized grains of magnetite, hematite, goethite, hornblende, augite, biotite, and epidote. The relative reactivity toward  $H_2S$  of these minerals was found to be similar to their relative solubility in hot concentrated HCl. Thus, HCl solubility is a guide to  $H_2S$  reactivity. It is probable that the iron now present in pyrite was originally present in the sediments, before reaction with  $H_2S$ , as HCl-soluble iron. In other words the iron most reactive toward  $H_2S$  should be most reactive towards HCl.

After HCl extraction samples were washed, dried, and weighed. Since acid extraction also removes  $CaCO_3$ , all results are reported relative to carbonate-free, HCl-soluble iron-free, dry sediment weight. Portions of the dried samples were subsequently analyzed for pyrite sulfur and organic carbon by combustion using a Leco Induction furnace. Prior to sulfur analysis all elemental sulfur was removed by acetone extraction. Sulfur oxide gases formed by burning were trapped in 3 percent hydrogen peroxide solution to convert all sulfur to dissolved sulfate. The sulfate was then precipitated as  $BaSO_4$  and weighed. Standardization runs using pure pyrite indicate a recovery of  $85 \pm 5$  percent sulfur. Carbon dioxide produced by complete burning of organic carbon was trapped in air-free  $Ba(OH)_2$  solution as  $BaCO_3$  and subsequently weighed.

TABLE 3

Analytical data for Connecticut coastal sediments (for localities see fig. 1). Percentages are for carbonate free and HCl-soluble iron-free, dry weight

Depth cm	FeS	% Sulfur S°	Pyrite	%C	%Fe <sub>HCl</sub>	P
<u>SC-1</u>						
1-4	0.10	0.10	0.52	2.16	—	—
<u>SC-2</u>						
1-2	0.15	0.10	0.75	3.17	2.22	0.21
<u>SC-3</u>						
0-2	—	—	0.78	2.18	2.67	0.20
<u>BH-1</u>						
0-2	0.54	0.08	1.61	4.65	3.35	0.30
4-6	0.19	0.18	1.84	2.61	2.96	0.35
7-9	0.05	0.15	1.92	2.18	3.08	0.35
12-15	0.05	0.17	1.93	2.21	3.30	0.34
18-21	0.05	0.23	1.51	2.04	3.06	0.30
25-28	0.02	0.18	1.98	2.39	3.35	0.35
<u>IB-1</u>						
1-2	0.25	0.14	1.04	3.34	3.12	0.22
<u>IB-2</u>						
1-2	0.29	0.03	0.79	2.70	3.65	0.16
<u>G-1</u>						
0-2	—	0.03	0.09	0.28	0.86	0.08
<u>G-2</u>						
0-2	—	0.03	0.08	0.37	1.00	0.07
<u>H-1</u>						
0-2	—	0.07	1.50	5.55	2.76	0.33
<u>H-2</u>						
0-2	—	0.02	1.55	5.55	2.46	0.35
<u>H-3</u>						
0-2	0.03	0.14	1.80	6.55	2.02	0.44
<u>LIS</u>						
0-2	—	—	0.31	1.45	2.53	0.10
2-4	—	—	0.45	1.53	2.22	0.15
4-6	—	—	0.58	1.54	1.98	0.20
6-8	—	—	0.55	1.51	1.84	0.21
8-10	—	—	0.38	0.97	1.46	0.18
10-12	—	—	0.48	1.08	1.56	0.21
12-14	—	—	0.58	1.23	1.73	0.23
14-16	—	—	0.70	1.04	1.58	0.28
16-18	—	—	0.88	1.16	1.76	0.30
18-20	—	—	0.92	1.24	1.95	0.29
20-22	—	—	0.77	1.07	2.06	0.25
22-24	—	—	0.78	1.05	2.02	0.25
24-26	—	—	0.78	1.05	1.82	0.27
26-28	—	—	0.87	0.99	1.87	0.29
28-30	—	—	0.60	0.77	1.76	0.23
30-32	—	—	0.80	0.86	1.67	0.29
34-36	—	—	0.76	1.06	2.33	0.22
38-40	—	—	0.72	1.08	2.15	0.23
42-44	—	—	0.49	0.85	1.88	0.18
46-48	—	—	0.70	1.13	2.24	0.21
50-52	—	—	0.82	1.12	2.29	0.24

Graphite was used as a standard, and recovery was  $86 \pm 8$  percent. Blanks and pyrite and graphite standards were run before and after every 5 to 10 analyses, and all analyses were done in duplicate. Results are reported relative to the standards.

