[AMERICAN JOURNAL OF SCIENCE, VOL. 283, MARCH, 1983, P. 193-217]

American Journal of Science

MARCH 1983

EXPERIMENTAL STUDY OF METASTABLE SULFUR OXYANION FORMATION DURING PYRITE OXIDATION AT pH 6-9 AND 30°C

MARTIN B. GOLDHABER

U.S. Geological Survey, Branch of Uranium and Thorium Resources,
Denver Federal Center — MS 916, Denver, Colorado 80225

ABSTRACT. Experimental studies of pyrite oxidation over the pH range 6 to 9 were carried out at 30°C in 0.1 M (molar) KCl under conditions of fixed pH and pO_2. Rate of addition of base necessary to maintain a fixed pH was monitored. Samples were withdrawn periodically and analyzed for total sulfur in solution, thiosulfate, polythionates sulfite, and sulfide. The results demonstrate an increase in rate of hydrogen-ion production with increase in pH. Metastable sulfur oxyanions were detected as intermediates in the sulfur oxidation pathway. For short-term (less than 2 day) runs, the proportion of these sulfur oxyanions was less sensitive to the length of a run than to the pH of the run. At the lower pH values (6-7), tetrathionate and sulfate were the major observed species. As pH is increased, these ions diminish with respect to thiosulfate and sulfite. The data from this and previous studies are consistent with a pyrite oxidation mechanism whose rate controlling step is a chemical reaction occurring subsequent to the initial adsorption of oxygen to the pyrite surface.

INTRODUCTION

Pyrite oxidation has been studied extensively in connection with its importance in producing the serious environmental problem of acid mine drainage. The literature is voluminous (see Nordstrom, 1982, for a recent comprehensive review). There is a general consensus as to the overall inorganic pathway under acidic (pH less than 4) conditions. The initial step consists of a simple dissolution leading to ferrous iron and disulfide ion (S_2^{2-}) in solution (or perhaps a rapid sequence of oxidations subsequent to dissolution that ultimately produces aqueous ferrous iron and sulfate). The ferrous iron reacts with oxygen in a slow step to produce aqueous ferric iron, which in turn rapidly oxidizes pyrite to sulfate and ferrous iron. The reoxidation of this ferrous iron, which is the rate limiting step (Singer and Stumm, 1970), thus propagates the cycle. Bacteria of the genus *Thiobacillus* intervene in the propagation step by catalyzing the oxidation of ferrous iron. The oxidation of pyrite at low pH occurs at a rate that is independent of pH (for example, McKay and Halpern, 1958; Smith and Shumate, 1970). Sulfate is the stable sulfur oxidation product in the presence of excess oxygen. Sulfur intermediates whose oxidation state is less than that of sulfate are not typically reported, although elemental sulfur has been detected in a few studies (Bergholm, 1955; McKay and Halpern, 1958). This lack of observed sulfur intermediates does not imply that such intermediates do not occur in the pathway. As stressed by Nordstrom (1982) oxidation steps must occur by one or at most two electron transfers per reaction, and there is a seven-electron difference in oxidation state between sulfur in pyrite and that in sulfate. Therefore, these sulfur oxidation steps must be rapid at low pH compared to the time scale of presently available measurements.

Despite the fact that the pathway just outlined is well established for acid pH's, several lines of evidence suggest that it may be inappropriate for pyrite oxidation in ground water flow systems. It must first be noted that the solubility of a major pyrite oxidant, ferric iron, drops dramatically as pH is increased above 4, whereas studies of modern ground-water systems containing a redox (oxygen-sulfide) boundary do not report pH values below 6.5 at the boundary (Edmunds, 1973; Lisitsyn and Kuznetsova, 1967; Dahl and Hagmaier, 1974). Ground-water systems contain a range of sinks for hydrogen ion such as carbonates, clay minerals, and feldspars that are not present in the same relative abundance in the acid mine-drainage environment. Furthermore, polished sections from sedimentary uranium deposits show pseudomorphic textures in which iron oxides formed by oxidation of pyrite closely mimic the morphology of precursor sulfides (Reynolds and Goldhaber, 1978). These textures suggest that iron dissolution was at best incomplete, and thus the process differs fundamentally from that under acidic conditions. Also notable is the fact that sulfur intermediates in the pathway are reported during metal sulfide oxidation at higher pH's in contrast to what has been observed at low pH (Forward and Mackiw, 1955; Nelson, ms; Makhija and Hitchen, 1978). Although such intermediates have been noted for other metal sulfides, there appears to have been no systematic laboratory study of the conditions of production of such intermediates during pyrite oxidation. The possible production of sulfur intermediates during pyrite oxidation is of extreme interest in uranium geochemistry because of their postulated role in roll-type uranium deposit formation (Granger and Warren, 1969; Goldhaber, Reynolds, and Rye, 1978) and is the main focus of this study. This emphasis on sulfur chemistry may have diminished the information available on the mechanism of pyrite oxidation if the reactions that determine sulfur speciation occur after the rate determining step (Nelson, ms; Hoffman, 1979).

EXPERIMENTAL PROCEDURES

Pyrite oxidation was carried out under conditions of constant pH, pO_2, and temperature in a thermostated glass reaction vessel, with a magnetic stirrer suspended from the cap and with two side ports. The two side ports were equipped with a gas-inlet tube plus inlet tube for NaOH titrant and combination pH electrode, respectively. pH control was realized via a pH stadt similar to that described by Morse (1974). For experiments described below, the pH was held to within ± 0.03 of the reported value by addition of CO_2-free NaOH (0.1 M). The concentration of dissolved oxygen was fixed by bubbling water-saturated high purity oxygen or a prepared mixture of oxygen plus nitrogen through the sample solution. The gas was scrubbed free of CO_2 prior to entering the cell. In all runs, the total gas-flow rate was fixed at 275 cm^3 per min. This rate was determined in preliminary experiments to be sufficiently rapid that oxygen concentration was not limited by mass transfer. The pyrite used was from the Climax Molybdenum Mine. No phases other than pyrite were detected by X-ray diffraction. Observations of the starting material in polished section revealed <2 percent impurities, dominantly silicates and iron-titanium oxides. This pyrite was ground and sized by sieving at less than 44 micrometer, and the fine fraction was washed under a nitrogen atmosphere in a glove bag with dilute hydrochloric acid, followed by deoxygenated water, and finally acetone. Between experiments, the pyrite was stored in a vacuum desiccator. A large batch of this fine-grained pyrite was prepared initially, and the majority of experimental data, except where specifically noted, was obtained with this same batch. No surface area measurements were made on this pyrite. The stirring rate in all experiments was the same. This rate was sufficient to suspend all material 44 micrometers or less. In polished section, the pyrite was characterized by a very large spectrum of particle sizes ranging down to the resolving power of the microscope.

At the start of a run, 5 g of pyrite were added to 1200 ml of 0.1 M KCl solution that had previously been thermally equilibrated to 30°C and presaturated with the appropriate gas mixture. The amount of sodium hydroxide added to maintain pH was noted as a function of time. In addition, 20-ml sample aliquots were periodically removed, immediately filtered through 0.45-micrometer membrane filters, and analyzed for a range of aqueous sulfur constituents. Polythionates and thiosulfate were determined by cyanolysis and spectrophotometric determination of resulting thiocyanate (Nor and Tabatabai, 1976). These reactions proceed as follows:

$$S_XO_6{}^{2-} + (X-3)\,CN^- + H_2O \rightarrow S_2O_3{}^{2-} + SO_4{}^{2-} + 2H^+ + (X-3)\,SCN^- \tag{1}$$

$$S_2O_3{}^{2-} + CN^- \;\textbf{Cucatalyst} \rightarrow SO_3{}^{2-} + SCN^- \tag{2}$$

At room temperature, reaction (1) occurs only with polythionates of $M \geqslant 4$. In the presence of a copper catalyst, two moles of thiocyanate are formed from tetrathionate, three from pentathionate, and four from hexathionate. In the absence of the copper catalyst, the thiocyanate equivalents formed from tetra-, penta-, and hexathionate are one, two, and three, respectively. Nor and Tabatabai (1976) assumed that all polythionate was present as tetrathionate and determined an empirical factor of 1.75 to estimate the amount of tetrathionate in samples that also contained thiosulfate. In the present work, the same factor, 1.75, has been used. If higher polythionates than tetrathionate are present, this would result in an underestimate of polythionates relative to thiosulfate. This point is addressed further below. Sulfite was determined by the colorimetric procedure of West and Gaeke (1956). In the presence of thiosulfate, an elemental sulfur precipitate was removed by membrane filtration prior to color development. Total dissolved sulfur in all forms was estimated by reduction to H_2S and determination of H_2S by methylene-blue colorimetry (Johnson and Nishita, 1952). This technique gave generally reasonable agreement (± 10 percent), with values obtained at the end of selected runs by oxidizing the supernatant solution to sulfate with hot nitric acid and gravimetric determination of sulfate as $BaSO_4$. However, obviously erratic values were, for unknown reasons, occasionally obtained by the Johnson and Nishita procedure. Therefore, in certain instances when this was inferred to have occurred, the total sulfur data were interpolated from the remaining values.

