# OXIDATION OF SULFIDE MINERALS, 4. PYRITE, CHALCOPYRITE AND PYRRHOTITE*

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## ABSTRACT

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Samples of pyrite, chalcopyrite and pyrrhotite were subjected to 52° C and 68% Rela-
tive Humidity in air for periods of up to four weeks. The resultant oxidation products
were analyzed for metal and the various possible surface-bearing products such as sulfate,
etc. It was concluded that pyrite and chalcopyrite are initially oxidized to ferrous or a
combination of ferrous and cuprous thiosulfates which undergo(es) further oxidation to
ferric or ferric and cupric sulfate(s). In addition to this thiosulfate—sulfate oxidation,
pyrrhotite undergoes a much more rapid oxidation to goethite and elemental S.

## INTRODUCTION

As part of a general study to establish the "shelf-life" or stability of certi-
fied reference ores and concentrates (Steger, 1976c), it was decided to im-
prove the understanding of the air oxidation of the more common sulfide
minerals. Although much work has been done on the oxidation of sulfide
minerals at high temperatures ($T > 200° C$), particularly with respect to
roasting of ores, the knowledge of the oxidation at relatively low tempera-
tures ($T < 100° C$) is scant and, in general, has been derived from studies on
the weathering of sulfide minerals. The major difficulty encountered in the
study of the oxidation of sulfide minerals at $T < 100° C$ is the identification
and/or determination of the small amounts of products which are formed
during reasonable time periods. Methods have been developed in this labora-
tory to determine the metal (Steger, 1977b,c) and the S-bearing constituents

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(Steger and Desjardins, 1977) in very small amounts of oxidation product formed on the common sulfide minerals. This paper describes the results of the application of these analytical methods to ascertain the nature of the oxidation of pyrite, pyrrhotite and chalcopyrite at 52°C and 68% relative humidity (RH).

Previous studies on weathered pyrite by Saksela (1952), Frenzel (1957) and Nambu (1957) or on the low-temperature oxidation of pyrite by Banerjee (1971), Sinha and Walker (1972) and Frost et al. (1974) do not show a consensus on either the products or nature of the oxidation but instead, suggest that the oxidation of pyrite proceeds to give: (1) $FeSO_4$ or $Fe_2(SO_4)_3$; (2) $FeO$ or $Fe_2O_3$; or (3) pyrrhotite. It is also possible that the sulfates could decompose further to give $Fe_2O_3$ (Mapstone, 1954). Similarly, the oxidation of pyrrhotite at $T < 100°C$, although not widely investigated, is not well understood. Ivanov (1966) has suggested three possible oxidation mechanisms for pyrrhotite at ambient temperature to give: (1) $FeSO_4$ even with an insufficiency of oxygen; (2) $FeSO_4(OH)$ in an excess of oxygen; and (3) $Fe(OH)_3$ under the effect of sunlight. No reference to the oxidation of chalcopyrite at $T < 100°C$ was found in the open literature even though this mineral does have significant economic importance. It is evident, therefore, that any clarification of the oxidation of these three iron sulfides at ambient temperatures would serve to improve the understanding of their behavior in processes such as flotation or in the desulfurization of coals by oxidation of the associated pyrite (Sinha and Walker, 1972). The results of the current study on the oxidation at 52°C and 68% RH should also prove helpful in understanding the weathering of these minerals.

EXPERIMENTAL

*Preparation of mineral samples*

Lumps of high-purity (Rico, Colorado), monoclinic pyrrhotite (Falconbridge, Ontario) and chalcopyrite (Ajo, Arizona) were crushed mechanically and the 44—74-$\mu$m fraction was collected (by dry-sieving) for further study. The non-sulfide impurities were removed from this fraction by density separation with diiodo-methane (S.G. = 3.3 g/cm³). Polished sections were prepared to identify and estimate the purity of these samples. The pyrite contained a trace of chalcopyrite and sphalerite and 1—2% gangue; the pyrrhotite was monoclinic with traces of pyrite, galena and gangue; and the chalcopyrite contained 1—2% pyrite and 2—3% gangue. Elemental analysis gave:

| | | |
|---|---|---|
| 46.18% Fe and 51.98% S, | i.e., $FeS_{1.96}$ | for pyrite |
| 59.94% Fe and 39.41% S, | i.e., $FeS_{1.14}$ | for pyrrhotite |
| 30.01% Fe, 33.52% Cu and 34.16% S, i.e., $0982\ FeCuS_2 + 0.018\ FeS_2$, | | for chalcopyrite |