The sulfur determined by combustion is assumed to represent only pyrite sulfur. Acid soluble sulfide and elemental sulfur are removed prior to analysis, but organic sulfur compounds are decomposed along with pyrite during combustion. No correction for organic sulfur has been made. Independent evidence, however, indicates that organic sulfur must be negligible when compared with pyrite. The sulfur to carbon ratio of the samples (see table 3) ranges from 0.25 to 1.0, whereas that of freshly killed marine organic matter, freed of all inorganic sulfur, averages about 0.02 (Kaplan, Emery, and Rittenberg, 1963). Thus, more than 90 percent of the analyzed sulfur must represent pyrite. Since it is quite possible that the sulfur to carbon ratio of organic matter decreases during diagenesis as a result of bacterial activity, the proportion of sulfur that is pyrite may be close to 100 percent. The abundance of framboidal microspheres in all sediments examined with a microscope qualitatively supports this contention. Also, one sediment sample was sent to Tracerlab, Inc. in order to remove all organic matter through the use of their low temperature asher (Gluskoter, 1965). The sulfur content during oxidation of organic matter remained constant within experimental repro-

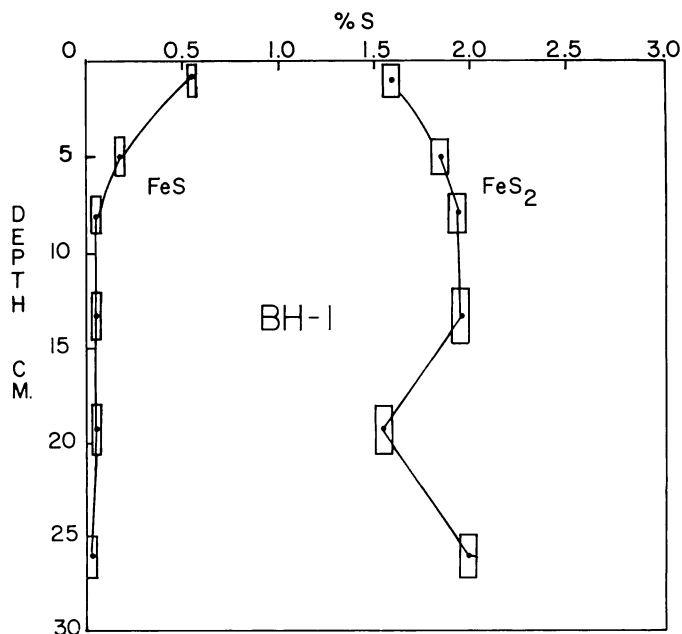


Fig. 2. Percent monosulfide (FeS) sulfur and pyrite sulfur versus depth in a sediment core from location BH-1. Values are based on carbonate free, HCl-soluble iron free, dry weight.

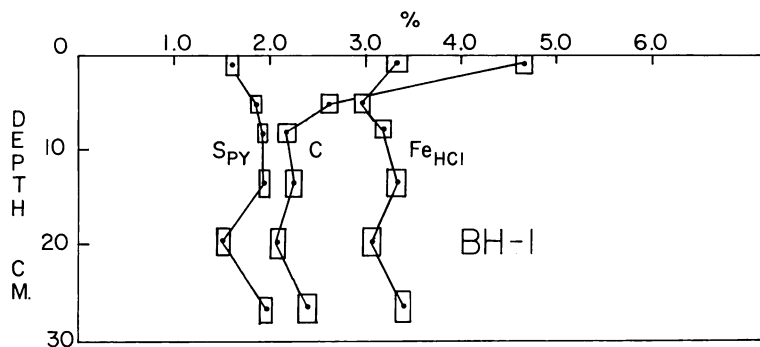


Fig. 3. Percent pyrite sulfur ( $S_{py}$ ), percent organic carbon (C), and percent HCl-soluble iron ( $Fe_{HCl}$ ) versus depth in a sediment core from location BH-1. Values are for carbonate free, HCl-soluble iron free, dry weight.

ducibility indicating that the sulfur must be contained within pyrite, which is not decomposed by the ashing technique.