The solid products of two of the runs were examined petrographically in polished grain mounts under reflected light. In addition, a separate experiment was conducted to observe petrographically results of longer term oxidation. A 140-milligram sulfide concentrate consisting of intergrown pyrite and marcasite from the Benavides uranium deposit, south Texas, was held at saturation with air. pH was increased by addition of sodium carbonate. The initial pH of the solution was 8.3; after 2 weeks the pH rose to about 10 and stayed approximately constant for the remaining 6 weeks of the experiment. A parallel experiment was run in which sodium carbonate was not added. The pH of this run started at 5.2 and was 4.4 after 2 weeks. These experiments were not analyzed for their aqueous sulfur species.

Results.—Results of this study clearly indicate that soluble metastable sulfur oxyanions are produced as intermediates during inorganic pyrite

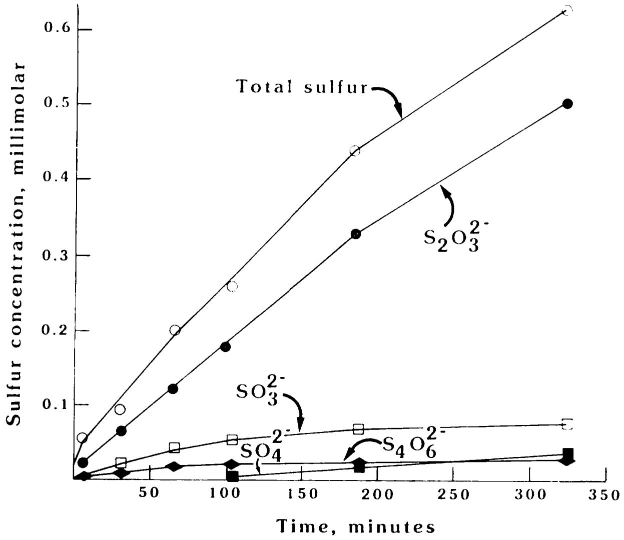


Fig. 1. Plot of sulfur species in solution produced during pyrite oxidation at pH 9 versus time. Oxygen held at saturation.

oxidation in the pH range 6 to 9. As an illustration of the point, first consider an experiment conducted at pH 9 utilizing pyrite in the <44-micrometer size range. Oxygen was held at saturation, corresponding to a concentration of 0.44 mm O_2 under the conditions of the experiment. The presence of metastable sulfur intermediates is indicated by the data points representing thiosulfate sulfur, polythionate sulfur, and sulfite sulfur (fig. 1 and table 6). The lines drawn through the data points deviate from a straight line. Nonlinearity is seen also in the plot of NaOH addition with time (fig. 2). In view of linear rates observed by other workers using more carefully sized material (see below) this behavior may be caused by the large spectrum of particle sizes present in the starting material as documented in the case of feldspar dissolution (Holdren and Berner, 1979). However, petrographic data (see below) demonstrate that oxide reaction-product coatings (which introduce a diffusion barrier and therefore nonlinear rates) can develop with time, particularly at elevated pH. Therefore, the observation that nonlinearity is more marked at pH 9 compared to pH 6 (fig. 2) may in fact be related to diffusion control of the rate. At present, the data are not sufficient to resolve this point satisfactorily.

The thiosulfate was calculated, as discussed above, by assuming that the polythionate fraction is composed exclusively of tetrathionate. This calculation requires only a minor correction to the thiosulfate data in the experiment under consideration. "Sulfate", the difference between total S and the sum of the analyzed constituents, is present as an appreciable percentage of the total sulfur only for the first measurement taken at 7 min elapsed time. The sulfate result for this time interval is most likely

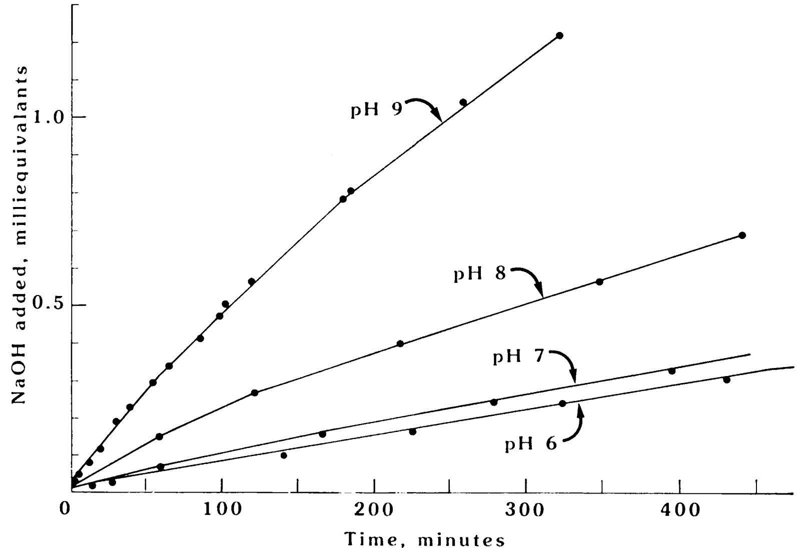


Fig. 2. Plot of milliequivalents of NaOH added to maintain pH constant versus time for pyrite oxidation experiments conducted at pH 6, 7, 8, and 9.

an experimental artifact, because sulfate once formed would not disappear from solution as required by the data in table 1. "Sulfate" in the first time interval may, therefore, be taken to indicate the transient presence of a sulfur species not considered in the analytical scheme, perhaps trithionate. Anomalous "sulfate" concentrations of this type were found during the first few minutes in a number of other experiments as well. These concentrations seem to reflect an initial "pre-oxidation" that occurs during handling of the pyrite in air (see, for example, Steger and Desjardins, 1978). In support of this hypothesis, the intensity of this initial anomalous behavior was noted to increase markedly when the pyrite was not carefully cleaned and stored.

Disregarding, therefore, the initial data point at 7 min elapsed time the following results stand out: (1) Thiosulfate is the major component of total S in solution (66-79 percent of total S). (2) Sulfate constitutes only a small fraction of total S (1-6 percent), as does tetrathionate (4-11 percent). (3) Sulfite is relatively abundant (12-22 percent). (4) Systematic trends in the data indicate some minor tendency toward an increasing proportion of sulfate and thiosulfate and a decrease in relative amounts of tetrathionate and sulfite with time.

Results for a pH 6 run (O_2 at saturation) are given in table 2 and plotted on figure 3. These data differ significantly from those at pH 9. Note first that the rate of production of total sulfur is much lower at pH 6 than at pH 9. Only 0.23 mM total sulfur was produced in 600 min, whereas at pH 9, 0.64 mM was detected at 325 min. The rate of NaOH consumption is likewise lower at pH 6 (fig. 2). The distribution of aqueous sulfur species is also markedly different. Sulfite was not detected above the blank at pH 6. Sulfate and tetrathionate sulfur are found in subequal concentrations, and both represent a higher percentage of total sulfur at pH 6 compared to pH 9.