The difference between 100% and the sum of the elemental analyses can be attributed to the gangue which can be considered to be inert.

In order to remove as much as possible of the oxidation products formed

during the preparation of these samples, approximately 20-g lots of each mineral were shaken for 2 h with 100 ml of $(NH_4)_2 S$ solution (Fainberg, 1953), freshly prepared by saturation of 400 ml water and 14 ml concentrated $NH_4 OH$ with $H_2 S$ gas. The specimens were then filtered, thoroughly washed with de-aerated water, anhydrous methanol and ethyl acetate and dried under suction; they were then stored in vials (flushed in $N_2$ gas) in a desiccator.

*Oxidation of mineral samples*

For each mineral, ~16 g were weighed into a tared 90 × 50-mm crystallization dish which was then placed in a controlled temperature-humidity chamber (Blue M Electric Co., Blue Island, Illinois) set at $52 \pm 2°C$ and $68 \pm 3\%$ RH. The samples were removed from this chamber after various pre-selected time intervals, dried in a desiccator over Drierite® for 18—20 h, weighed to determine $\Delta$wt, the change in weight due to oxidation and then thoroughly mixed manually. After the removal of sub-samples of ~2 g, the mineral samples were re-weighed and returned to the chamber.

*Determination of parameters of oxidation*

In addition to the value of $\Delta$wt, the oxidation products formed from each sub-sample were analyzed for Fe(II) and Fe(III) by selective extraction with $10 M H_3 PO_4$ (Steger, 1977a), for sulfate and thiosulfate by ion-exchange treatment with $(NH_4)_2 S$ (Steger and Desjardins, 1977) and for elemental sulfur, $S^0$, by sublimation (Steger, 1976b). The results of these analyses are summarized in Tables I—III. It should be noted that corrections were applied to take into account the decreasing amount of original unoxidized mineral as sub-sample are successively removed. The numbers in brackets are the estimated reproducibility of the results. Because the reproducibilities for Fe(III) and $S^0$ are essentially constant for all samples of a given mineral, they have been shown only for the unoxidized minerals.

In addition, the oxidation products of both the untreated and treated samples showed an invariant Fe(II) content of $3.4 \pm 0.5$, $3.1 \pm 0.4$ and $1.4 \pm 0.2 \cdot 10^{-3}$ mole per mole of initial pyrite, pyrrhotite and chalcopyrite, respectively.

DISCUSSION

The data in Tables I—III illustrate that the initial minerals are already oxidized to some extent. Indeed, a "clean" sulfide mineral cannot be expected to remain so, especially after drying in air (under suction) after treatment with $(NH_4)_2 S$ solution. The relatively high Fe(III) content of the unoxidized pyrite suggests the presence of appreciable $Fe_2 O_3$ which is not removed with $(NH_4)_2 S$. All changes due to oxidation are, of course, those differences in

## TABLE I

Results of analysis for oxidized pyrite

| Time (h) | $\Delta_0$ wt (g/mole FeS$_2$) | $10^{-3}$ mole per mole FeS$_2$ | | | |
|---|---|---|---|---|---|
| | | Fe(III) | SO$_4$$^{2-}$ | S$_2$O$_3$$^{2-}$ | S$^0$ |
| Unoxidized | 0.0 | 12.75 (0.8) | 1.31 (0.22) | 1.08 (0.44) | 0.83 (0.3) |
| 72 | 0.41 | 14.53 | 3.09 (0.58) | 2.77 (1.16) | 1.60 |
| 168 | 0.62 | 16.44 | 6.20 (0.57) | 2.52 (1.14) | 2.08 |
| 240 | 0.85 | 18.11 | 8.15 (0.56) | 3.05 (1.12) | 2.08 |
| 336 | 1.02 | 19.28 | 10.52 (0.70) | 3.11 (1.40) | 2.49 |
| 504 | 1.29 | 21.20 | 13.77 (0.69) | 3.06 (1.38) | 2.91 |
| 672 | 1.54 | 23.48 | 16.18 (0.97) | 3.57 (1.94) | 3.32 |