*Results.*—Analyses for acid soluble sulfide (FeS sulfur), elemental sulfur, pyrite sulfur, organic carbon, and HCl-soluble iron are listed along with sample depth in table 3 and plotted in figures 2 to 4. In addition to the above results the parameter

$$P = \frac{\% Fe_{pyrite}}{\% Fe_{pyrite} + \% Fe_{HCl\ soluble}}$$

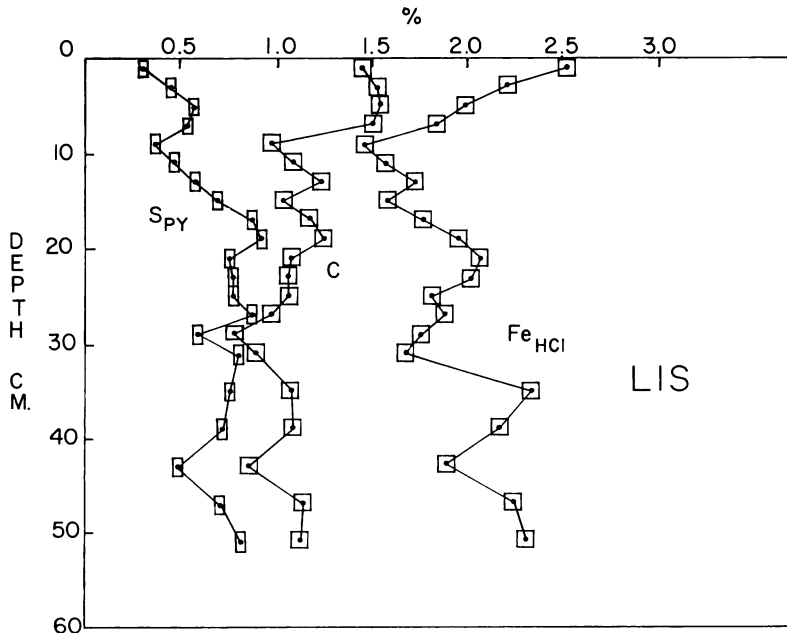


Fig. 4. Percent pyrite sulfur ( $S_{py}$ ), percent organic carbon (C), and percent HCl-soluble iron ( $Fe_{HCl}$ ) versus depth in a sediment core from location LIS-1. Values are for carbonate free, HCl-soluble iron free, dry weight.

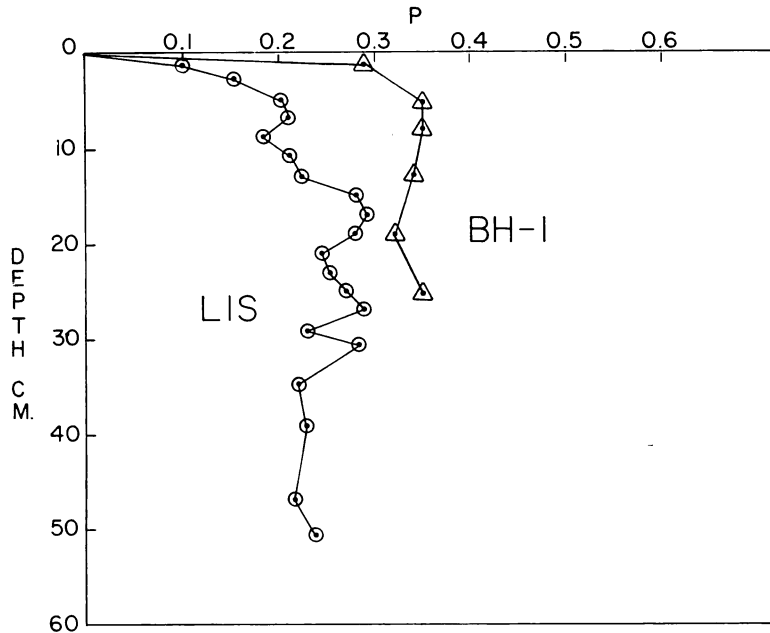


Fig. 5. Degree of pyritization, P, versus depth for sediments from locations BH-1 and LIS-1. For definition of P see text.

is included in table 3 and plotted versus depth in figure 5. P is the degree of pyritization and represents the fraction of HCl-soluble or reactive iron transformed to pyrite iron. Plots of percent organic carbon versus P, percent pyrite sulfur, and percent HCl-soluble iron, for the top 2 cm of sediment are shown in figures 6 to 8.