Because of the importance of polythionates at the lower pH values studied, a separate experiment was conducted to examine the assumption that tetrathionate is the dominant species. This was done using the anion-exchange chromatigraphic technique of Pollard, Nickless, and Glover (1964), in which the polythionates were eluted, in turn, from Bio-Rad AG 2-X (20-50 mesh) resin with successively more concentrated HCl. Poly-

TABLE 1

Results of pyrite oxidation at pH 9 and O_2 at saturation

[mM, millimolar; leaders (- - -) indicate not detected]

Elapsed time (minutes)	Total sulfur (mM)	$S_4O_6^{2-}$ — **sulfur** (mM)	$S_2O_3^{2-}$ — sulfur (mM)	SO_3^{2-} — sulfur (mM)	"SO_4^{2-}" — sulfur (mM)	NaOH added (milliequivalents)
7	0.056	Trace	0.021	- - -	0.035	0.14
33	0.095	0.008	0.063	0.021	0.003	0.29
68	(0.20)*	0.021	0.12	0.041	(0.021)	0.44
106	0.26	0.21	0.18	0.053	0.002	0.60
189	0.44	0.024	0.33	0.069	0.021	0.90
327	0.64	0.027	0.50	0.075	0.035	1.32

* Interpolated value.

TABLE 2

Results of pyrite oxidation at pH 6 and O_2 at saturation
[mM, millimolar; leaders (- - -) indicate not detected]

Elapsed time (minutes)	Total sulfur (mM)	$S_4O_6^{2-}$ — sulfur (mM)	$S_2O_3^{2-}$ — sulfur (mM)	SO_3^{2-} — sulfur (mM)	"SO_4^{2-}" — sulfur (mM)	NaOH added (milliequiv-alents)
30	Trace	Trace	- - -	- - -	- - -	0.025
140	0.06	0.022	0.009	- - -	0.029	0.10
225	0.09*	0.045	- - -	- - -	0.045	0.17
325	0.14	0.080	- - -	- - -	0.073	0.24
430	0.16	0.093	- - -	- - -	0.075	0.31
600	0.23	0.12	- - -	- - -	0.12	0.39

* Interpolated value.

thionates that eluted off the column were detected by their charge transfer to solvent spectra in the UV using a Beckman model 25 spectrophotometer. The separation procedure was checked using synthetic tetrathionate prepared and purified by the procedure of Stamm, Goehring, and Feldman (1942). Figure 4 presents results from the supernatant collected at the end of a pyrite oxidation experiment conducted at pH 6.5. Detection of the polythionates was at a fixed wavelength of 214 mm. This is the wavelength of maximum absorption for tetrathionate and very near to that of thiosulfate (216 mm). The assumption was made that the other polythionates would likewise have their maximum absorption in this region. The integrated ultraviolet absorbances at 214 mm of the polythionates occur in the ratio 1: 11.1: 3.0 for $S_3O_6^{2-}$: $S_4O_6^{2-}$: $S_5O_6^{2-}$. Literature values for the molar extinction coefficients of tri- and pentathionate were not found. However, assuming that the molar extinction coefficients of the polythionate ions are similar, these absorbance ratios would also correspond to their concentration ratios or recalculated as percentage of total poly-

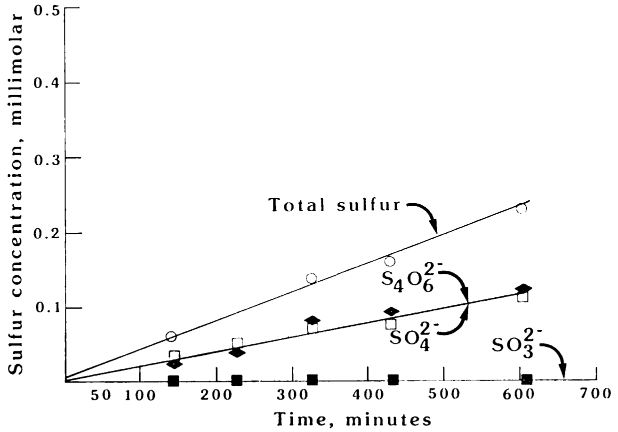


Fig. 3. Plot of sulfur species in solution (as S) produced during pyrite oxidation at pH 6 versus time. Oxygen at saturation.

thionate sulfur; 4.8, 71.2, and 24 percent, respectively. If, however, the molar extinction coefficients increase with increasing position in the homologous series as is the case for polysulfide ions (Giggenbach, 1972), the calculated tetrathionate concentration relative to pentathionate would increase. These data, although obviously extremely limited, serve to indicate the error incurred in assuming that tetrathionate is the dominant polythionate. They also suggest that the difference between total sulfur and the sum of the analyzed species is not trithionate.

In addition to the pyrite oxidation results for pH 6 and pH 9 discussed above, additional runs with O_2 held at saturation were made at pH values of 6.5, 7, 7.5, and 8. Data for these experiments are given in tables 3 to 6, respectively. The runs at pH 6.5 and 7.5 were done using a separate batch of pyrite, and so the rate data are not directly comparable because the specific surface area was different. Some limited work was also done at pH 8 with O_2 at 50 and 20 percent of saturation. These experiments will not be discussed except to note that the results suggest a linear relationship between NaOH consumption rate and oxygen partial pressure at constant pH.

The relative abundance of aqueous sulfur species produced during short-term pyrite oxidation experiments is clearly pH-dependent. This dependency is illustrated in figure 5 in which the percentage distribution of sulfur oxyanions produced during pyrite oxidation is plotted against the pH of the experiment. The range in this percentage value during the course of the run is indicated by a vertical bar. The initial experimental

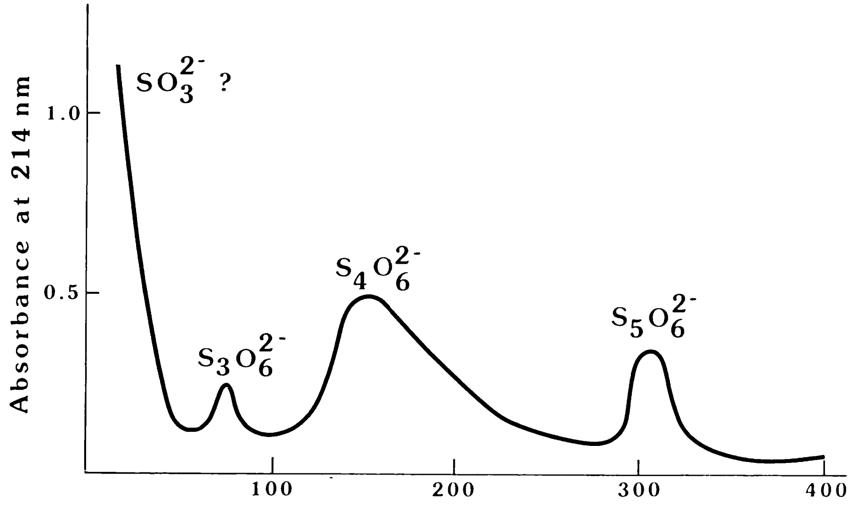


Fig. 4. Plot of absorbance at 214 nm versus volume of acid passed through anion exchange column showing resolution of polythionate anions.

point in each run was not considered for reasons discussed previously. Figure 5 shows that variations between runs at different pH values are more significant than changes in the proportion of sulfur constituents with time at a given pH. A notable exception to this behavior occurred at pH 7.5 which is not plotted on figure 5 for this reason (see below). As discussed previously, thiosulfate is dominant at pH 9, with subordinate sulfite and minor sulfate. As pH decreases, thiosulfate and sulfite diminish in relative importance compared to tetrathionate and sulfate. The results obtained at pH 7.5 differ somewhat from those at other pH values in that there is a more pronounced variability with time in the relative proportions of sulfur oxyanions. Initially, thiosulfate and tetrathionate sulfur are produced in approximately equal proportions (fig. 6). As the experiment progressed, however, thiosulfate declined relative to other forms of sulfur and in absolute concentration. Sulfite was detected only toward the end of the experiment. This pH is in the transitional region between products dominated by tetrathionate (pH $\leqslant 7$) and thiosulfate (pH $\geqslant 8$), and this transition is evidently reflected in the data from pH 7.5.