## TABLE II

Results of analysis for oxidized chalcopyrite

| Time (h) | $\Delta_0$ wt (g/mole FeCuS$_2$) | $10^{-3}$ mole per mole FeCuS$_2$ | | | |
|---|---|---|---|---|---|
| | | Fe(III) | SO$_4$$^{2-}$ | S$_2$O$_3$$^{2-}$ | S$^0$ |
| Unoxidized | 0.0 | 2.35 (0.8) | 0.74 (0.46) | 2.30 (0.92) | 0.87 (0.3) |
| 72 | 0.11 | 3.32 | 1.77 (0.54) | 2.71 (1.04) | 0.18 |
| 168 | 0.21 | 3.90 | 2.80 (0.39) | 2.64 (0.78) | 0.38 |
| 240 | 0.30 | 4.17 | 3.32 (0.55) | 2.66 (1.10) | 0.28 |
| 336 | 0.41 | 4.50 | 3.69 (0.57) | 2.84 (1.14) | 0.28 |
| 504 | 0.58 | 4.87 | 4.54 (0.54) | 3.05 (1.08) | 0.28 |
| 672 | 0.66 | 5.21 | 5.00 (0.63) | 3.28 (1.26) | 0.36 |

## TABLE III

Results of analysis for oxidized pyrrhotite

| Time (h) | $\Delta_0$ wt (g/mole FeS$_{1.14}$) | $10^{-3}$ mole per mole FeS$_{1.14}$ | | | |
|---|---|---|---|---|---|
| | | Fe(III) | SO$_4$$^{2-}$ | S$_2$O$_3$$^{2-}$ | S$^0$ |
| Unoxidized | 0.0 | 0.0 (0.8) | 0.36 (0.21) | 0.72 (0.42) | 1.7 (0.5) |
| 5 | 0.67 | 19.2 | 0.68 (0.48) | 2.88 (0.96) | 11.9 |
| 12 | 1.46 | 42.0 | 2.03 (0.49) | 2.31 (0.98) | 29.6 |
| 24 | 2.56 | 70.8 | 2.22 (0.51) | 2.64 (1.02) | 54.6 |
| 48 | 2.90 | 84.7 | 3.31 (0.47) | 2.59 (0.94) | 62.2 |
| 96 | 3.71 | 104.8 | 5.14 (0.50) | 1.64 (1.00) | 86.8 |
| 185 | 4.43 | 122.3 | 4.17 (0.86) | 2.90 (1.72) | 97.9 |
| 336 | 4.91 | 139.2 | 4.53 (0.79) | 2.66 (1.58) | 116.4 |
| 504 | 5.37 | 153.7 | 5.37 (0.76) | 2.93 (1.52) | 124.6 |
| 672 | 6.11 | 167.5 | 6.19 (1.00) | 3.05 (2.00) | 135.9 |

Fe(III), $SO_4^{2-}$, $S_2O_3^{2-}$ and $S^0$ between the initial and oxidized minerals; these differences will be denoted hereafter by $\Delta Fe$, $\Delta SO_4^{2-}$, $\Delta S_2O_3^{2-}$ and $\Delta S^0$. One quantity which must be calculated is the expected total oxidized sulfur, $\Delta S_T$, which is given by $\Delta Fe$ times the S/Fe ratio in the mineral.