#### FACTORS LIMITING PYRITE FORMATION IN MARINE SEDIMENTS

*Organic matter.*—As pointed out in the introduction, the principal source of sulfide for pyrite formation in marine sediments is sulfate dissolved in sea water. To bring about reduction of sulfate to sulfide organic matter is required as an energy source for bacteria. (Non-bacterial reduction does not occur.) Without metabolizable organic matter there is no sulfate reduction and no pyrite formation. Thus, available organic matter, defined as that which can be metabolized by sulfate reducing bacteria, is a primary factor limiting the amount of pyrite that can be formed in a sediment. A crude measure of available organic matter is the concentration of organic carbon. Organic carbon is a reasonably accurate measure of total organic matter in sediments (Emery, 1960). Of course all organic matter is not available for sulfate reduction, but it can be assumed, as a first approximation, that a constant ratio of metabolizable to total organic matter exists at the time of deposition. This would be the case if organic remains of essentially the same biochemical com-

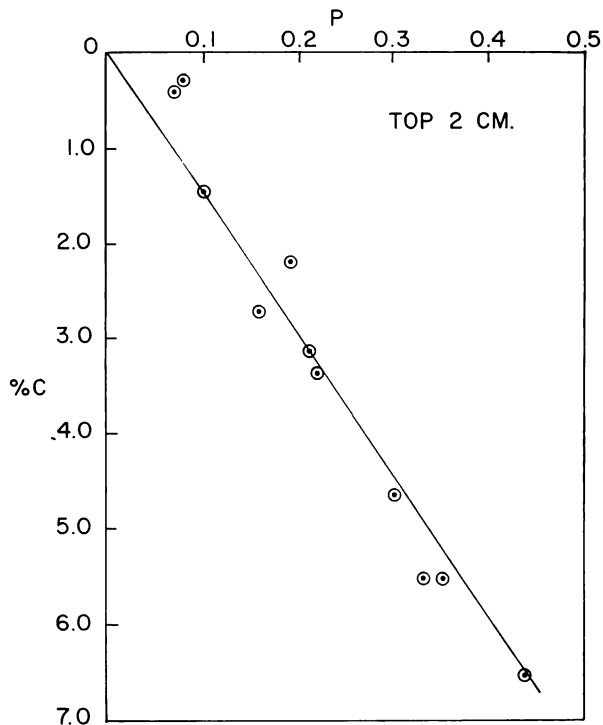


Fig. 6. Plot of P, the degree of pyritization, versus percent organic carbon for the top 2 cm of some Connecticut coastal sediments.

position serve as sources of organic matter for all the sediments of a given area.

Besides acting as a capacity factor in controlling how much pyrite may theoretically form, organic matter may also act as an intensity factor limiting the actual amount formed. It has been suggested by the writer (Berner, 1964c) that the rate of sulfate reduction in sediments is a direct function of the concentration of available organic matter. If this is true, sediments high in available organic matter should also be high in dissolved sulfide. This is because a high reduction rate enables the attainment and maintenance of high  $H_2S$  concentrations in the presence of continuous loss of  $H_2S$  by diffusion out of the sediment. Because different detrital iron compounds exhibit widely differing reactivities toward  $H_2S$ , it would be expected that at higher  $H_2S$  concentrations a greater proportion of total iron in a sediment would react with  $H_2S$  to form pyrite. If so, then the degree of pyritization of iron should be related directly to the concentration of available organic matter, if organic matter is a limiting factor.

In the Connecticut coastal sediments originally deposited organic carbon, as a measure of available organic matter, appears to be a limiting

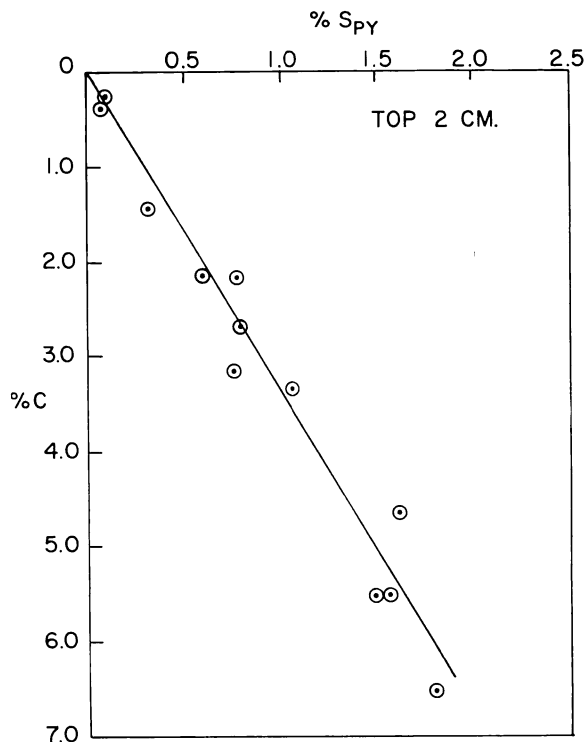


Fig. 7. Plot of percent pyrite sulfur ( $S_{py}$ ) versus percent organic carbon for the top 2 cm of some Connecticut coastal sediments.