The relationships illustrated on figure 5 are representative of short time periods only. Eventually, all sulfur in solution will be oxidized to sulfate, which is the thermodynamically stable species in equilibrium with

Table 3

Results of pyrite oxidation at pH 6.5 and O_2 at saturation

[mM, millimolar; leaders (- - -) indicate not detected]

Elapsed time (minutes)	Total sulfur (mM)	$S_4O_6^{2-}$— sulfur (mM)	$S_2O_3^{2-}$— sulfur (mM)	SO_3^{2-}— sulfur (mM)	"SO_4^{2-}"— sulfur (mM)	NaOH added (milliequivalents)
35	- - -	0.017	- - -	- - -	- - -	0.006
180	0.041	0.038	- - -	- - -	0.003	0.063
360	0.076	0.052	- - -	- - -	0.024	0.14
1140	0.28	0.16	- - -	- - -	0.12	0.47
1440	0.32*	0.20	- - -	- - -	0.12	0.57
2040	(0.45)*	0.29	- - -	- - -	0.16	0.76
2640	0.55	0.32	- - -	- - -	0.23	1.0
2940	0.65	0.35	- - -	- - -	0.30	1.1

* Interpolated value.

Table 4

Results of pyrite oxidation at pH 7 and O_2 at saturation

[mM, millimolar; leaders (- - -) indicate not detected]

Elapsed time (minutes)	Total sulfur (mM)	$S_4O_6^{2-}$— sulfur (mM)	$S_2O_3^{2-}$— sulfur (mM)	SO_3^{2-}— sulfur (mM)	"SO_4^{2-}"— sulfur (mM)	NaOH added (milliequivalents)
15	Not determined	Trace	- - -	- - -	- - -	0.005
60	0.09	(0.03)*	- - -	- - -	0.06	0.06
165	0.11	0.067	- - -	- - -	0.039	0.16
278	0.17	0.11	- - -	- - -	0.07	0.25
395	0.23	0.14	- - -	- - -	0.09	0.34

* Extrapolated value.

excess oxygen. Evidently this conversion to sulfate is subject to catalysis. This catalysis can be deduced from preliminary work on a more complex solution than the simple KCl matrix used in most of the study. A sterile bacterial medium (Stanier, Doudoroff, and Adelberg, 1963) was used in one experiment at pH 6.5 (Cathy Shepard, ms thesis in preparation). Although the dominant species are the same as those shown on figure 5, the abundance of tetrathionate sulfur relative to total sulfur in solution declined rapidly after 600 min in contrast with the results shown in table 3. This difference between the complex bacterial media and KCl solutions presumably indicates a catalytic effect in the complex media by trace metals in which tetrathionate is converted to some other product — probably sulfate. The catalysis of oxidation of reduced sulfur species by trace metals has been previously demonstrated (Chen and Morris, 1970; Hoffman, 1980).

The data of figure 5 can be recast to show that the mean oxidation state of sulfur in solution increases with decreasing pH (fig. 7). This plot was constructed by combining the mean oxidation state of sulfur in each of the individual sulfur oxyanions in the proportions shown on figure 5.

TABLE 5

Results of pyrite oxidation at pH 7.5 and O_2 at saturation
[mM, millimolar; leaders (- - -) indicate not detected]

Elapsed time (minutes)	Total sulfur (mM)	$S_4O_6^{2-}$ — sulfur (mM)	$S_2O_3^{2-}$ — sulfur (mM)	SO_3^{2-} — sulfur (mM)	"SO_4^{2-}" — sulfur (mM)	NaOH added (milliequivalents)
12	0.34	0.003	0.004	- - -	0.024	0.012
65	0.03	0.008	0.011	- - -	0.011	0.040
160	0.048	0.017	0.014	- - -	0.017	0.074
243	0.075*	0.026	0.017	- - -	(0.032)	0.11
328	0.107	0.042	0.023	- - -	0.042	0.14
520	0.113*	0.067	0.025	- - -	(0.021)	0.22
1398	0.334	0.25	0.015	0.008	0.069	0.65
1693	0.425	0.31	0.011	0.016	0.104	0.77

* Interpolated value.

TABLE 6

Results of pyrite oxidation at pH 8 and O_2 at saturation
[mM, millimolar; leaders (- - -) indicate not detected]

Elapsed time (minutes)	Total sulfur (mM)	$S_4O_6^{2-}$ — sulfur (mM)	$S_2O_3^{2-}$ — sulfur (mM)	SO_3^{2-} — sulfur (mM)	"SO_4^{2-}" — sulfur (mM)	NaOH added (milliequivalents)
2	Not determined	- - -	- - -	- - -	- - -	0.01
16	0.037	(0.007)*	0.024	- - -	0.005	0.05
58	0.13	(0.010)*	0.074	- - -	0.046	0.15
122	0.19	(0.015)*	0.12	- - -	0.060	0.27
217	0.30	(0.020)*	0.17	- - -	0.11	0.40
346	0.42	0.026	0.23	- - -	0.14	0.57

* Data are based upon a linear interpolation between an initial value of zero and the final value at 346.

That the trend shown in figure 7 continues to lower and higher pHs can be inferred from the results of previous workers. At low pH, sulfate and, rarely, elemental sulfur are the sole sulfur-oxidation products, as noted in the introduction. Results of low pH are indicated as a generalized point on figure 7 in which elemental sulfur formation was neglected in accordance with the majority of data. At highly alkaline pH, some aqueous

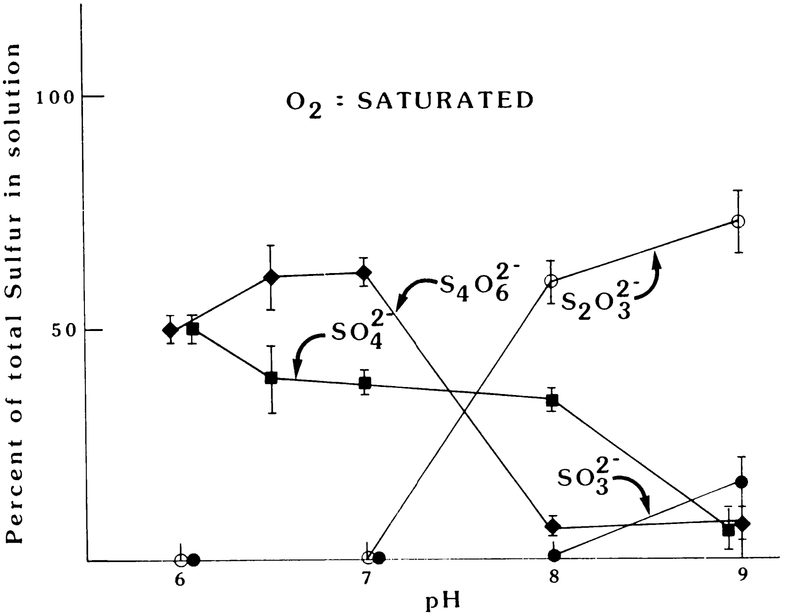


Fig. 5. Relative abundance of aqueous sulfur species (as S) produced during short term pyrite oxidation experiments as a function of pH.

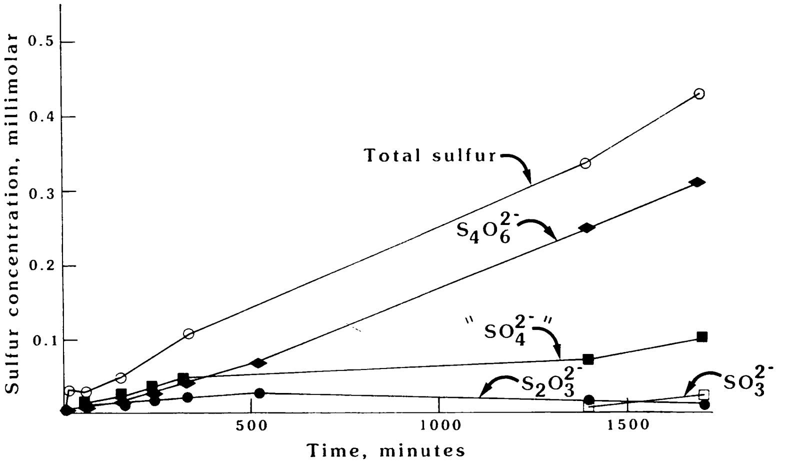


Fig. 6. Plot of sulfur species in solution (as S) produced during pyrite oxidation at pH 7.5 versus time. Oxygen at saturation.

bisulfide (oxidation state −2) is produced (Stokes, 1907), possibly by an alkaline hydrolysis reaction.