factor. In the topmost portion of the sediments (upper 2 cm) where organic carbon concentrations are as near as possible to those at the time of deposition, there is a good linear correlation between the degree of pyritization,  $P$ , and the concentration of organic carbon. This is shown in figure 6. The amount of pyrite formed in the top 2 cm is also a linear function of organic carbon as shown in figure 7. Both regression lines extrapolate to zero at zero percent carbon as would be expected if organic carbon were limiting.

Below 2 cm some additional pyrite is formed (see figs. 2-5). Accompanying this is a loss of  $FeS$  and of organic carbon. The decrease in  $FeS$  is presumably due to transformation to pyrite, and the loss of organic carbon is due to metabolism by sulfate reducing and other bacteria. After a depth of about 10 cm is reached, the degree of pyritization essentially levels off (fig. 5) indicating cessation of further pyrite formation. The reason for this levelling off is that no more iron is able to react at the concentration of  $H_2S$  in the sediment to form pyrite. Additional iron, soluble in  $HCl$ , is available for further possible pyrite formation as shown by the relatively low maximum values of  $P$ . At higher  $H_2S$  con-

centration more pyrite can form. This is indicated by a distinct darkening of several samples, due to FeS formation, after prolonged subjection to considerably higher concentrations of  $H_2S$  in the laboratory. Thus, available organic matter, since it controls the concentration of  $H_2S$ , also controls the final degree of pyritization.

Organic carbon may be a limiting factor also in the transformation of FeS to pyrite. The transformation, as pointed out earlier, involves the addition of sulfur, rather than the removal of iron. In some situations the excess elemental sulfur needed for complete transformation may be lacking due to an insufficient amount of sulfate reduction resulting from a low original concentration of available organic matter. In other words, sufficient  $H_2S$  is initially formed to convert rapidly a small proportion of very reactive detrital iron to FeS, but not enough is present to transform further all FeS to  $FeS_2$ . As a consequence of "sulfur starvation" FeS may persist in a sediment and crystallize as mackinawite, pyrrhotite, or greigite. In order for FeS to persist, there should be little excess  $H_2S$  from which elemental sulfur and, thus, pyrite can be produced. Volkov (1961) has shown that old buried sediments from the Black Sea, in which appreciable black FeS occurs, are low in total sulfur and very low in dissolved  $H_2S$  and the degree of pyritization. This is ascribed by Volkov to limited sulfate reduction during early diagenesis with insufficient elemental sulfur formed to enable complete transformation of FeS to pyrite. Apparently in the Connecticut coastal sediments and in most other marine pyrite occurrences (for example, van Straaten, 1954; Kaplan, Emery, and Rittenberg, 1963; Berner, 1964b), there is sufficient available organic matter to enable essentially complete transformation. Black FeS is not found at depth.

*Iron.*—For a given fixed concentration of  $H_2S$  the amount of pyrite that forms in a sediment should be directly controlled by the concentration and reactivity of detrital iron compounds. The higher the iron content and the greater its reactivity, the higher should be the resulting concentration of pyrite. If abundant available organic matter is present so that the  $H_2S$  concentration is maintained at a very high value for a long time, the total amount of pyrite may be limited by the total quantity of iron. In such a case the value of P should approach, or even exceed one. This situation, however, is almost never achieved as evidenced by the very common occurrence in ancient pyritic sediments of metastable, HCl-soluble iron minerals (for example, Strakhov, 1958; Berner, 1964d; Curtis, 1967).

In the Connecticut coastal sediments total iron is not a limiting factor in pyrite formation. If it were, all reactive iron would be used up to form pyrite. However, relatively low values of P ( $<0.5$ ) shown in table 3 indicate incomplete pyritization of HCl-soluble iron. Further proof of incomplete pyritization is shown by a blackening of sediment samples in the laboratory when exposed to saturated  $H_2S$  solution for a few days. Figure 8 shows no clear-cut correlation between pyrite sulfur



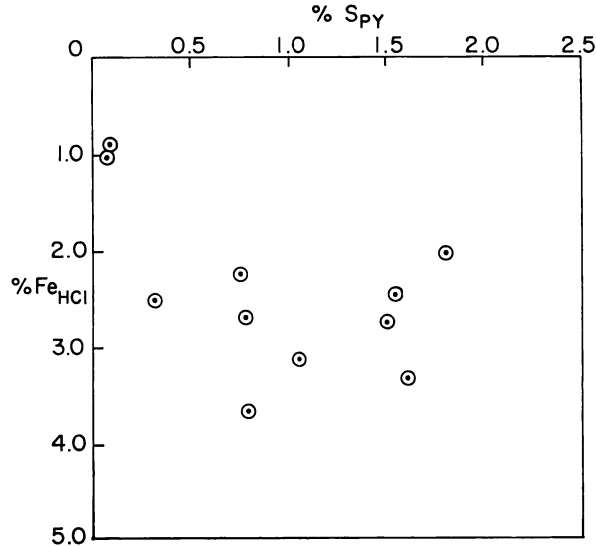


Fig. 8. Plot of percent pyrite sulfur ( $S_{py}$ ) versus percent HCl-soluble iron ( $Fe_{HCl}$ ) for the top 2 cm of some Connecticut coastal sediments.

and HCl-soluble iron for the topmost sediment from different locations. This also indicates that iron is not a limiting factor.

Although no apparent correlation between pyrite sulfur and HCl-soluble iron exists when comparing sediments from different locations, there does appear to be some correlation within a single core for samples taken below depths of about 10 cm. This is shown by a rough parallelism of the curves for pyrite sulfur and HCl-soluble iron in figures 3 and 4 and the approximate constancy of P with depth. If P is constant, then:

$$\frac{Fe_p}{Fe_p + Fe_{HCl}} = k \quad (13)$$

and:

$$Fe_p = \left( \frac{-k}{k-1} \right) Fe_{HCl} \quad (14)$$

$$S_p = 1.15 \left( \frac{-k}{k-1} \right) Fe_{HCl} \quad (15)$$

where:

$k$  = constant

$Fe_p$  = pyrite iron

$Fe_{HCl}$  = HCl-soluble iron

$S_p$  = pyrite sulfur

Curve parallelism and equation (15) are not brought about by a direct relation between pyrite formation and reactive iron. Instead they more probably result from a secondary correlation resulting from the primary

correlations of  $\text{Fe}_{\text{HCl}}$  with organic carbon and pyrite sulfur with organic carbon. Pyrite sulfur correlates with organic carbon because carbon is a limiting factor. The weaker correlation of HCl-soluble iron with organic carbon at depths below 10 cm is probably the result of the association of higher iron and higher organic matter with finer grain sizes. Finer particles consist of more HCl-soluble chlorite and adsorbed iron oxides and tend to settle out along with light suspended organic detritus. The covariation of both pyrite sulfur and HCl-soluble iron with organic carbon is, thus, due to a variable sand plus silt content in the sediments. This is supported by grain size determinations.

Although the Connecticut coastal sediments may be typical of iron-rich terrigenous muds (Love, 1967), they are not representative of iron-poor sediments, especially carbonates. The iron content of pure carbonate sediments is low because of a lack of detrital iron minerals. As a result, carbonate muds may be rich in organic matter and  $\text{H}_2\text{S}$  but very low in pyrite. Certainly in this case iron content must be the principal limiting factor in pyrite formation. Much of the iron may emanate from organic iron compounds and be completely reactive toward  $\text{H}_2\text{S}$ . A good example of pyrite-poor, high  $\text{H}_2\text{S}$  sediments are the carbonate muds of Florida Bay.

Probably in most sediments pyrite formation takes place in the presence of overlying partly aerobic water. An outstanding exception is the Black Sea where waters below about 150 m depth are anaerobic and contain dissolved  $\text{H}_2\text{S}$  (Skopintsev, 1961). In this situation it is possible that pyrite formation may take place at, or even above, the sediment-water interface. If most pyrite is formed at the sediment-water interface, the amount formed should be controlled by the amount of detrital iron that can react at the  $\text{H}_2\text{S}$  concentration of the overlying water (Ostroumov, Volkov, and Fomina, 1961). The  $\text{H}_2\text{S}$  concentration is a property of the water mass and not related to local organic carbon concentrations in the sediments. In this situation iron, and not organic carbon, should be the limiting factor. However, additional sulfate reduction occurs within the sediments (Shishkina, 1959), which suggests additional pyrite formation within the sediments. Therefore, reactive iron may be a primary limit on pyrite formation in euxinic environments such as the Black Sea, but metabolizable organic carbon should exert an additional influence.