Figure 8 summarizes results of rate of addition of NaOH as a function of pH. This rate is the slope of the NaOH versus time curves in figure 2. For those plots that are nonlinear, the initial part of the experiment was neglected in this calculation on the assumption that this behavior is related to a more rapid reaction of the finest particles, as mentioned above. The plot demonstrates an increase in NaOH addition rate with increasing pH. This increase is particularly marked between pH 8 and 9. A similar result was noted by previous workers (Smith and Shumate, 1970).

At first glance, figure 8 suggests that the rate of "pyrite oxidation" (which in this context is defined as the rate of oxidation of ferrous iron in pyrite to ferric iron in iron oxide) increases at pH 9 relative to pH 6. However, the relationship between hydrogen ion production (NaOH consumption) and rate of pyrite oxidation is dependent upon the particular sulfur oxidation product produced as illustrated by the following equations, which are written so as to produce a constant amount of lepidocrocite ($FeO \cdot OH$), which is known to be the product phase of iron monosulfide oxidation (Nelson, 1978).

$$2FeS_2 + 7\tfrac{1}{2}O_2 + 5H_2O = 2FeOOH + 8H^+ + 4SO_4^{2-} \quad (3)$$

$$2FeS_2 + 5\tfrac{1}{2}O_2 + 5H_2O = 2FeOOH + 8H^+ + 4SO_3^{2-} \quad (4)$$

$$2FeS_2 + 4O_2 + 2H_2O = 2FeOOH + 2H^+ + S_4O_6^{2-} \quad (5)$$

$$2FeS_2 + 3\tfrac{1}{2}O_2 + 3H_2O = 2FeOOH + 4H^+ + 2S_2O_3^{2-} \quad (6)$$

$$2FeS_2 + 1\tfrac{1}{2}O_2 + H_2O = 2FeOOH + 4S^\circ \quad (7)$$

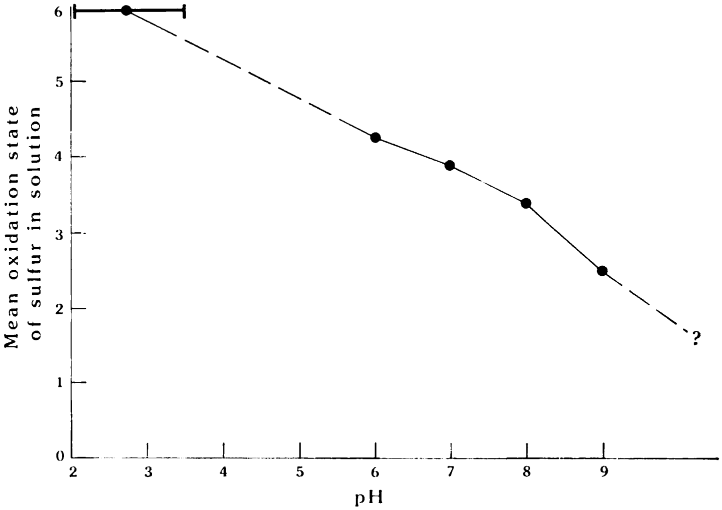


Fig. 7. Mean oxidation state of sulfur in solution as a function of pH.

Of particular interest is the fact that pyrite oxidation leading exclusively to elemental sulfur (S°, eq 7) produces no hydrogen ions. Therefore, the possibility exists that at low pH, where low rates of hydrogen ion production (NaOH consumption) are observed, the oxidation of iron may nevertheless be proceeding at a rapid rate with an associated buildup of sizeable quantities of elemental sulfur in the solid phase. Nelson (ms) observed elemental sulfur to be the major sulfur oxidation product of iron monosulfide at pH <7. Two procedures were employed to test for elemental sulfur. In the first, an attempt was made to measure ferric iron in oxidized pyrite and to compare this measured value to one predicted from the NaOH consumption data. Oxidized iron was determined by leaching pyrite previously oxidized in the pH-stadt in boiling 6 N HCl for 10 min. Pyrite is insoluble under these conditions, whereas iron oxides are soluble (Berner, 1970). Iron was determined on the supernatant by colorimetry utilizing the ferrozine technique (Stookey, 1970). A blank consisting of unreacted pyrite was run for comparison. The predicted values were calculated as follows: (1) The ratio of moles of iron oxidized to moles of hydrogen ion produced was calculated by combining eqs 3 to 6 in the proportion dictated by the observed proportions of analytically detected aqueous sulfur species. (2) This ratio was then multiplied by the actual amount of hydrogen ions produced, as determined by the volume of NaOH consumed times its known concentration. The results of this calculation, as well as the observed values, are compared in table 7. The agreement between the two estimates is considered reasonable considering

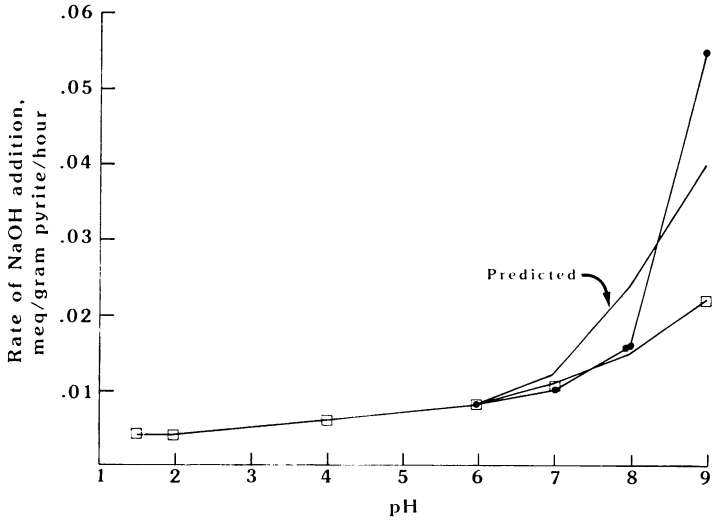


Fig. 8. Rate of NaOH addition in milliequivalents per gram pyrite per hour during pyrite oxidation as a function of pH.

(●) Data of this study.

(☐) Data of Smith and Shumate (1970). Normalized to correspond to results from this study at pH 6.

that the leaching procedure is rather crude. In particular, the results for the pyrite oxidized at pH 6 show no buildup of oxidized iron over that predicted from the analytically determined sulfur species.

In a second set of experiments, elemental sulfur was determined directly on the same previously oxidized pyrite samples as shown in table 7. A separate aliquot of each of these samples was refluxed in acetone, as was a standard consisting of flowers of sulfur. Sulfur dissolved in the acetone was then determined by the procedure of Bartlett and Skoog (1954). All values determined were extremely low, and none was significantly above the values of the blank determined from unreacted pyrite. The two experiments together indicate that solid elemental sulfur was not a major product in these experiments.

The data for H+ production as a function of pH is compared (fig. 8) to the oxygen-consumption results of Smith and Shumate (1970). The oxygen consumption data were normalized to correspond to the H+ production results at pH 6. Comparison of the two plots shows close correspondence at pH 7 and 8, but the H+ production shows a relative increase at pH 9. In a general sense, the two measures of pyrite-oxidation rate should shift with respect to each other as a function of pH. Inspection of eqs 3 to 7 shows that the relationship of O_2 consumed to H+ produced is a function of the particular sulfur species produced as shown on figure 8 by the "predicted" curve in which the rate of H+ production is calculated relative to oxygen consumption based upon the observed distribution of sulfur oxyanions at each pH (fig. 5). Viewed in this way, there is rather poor agreement between the two data sets at pH 8 and 9. Although the origin of the discrepancy is not presently known, it may indicate a sensitivity of the distribution of sulfur products to the particular experimental design.

Observations on solid reaction products were consistent with the chemical data in that elevated pH led to much more rapid oxidation effects. Essentially no discernible differences were seen between unreacted pyrite and that oxidized at pH 6. Likewise, the sulfide concentrate from the Benavides deposit oxidized for 2 weeks between pH 5.2 and 4.4 was not detectably affected. In comparison, pyrite oxidized at pH 9 had a distinctive surface tarnish, but no discrete reaction rim was resolvable using the petrographic microscope. The sulfide concentrate from the south

TABLE 7

Comparison of iron oxide iron predicted to have formed during pyrite oxidation experiments with that leached by HCl

	Predicted (mg)	Observed (mg)
pH6	5	3
pH8 (O_2=50 percent)	4	4
pH8 (long term)*	84	101
pH9	28	18

* This was a sample oxidized for longer (4700 min) than in other experiments (typically less than 450 min) to allow more extensive buildup of oxidation products.