*Sulfate.*—If pyritic sulfur emanates mainly from dissolved sulfate, the amount of pyrite formed may be limited by the diffusion of sulfate into a sediment from the overlying water. The importance of diffusion in building up high concentrations of pyrite has already been pointed out in the introduction. A situation might exist where an iron and organic-rich sediment is deposited so rapidly that diffusion of sulfate cannot keep pace with reduction. As a result dissolved sulfate will disappear rapidly at shallow depths and not be replenished from above. The limiting amount of sulfate would then be simply that contained within pore waters buried with the sediment at the time of deposition. For typical

marine sediment this would be equivalent to 0.3 percent pyrite sulfur by dry weight.

Diffusion of sulfate is not a limiting factor in the Connecticut coastal sediments. This is shown by the presence of appreciable concentrations of dissolved sulfate in sediment pore waters at and below depths where active pyrite formation occurs and by the presence of pyrite sulfur in concentrations far exceeding 0.3 percent. The Connecticut sediments are probably typical of most marine sediments.<sup>2</sup> In the Gulf of California (Berner, 1964b) and the Santa Barbara Basin off southern California (Kaplan, Emery, and Rittenberg, 1963) concentrations of dissolved sulfate in sediments at depths many tens of centimeters below the depth where pyritization is essentially complete are at least half that in the overlying water. Reduction and removal of all interstitial sulfate at shallow depths, which is necessary for sulfate diffusion to become limiting, does not occur. Also, the concentration of pyrite sulfur generally far exceeds 0.3 percent.

*Elemental sulfur.*—The transformation of FeS to FeS<sub>2</sub> is an oxidation, and if no active oxidizing agent is present in a sediment, even though there may be a high concentration of H<sub>2</sub>S, no pyrite can form. In the present study it is suggested that the only oxidizing agent capable of bringing about this transformation is elemental sulfur. If true, elemental sulfur may be a limiting factor in pyrite formation.

In most sediments elemental sulfur is not limiting since, as pointed out earlier, incomplete transformation of FeS to pyrite is a relatively rare phenomenon. This is especially true of sediments overlain by aerobic waters, such as those from the Connecticut coast, where elemental sulfur readily forms as a result of the oxidation of H<sub>2</sub>S and FeS by dissolved oxygen. The oxygen is mixed into the anaerobic sediment by the burrowing activity of benthonic organisms, by current and wave stirring, and by diffusion. The oxidation process can be inorganic but is more commonly mediated by microorganisms such as the Thiobacilli (Thimann, 1963) which not only produce elemental sulfur but also oxidize elemental sulfur to sulfate ion. Oxidation to sulfate explains why elemental sulfur does not normally accumulate in sediments (note low concentrations in table 3).

In sediments overlain by anaerobic waters (that is, euxinic basins) the origin of elemental sulfur is more problematical. It is generally assumed that bacteria that produce elemental sulfur are aerobic, photosynthetic, or use dissolved nitrate as an energy source (ZoBell, 1946; Thimann, 1963). In a sulfidic sediment or a deep sulfidic water there is no oxygen or light, and nitrate is either absent or present in very low concentrations; yet complete transformation of FeS to FeS<sub>2</sub> in sediments of euxinic basins is common as shown by the Black Sea (Ostroumov,

<sup>2</sup>From unpublished studies, the writer has found that in some unusually organic-rich sediments, especially those affected by human pollution, all dissolved sulfate may be removed at shallow depths. However, these sediments are atypical of pyritic sediments in general.

1953; Volkov, 1961). If pyrite formation is dependent upon elemental sulfur, the elemental sulfur must either be added by deposition from above or it must form by some unknown anaerobic process.

The most plausible origin for "detrital" sulfur is formation in the water column at the shallow depth where  $H_2S$ -containing deep water contacts oxygenated surface water. In the Black Sea this elemental sulfur is distributed by surface currents and subsequently falls to the bottom (Ostroumov, Volkov, and Fomina, 1961). Volkov (1961) states that elemental sulfur is also formed directly by bacteria in the sediments of the Black Sea. However, microbiological studies of the Black Sea have so far failed to demonstrate conclusively anaerobic sulfur formation at depth (H. Jannasch, personal commun.).