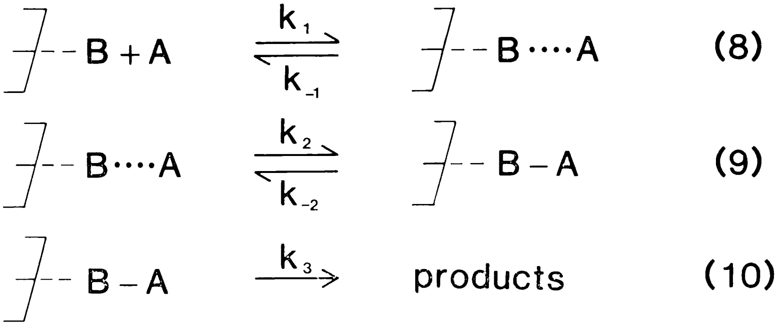
Texas uranium deposit held at elevated pH, however, showed marked effects of oxidation after both 2 and 6 weeks. After 2 weeks, most grains had developed at least a discontinuous iron-oxide rim, presumably by replacement of iron disulfide. On some grains, these rims were continuous and crudely uniform in thickness; the rims were typically 1 micrometer thick. In many grains, the oxide rim had pulled away from the sulfide substrate, leaving a 1 to 3 micrometer gap between the two phases. This gap may have occurred either during reaction or perhaps as an artifact of desiccation during sample preparation. Marcasite oxidized more rapidly than pyrite, as evidenced by grains containing both phases in which the pyrite was significantly less replaced by oxide than was marcasite. Along one such grain perimeter, an oxide rim was 2 micrometers thick against marcasite and 1 micrometer thick against pyrite. In a large number of grains, there was extensive embayment of sulfides rather than uniform rimming, suggesting preferential attack along fractures or other zones of weakness.

After 6 weeks, the types of features observed were essentially similar to those at 2 weeks, although oxidation was more advanced in that a higher proportion of grains bore a continuous oxide rim, and oxide rims were as much as 3 or 4 micrometers thick. Residual unreacted pyrite was occasionally contained within the oxide rim. In a few grains the outer margin of the oxide rim seemed to be pseudomorphic after the original grain boundary, but in most grains this relationship could not be established. Oxide rims on marcasite grains were as much as 11 micrometers thick; in some grains this rim had the definite appearance of a pseudomorphic replacement.

DISCUSSION

Rate controls on pyrite oxidation.—As noted in the introduction, the nature of sulfur products observed during pyrite oxidation experiments may be determined by reactions that occur subsequent to the overall rate determining step in the pyrite oxidation pathway. This indeed appears to be the case for iron disulfide (see below) as it is for iron monosulfide (Nelson, ms). Therefore, the observed distribution of sulfur oxidation products may not provide information regarding the rate determining step in either case. However, the converse is not necessarily true. Therefore, the possible rate controls on pyrite oxidation are very briefly discussed, in large part based on data from the literature. This is followed by a analyses of controls on sulfur speciation and finally by a schematic oxidation pathway which serves to rationalize the range of observations considered.

Nelson (ms) and Berner (1978), among others, have reviewed the general concepts involved in heterogeneous reaction kinetics, aspects of which are summarized here. Chemical reaction between a solid phase and a solute in aqueous solution must of necessity involve both mass transfer from the solution to the solid and reaction at the surface of the solid, as well as possible desorption of products from the solid. The rate limiting step for a sequential reaction path is determined by the slowest step in the reaction sequence. If this slow step is mass transfer, the reaction is said to be diffusion controlled and generally leads to a parabolic ($t^{1/2}$) rate expression (Luce and others, 1972). Diffusion control may arise either when the resistance to mass transfer is caused by a thin stagnant film of solution at the surface of the solid, or when a buildup of insoluble product residue occurs. In contrast, when the slow step is a chemical reaction at the surface of the solid, the rate is referred to as chemically controlled. Two subclasses of chemical control may be recognized: adsorption and reaction control. These may be understood by reference to the following simplified scheme (Nelson, ms), for reaction between a solid, B, and solute, A.



For adsorption control, the slow step in the sequence is the initial one defined by the rate constant k_1. The form of the rate expression resulting from the situation is;

$$\text{Rate} = k[A]S \tag{11}$$

where S is surface area, and brackets denote concentration in aqueous solution. If, however, the rate limiting step is the final one leading to formation of products, the general rate expression is of the form

$$\text{Rate} = \frac{K_1[A]S}{1 + K_2[A] + K_3[S]} \tag{12}$$

where K_1, K_2, and K_3 are composite constants composed of combinations of the individual rate constants in eqs 8, 9, and 10. It may be shown that at low concentration of A, eq 12 reduces to the form of eq 11, and at high concentrations of A, the rate becomes independent of A. The latter case corresponds physically to total complexation of all reactive surface sites.

The available evidence points to chemical control of the rate of pyrite oxidation (although exceptions will be discussed) and to a rate limiting step subsequent to the initial adsorption of oxygen to the surface. Evidence for chemical rather than transport control can be deduced from the activation energy for the reaction that has been measured at 14 kcal/mole (T = 20-35°C) and 13.3 kcal/mole (T = 130-210°C) by Smith and Shumate (1970) and Warren (1956, cited by Umana, ms) respectively. Activation energies for transport controlled processes are much smaller, typically 4 kcal/mole or less.

It seems reasonable to conclude that linear (0th order) overall rates of pyrite oxidation (other variables held constant) are associated with a chemically controlled rate of oxidation. Smith and Shumate noted this behavior in the study just cited which yielded a high activation energy. Linear rates of pyrite oxidation have also been reported in strongly acid solutions at 100° to 130°C (McKay and Halpern, 1958) and in mild to strong alkaline solutions at 60° to 120°C (Burkin, 1969). These constant rates hold over an extent of reactions of greater than 30 percent of the starting pyrite in some of the cited studies. Dresher, Wadsworth, and Fassell (1956) found similar behavior for molybdenite (MoS_2) oxidation under alkaline conditions at 110° to 200°C, indicating that the phenomenon is not unique to iron disulfide.

Several exceptions to the linear-rate behavior have been noted. In the present study, this effect may in part be attributed to non-homogeneity of particle sizes. The remainder can perhaps be related to buildup of products on the pyrite surface which, based on the petrographic study, is most pronounced at pH 9. Nonlinearity was observed under acidic conditions by Bergholm (1955) and was related to a diffusion barrier arising from a buildup of elemental sulfur. Burkin (1969) noted that when impure pyrite ore is oxidized at alkaline pH, iron-oxide product is mechanically retained around the pyrite surface, causing a diffusional barrier and a decrease in rate with time. In pure pyrite, however, this oxide layer was observed to spall off, exposing fresh surface except where cracks penetrating into the grain mechanically retained the iron oxide. The petrographic observations of the present study indicate that for pyrite oxidation at alkaline pHs and at room temperature, an oxide diffusion barrier may indeed form. The discrepancy between this result and the observations of Burkin (1969) are perhaps relatable to the differing temperature regimes of the two studies. At the higher temperatures, differential stress between the oxide and sulfide layers may be greater, owing to a temperature-dependence on the crystal structure of the oxide produced. The transition from a chemically controlled (linear) rate to a physical (diffusion) controlled one is, therefore, related to effects resulting from conditions of oxidation which allow buildup of product phases on the pyrite surface.

The approximate first-order dependence of oxidation rate on O_2 has been found for $O_2 \leqslant 1$ atm partial pressure in several studies (Stenhouse and Armstrong, 1952; McKay and Halpern, 1958; Smith and Shumate, 1970; Bergholm, 1955; this study). An interesting similarity is evident in comparing the data of Stenhouse and Armstrong (1952) and the MoS_2 study of Dresher, Wadsworth, and Fassell (1956). Both studies found linear dependence of rate on O_2 partial pressure up to 13.6 atm O_2, with a flattening out of the rate curve at greater pO_2. A possible implication is that adsorption of O_2 by the sulfide surface is more closely related to the $-S_2$ group than to the nature of the metal. This conclusion needs to be tempered by the data of Smith and Shumate (1970) and of Clark (1966) who reported a form similar to the rate versus-pO_2 curve but a lower limiting pO_2. The general form of the rate versus pO_2 curve is consistent with a rate controlling mechanism involving surface adsorption of O_2 on active sulfur sites on the pyrite surface. The data taken together therefore indicate that the first order dependence on O_2 at low pO_2 is actually a pseudo first order dependence which breaks down at higher pO_2. This in turn implies that the rate of pyrite oxidation is governed by an expression of the form of eq 12 and is therefore not adsorption limited.

Controls on sulfur speciation.—The results of this study demonstrate that metastable sulfur oxyanions accumulate as intermediates in the pathway of pyrite oxidation over the pH range 6 to 9. These species show a systematic pH dependence with a more oxidized assemblage detected at lower pH. A review of the literature on the chemistry of sulfur oxyanions suggests that the broad outlines of the observed distribution can in part be rationalized on the basis of well-established kinetic behavior of these ions under conditions of *homogeneous* oxidation in aqueous solution.

Under weakly acidic conditions, thiosulfate is readily oxidized to tetrathionate by weak oxidizing agents (Lyons and Nickless, 1968) eq 13.

$$2S_2O_3^{2-} + 2H^+ + \tfrac{1}{2}O_2 \rightarrow S_4O_6^{2-} + H_2O \qquad (13)$$

Alternatively, under strongly acid conditions, thiosulfate may disproportionate to elemental sulfur (actually S_8) and sulfite (Davis, 1958).

$$S_2O_3^{2-} + H^+ \rightarrow HSO_3^- + S^\circ \qquad (14)$$

Thiosulfate is known to persist, however, under alkaline conditions (Dowson and Jones, 1974). This may be a kinetic phenomenon. Calculations on the position of the tetrathionate-thiosulfate metastable equilibrium (eq 13), based upon the free-energy data in Garrels and Christ (1965), show that tetrathionate ought to predominate at the pO_2 and pH of the experiments.

Sulfite in basic solution is not stable in the presence of other sulfur species and is rapidly oxidized in the presence of dissolved oxygen. The oxidation of sulfite is known to proceed via a free radical chain mechanism which is very sensitive to catalysis and inhibition. The occurrence of sulfite as a reaction product in this study at pH 9 is likely related to such an inhibitory effect. However, this aspect of the results is not understood and will not be pursued further.

Polythionates, in contrast to thiosulfate and sulfite, are unstable in alkaline solution, being converted dominantly to thiosulfate (Lyons and Nickless, 1968; Dowson and Jones, 1974) but are relatively stable under acidic conditions.

$$4S_4O_6^{2-} + 5OH^- \rightarrow 5S_2O_3^{2-} + 2S_3O_6^{2-} + 3H_2O \qquad (15A)$$

or

$$2S_4O_6^{2-} + 6OH^- \rightarrow 3S_2O_3^{2-} + 2SO_3^{2-} + 3H_2O \qquad (15B)$$

$$2S_5O_6^{2-} + 6OH^- \rightarrow 5S_2O_3^{2-} + 3H_2O \qquad (16)$$

Therefore, the observed buildup of sulfite and thiosulfate at pH 8 to 9 can be postulated as due to the fact that these ions are intermediates in the sulfur-oxidation pathway, along which further oxidation is to some extent arrested in this pH range. The antipathetical relationship between thiosulfate sulfur and tetrathionate sulfur (fig. 5) suggests the possibility that thiosulfate is likewise an intermediate at pH less than 8 which is converted to tetrathionate (eq 8) at a rapid rate compared to production from its precursor in the pathway. Furthermore, the sum of sulfite-plus-sulfate at pH 9 is roughly similar to the proportion of sulfate to total sulfur at pH less than 9. This similarity suggests that sulfite oxidation provides a sizeable component of the observed sulfate. These observations imply, but do not prove, that the sequence of sulfur-oxidation steps is less sensitive to pH than is the relative rates of these steps.

A useful comparison is that between sulfur-oxidation products observed during oxygenation of aqueous HS^-/H_2S and those found during pyrite oxidation. A number of studies of the HS^-/H_2S pathway have been conducted (see Hoffman, 1980 for a summary); the most comprehensive work on the uncatalyzed homogeneous oxidation of sulfide by O_2 is that of Chen and Morris (1970, 1972). They noted a pH-dependence of the nature of sulfur intermediates. At pH's greater than neutral, thiosulfate and sulfite were predominant. The ratio of thiosulfate sulfur to all other sulfur-oxidation products increased (at similar time of reaction to the present experiments) with increasing pH from about 52 to 75 percent over the pH range 7.9 to 8.8. The comparable figures from this study are strikingly similar, 54 and 70 percent, respectively (fig. 5). Hoffman (1979) studied the homogeneous oxidation catalyzed by metal-phthalocyanine complexes. In contrast to the uncatalyzed reaction, the catalyzed pathway yields substantially smaller proportions of thiosulfate sulfur (37-51 percent) and correspondingly greater concentrations of sulfate sulfur (44-64 percent) at pH 8.8. At pH less than seven, Chen and Morris detected polysulfide ions (S_X^{2-}, $X = 2 - 6$). Visible precipitation of elemental sulfur occurred at pH 6.7 and below. Elemental sulfur and sulfate were the only products noted during oxidation of aqueous sulfide species by hydrogen peroxide (Hoffman, 1977), although polysulfide ions were invoked as intermediates. Polysulfides are stabilized by reaction of elemental sulfur with aqueous bisulfide (eq 17):

$$XS^\circ + HS^- \rightarrow S_{X+1}{}^{2-} + H^+ \qquad (17)$$

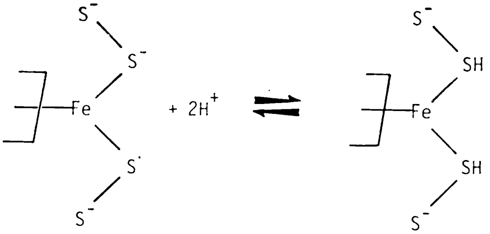
and therefore are not expected as persistent species or major intermediates in the pyrite-oxidation pathway.

Chen and Morris (1970, 1972) concluded that HS^-/H_2S oxidation in the neutral pH range operates by production of elemental sulfur via a chain mechanism and further reaction of this sulfur to form polysulfides that are much more rapidly oxidized than is HS^- or H_2S. Under alkaline conditions, elemental sulfur is still an important intermediate, but polysulfide ions do not build up, owing to removal of zero-valent sulfur by a mechanism such as the reverse of eq 14.

The gross similarity in product species between uncatalyzed HS^-/H_2S and pyrite oxidation at alkaline pH is taken to indicate a similar pathway involving a similar early intermediate in common between the two mechanisms. The unlikely formation of polysulfides during pyrite oxidation suggests that this intermediate must occur prior to the formation of polysulfide ions in the HS^-/H_2S sequence. Nelson (ms) reported on the sulfur oxidation products of the iron monosulfide phase mackinawite. The nature and pH dependence of these products are markedly different from the present study. This may imply that the disulfide group in FeS_2 plays a significant role in determining the observed distribution of sulfur products.

Mechanism of pyrite oxidation.—The observations and conclusions of the preceding paragraphs may be integrated in the form of a mechanistic interpretation of the pyrite oxidation pathway. Such a proposed mechanism must of necessity be highly schematic because evidence regarding the existence of key in intermediates is weak or totally lacking. Yet it is nonetheless useful to speculate in this area as a basis for guiding further studies.

The starting point for such a mechanism is an understanding of the properties of the pyrite surface. Such information, however, seems to be as yet largely unavailable in the literature. It is possible, however, to approximate one aspect of these properties, the pH dependency of charge on the pyrite surface. This charge is determined by protonation-deprotonation reactions (eqs 18 and 19).