Formation of elemental sulfur anaerobically by a strictly inorganic process is possible; however, the suggested mechanism of Feely and Kulp (1957), whereby elemental sulfur is formed by the reaction of  $H_2S$  with dissolved sulfate ion, is unlikely. The non-reactivity of sulfate toward inorganic reducing agents even stronger than  $H_2S$  is a well known phenomenon. The writer has never seen any evidence for the Feely and Kulp reaction in experiments at low or elevated temperature whenever air was scrupulously excluded from solutions. Also, Voge (1939) has demonstrated non-reactivity between  $H_2S$  and  $SO_4^{--}$  through the use of radioactive sulfur. The possible biological or inorganic formation of elemental sulfur by anaerobic processes requires further proof and much additional study. Only then can the role of elemental sulfur as a possible factor controlling pyrite formation be better evaluated.

#### RATE OF PYRITE FORMATION

The rate of pyrite formation, regardless of mechanism, can be estimated from data available for the Connecticut coastal sediments. Rates of deposition in this general area based on rates of coastal subsidence and sedimentation on tidal marshes (Bloom, 1967) average about 0.1 cm per year. For one of the specific areas studied by the writer some additional depositional rate data exists. The sediments from Joshua Cove (H-1, H-2, H-3) consist of about 2 to 3 cm of mud lying atop the surface of a dead marsh. The mud has been deposited since the opening of the main tidal creek to Long Island Sound during the late 1950's (A. Bloom, personal commun.). Before this the marsh had been artificially closed to the sea, and as a result the grass had died. Thus, the total time of deposition of the mud is about 10 years. Since the mud contains 1.5 to 1.8 percent pyrite sulfur (table 3), the minimum rate of pyrite formation is approximately 0.2 percent S per year. This is a minimum rate because formation may occur over an interval less than 2 cm sampled. There is little FeS in the mud, and degree of pyritization is comparatively high. Thus, pyrite formation may be complete. The rate of formation is undoubtedly higher than in many other areas because of the very high concentration of organic carbon which, due to rapid reduction of sulfate

to  $H_2S$ , helps to accelerate the overall pyrite forming process. However, it does give an idea of how fast pyrite can form in a sediment under optimum conditions. The rate is of the same order of magnitude as that expected for the reaction of FeS with elemental sulfur at neutral pH and sedimentary temperatures. This is based on room temperature experiments and reasonable extrapolations of rate data obtained at 65°C.

#### CONCLUSIONS

According to the above discussion and results and the results of other studies, the process of sedimentary pyrite formation in marine sediments proceeds as follows:

1. Organic matter derived from dead marine organisms and iron contained within or adsorbed upon fine grained detrital minerals is deposited in relatively quiet water where the light particles may settle out.

2. Upon removal of dissolved oxygen from associated waters by aerobic metabolism of the organic matter, anaerobic bacterial sulfate reduction occurs within sediments and more rarely in waters overlying the sediments. As a result of sulfate reduction,  $H_2S$  is formed.

3. Dissolved  $H_2S$  reacts immediately with the most reactive forms of iron present to form black non-crystalline FeS. If  $H_2S$  formation ceases at this point and no extra elemental sulfur is added to the sediment, no further reactions, other than the crystallization of FeS to various iron monosulfides, occur. The result is greigite, mackinawite, or pyrrhotite and little or no pyrite (or marcasite).

4. If continued sulfate reduction takes place, the  $H_2S$  concentration in the sediment increases which brings about the conversion of additional detrital iron to FeS. The amount of FeS (and ultimately pyrite) that can form is limited by the rate of production and concentration of  $H_2S$  and/or by the amount and reactivity of detrital iron.

5. Simultaneously with step 4 the concentration of sulfate in the sediment pore water falls and additional sulfate is made available for reduction by diffusion down the concentration gradient from the overlying water. Likewise, the produced  $H_2S$  builds up in the pore water and begins to diffuse out of the sediment. The concentration of available (metabolizable) organic matter controls the rate of sulfate reduction and, consequently, the concentration of  $H_2S$  that can be maintained in the presence of loss by diffusion.

6. Some of the  $H_2S$  is oxidized, either inorganically or by sulfur oxidizing bacteria, to elemental sulfur. Under aerobic bottom conditions considerable elemental sulfur is formed by the reaction of FeS and  $H_2S$  with dissolved oxygen which is stirred into the sediment from the overlying water by burrowing organisms or by storm waves and currents. Part of the elemental sulfur is subsequently oxidized by bacteria to dissolved sulfate.

7. The remaining elemental sulfur slowly reacts with FeS in the sediment to form pyrite which crystallizes as minute framboidal micro-

spheres. The time for complete transformation of FeS to FeS<sub>2</sub>, in the presence of abundant H<sub>2</sub>S and elemental sulfur, is on the order of several years.

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