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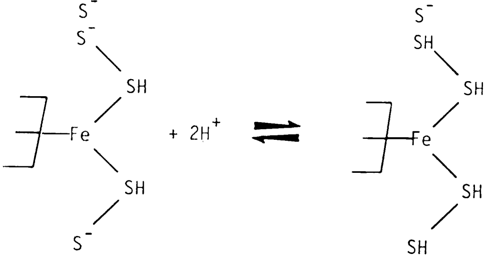

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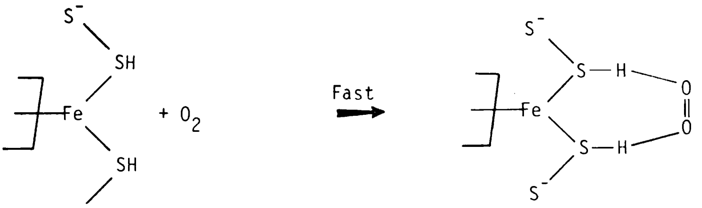
The pH of zero point of charge for the pyrite surface will be governed by the acidity of disulfane (H_2S_2) groups. This pH may be approximated by the equation:

$$pH_{ZPC} \approx \frac{1}{2}(pK_{a1} + pK_{a2}) \tag{20}$$

where pK_{a1} and pK_{a2} are the first and second ionization constants of disulfane. Based on data from Schwarzenbach and Fischer (1960):

$$pH_{ZPC} \approx \frac{1}{2} (5.0 + 9.7) \approx 7.3 \tag{21}$$

Examination of figure 8 shows that the most rapid rise in pyrite oxidation rate occurs in the vicinity of the pH_{ZPC} under conditions of net negative charge on disulfide groups of the pyrite surface. This observation seems reasonable in the light of studies of homogeneous sulfide oxidation, which have universally concluded that HS^- is oxidized more rapidly than is H_2S (Chen and Morris, 1972; Hoffmann, 1977; O'Brien and Birkner, 1977). Starting therefore with the partially deprotinated surface, the following pathway is proposed:



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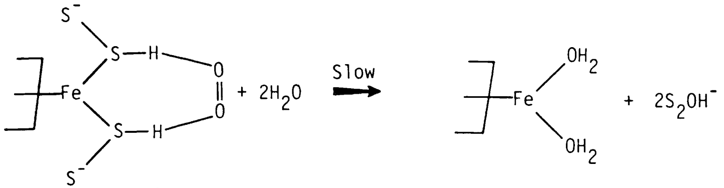

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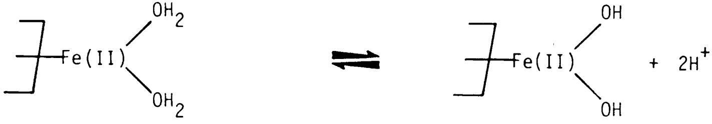

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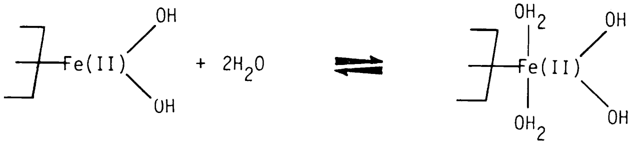

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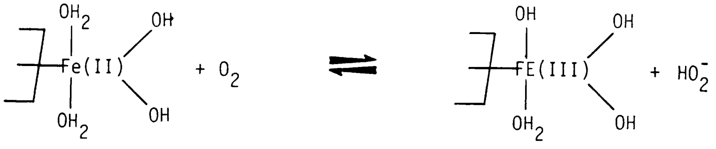

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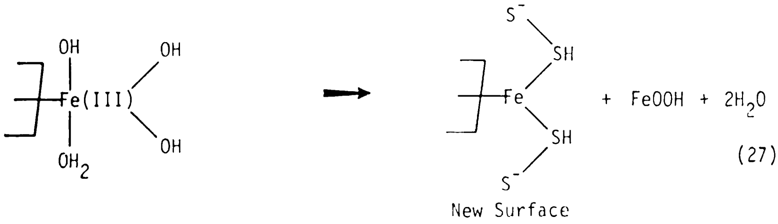

(27)

$$HO_2^- \rightleftharpoons H^+ + O_2^- \qquad (28)$$

$$H^+ + 2O_2^- \xrightarrow[\text{catalyst}]{\text{surface}} H_2O_2 + O_2 \qquad (29)$$

This mechanism incorporates the information that the rate determining step is reaction controlled (eq 23) and occurs subsequent to the initial adsorption of oxygen on the surface (eq 22). The oxidation step from Fe(II) to Fe(III) is similar to one proposed by Tamura, Goto, and Nagayama (1976) for the oxidation of surface adsorbed ferrous iron and is postulated to by these workers to form O_2^-. This ion has been implicated in the pyrite oxidation mechanism based on the electrochemical studies of Biegler, Rand, and Woods (1975). The same authors were able to demonstrate via direct chemical measurement as well as electrochemical studies that hydrogen peroxide forms as a soluble oxygen intermediate in acid solutions (eq 29). The reactions leading to the observed sulfur intermediates and product may be formulated as follows:

$$S_2OH^- + O_2 \xrightarrow{\text{fast}} HS_2O_3^- \qquad (30)$$

$$HS_2O_3^- \rightleftharpoons S_2O_3^{2-} + H^+ \qquad (31)$$

$$2S_2O_3^{2-} + H_2O_2 \xrightarrow{\text{fast}} S_4O_6^{2-} + H_2O \qquad (32)$$

$$S_2O_3^{2-} + 2OH^- + O_2 \longrightarrow 2SO_3^{2-} + H_2O \qquad (33)$$

$$HSO_3^- + H_2O_2 \longrightarrow SO_4^{2-} + H_2O + H^+ \qquad (34)$$

The initial sulfur intermediate, S_2OH^- (eq 23), differs from what others have postulated for the homogeneous oxygenation. Hoffman (1979) has proposed, for example, that the initial intermediate in the catalyzed homogeneous oxygenation is HSO_2^-. Formation of this species, which cannot be totally excluded for pyrite oxidation, does not require breaking of the O-O bond of O_2. This may be reasonable in the absence of specific adsorption of oxygen on the pyrite surface (eq 22). The sulfur reactions (eqs 30-34) postulate that thiosulfate is a key species in the formation of the remaining sulfur oxyanions. This sequence is therefore in accord with the results deduced previously that thiosulfate is a precursor to tetrathionate, and that sulfite is the precursor to sulfate.

IMPLICATIONS FOR ORE GENESIS

Modern genetic models for the origin of the Wyoming and Texas roll-type uranium deposits place considerable emphasis on the relationships between pyrite oxidation and ore deposition. The function of pyrite oxidation in this context has been discussed in terms of two contrasting hypotheses. One has been described as the biogenic or geochemical cell model (Rackley, 1972). In this formulation, sulfur is redistributed via bacterially catalyzed oxidation of iron-disulfide minerals producing sulfate ions that are carried with uranium-bearing ground water into reduced (organic carbon-bearing) rock. There, the sulfate is rereduced to aqueous sulfide which in part acts as a reductant for precipitating uranium as reduced (U(IV)) oxides or silicates and in part reacts with available non-sulfide iron to form the characteristic ore-stage iron-disulfide minerals. An alternative hypothesis (Granger and Warren, 1969) can be described as the nonbiogenic model. They postulated that inorganic pyrite oxidation produced aqueous sulfur species of intermediate oxidation state (for example, thiosulfate, $S_2O_3^{2-}$). Subsequent reactions of these species would be analogous in many ways to bacterially derived sulfide (uranium reduction and reaction with iron to produce ore-stage sulfides).

The results of this study indicate that metastable sulfur oxyanions can be produced during nonbiogenic oxidation of iron-disulfide minerals. This observation thus confirms in part the hypothesis of Granger and Warren (1969). However, some caveats must be placed upon applying the present results to ore-depositing systems. This study was conducted in extremely simple solutions. Oxidation of sulfur oxyanions is clearly subject to both bacterial and inorganic catalysis (Chen and Morris, 1970; Hoffman, 1980; Stanier, Doudoroff, and Adelberg, 1973), and the influence of such catalysis must be evaluated to determine if metastable sulfur oxyanions can persist long enough as intermediates in pyrite oxidation to function as sulfur carriers in ore-forming systems. Furthermore, additional studies will have to be carried out to determine if the metastable sulfur oxyanions are active as sulfidizing agents and uranyl ion reductants at earth surface temperatures.

ACKNOWLEDGMENTS

Much of the work described in this paper was carried out in laboratory space graciously provided by the Colorado School of Mines Department of Chemistry/Geochemistry. I would also like to acknowledge the assistance in the laboratory of Catherine Fogg and guidance in the petrographic aspects of the work by Richard Reynolds. The comments of an anonamous reviewer had a major impact on this paper, particularly the proposed reaction mechanism.

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