*Nature of the oxidation*

The sulfur component of the minerals is oxidized to three products, $SO_4^{2-}$, $S_2O_3^{2-}$ and $S^0$ or possibly $SO_2$, the relative proportions of which vary with the mineral. The product designated by $S_2O_3^{2-}$ can, in effect, be thiosulfate, sulfite or polythionate because the analytical method used cannot distinguish between them. Because polythionate is, in general, a redox product of thiosulfate (Cotton and Wilkinson, 1962), it seems reasonable to assume that $S_2O_3^{2-}$ represents the formation of thiosulfate or sulfite during mineral oxidation.

Both thiosulfate and sulfite reduce Fe(III) and Cu(II) to Fe(II) and Cu(I), respectively (Kolthoff and Belcher, 1957), and the product designated by $S_2O_3^{2-}$, must be associated with these lower-valence metal ions which make no contribution to the experimentally determined Fe(III) content. That the increase in $S_2O_3^{2-}$ between the initial and oxidized minerals is not accompanied by a corresponding increase in the Fe(II) content, points out that other Fe(II) products such as FeO, Fe(OH)$_2$ or FeSO$_4$ are present in the initial mineral and that part of these are oxidized to Fe(III) as the $S_2O_3^{2-}$ content increases during the initial oxidation period of 3 days for pyrite and chalcopyrite and 5 h for pyrrhotite. It is apparent that Fe(III) values other than those for the initial minerals include a contribution from the oxidation of these Fe(II) products. The value of $\Delta_o Fe$, the difference between the Fe(III) content of any oxidized and the intial samples is not a true indication of the oxidation at 52°C and 68% RH. Instead $\Delta Fe$, the difference between the Fe(III) content of any oxidized and the oxidized sample of the initial oxidation period, would be a more appropriate indicator because the Fe(III), due to the Fe(II) products, would cancel out. It should be noted that the oxidation of these Fe(II) products and the oxidation being studied at 52°C and 68% RH are independent reactions occurring at different sites. That FeO, Fe(OH)$_2$ or FeSO$_4$ are found in the initial sample but not in the oxidized samples can likely be attributed to the milder oxidation conditions experienced by the initial samples during their air drying at ambient temperature.
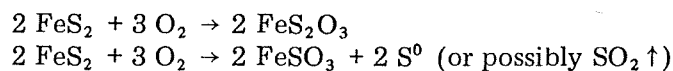
It is interesting to observe that the average values of $S_2O_3^{2-}$ for the oxidized samples, i.e., 3.0, 2.9 and 2.7 $\cdot$ 10$^{-3}$ mole per mole mineral, are consistent with the Fe(II) content of 3.4, 1.4 and 3.1 $\cdot$ 10$^{-3}$ mole per mole mineral for these samples, remembering that the Fe(II) content for chalcopyrite must be doubled to 2.8 $\cdot$ 10$^{-3}$ mole per mole mineral to calculate the potential Fe(II) + Cu(I) content. That this holds true for all three minerals suggests that there is a limitation in the amount of lower-valence metal that

can be present in the oxidation products at the temperature and RH used in this study. This limitation must apply to the lower-valence metal rather than to $S_2O_3^{2-}$ because the amount of metal exceeds that of $S_2O_3^{2-}$ in the initial samples.

### Oxidation reactions

Here, an attempt is made to speculate on the identity of the oxidation products and, subsequently, on the oxidation reactions of pyrite, chalcopyrite and pyrrhotite. This speculation is based on such parameters as the slope of the linear relationships between the various determined quantities such as Fe(III), $SO_4^{2-}$, etc. As will be observed below, the slope has relatively wide 95%-confidence limits because only a small fraction of the sulfide mineral specimens are oxidized and the analytical methods used to determine these changes are subject to the error commonly associated with chemical phase analysis (Steger, 1976a). It is to be understood that the present interpretation of the experimental results relies to a significant extent on the chemical intuition of the author.

*Pyrite.* The product represented by $S_2O_3^{2-}$ could be $FeS_2O_3$ or $2\,FeSO_3$ (to maintain the mass balance for sulfur in $S_2O_3^{2-}$) and could be formed according to:

$$2\,FeS_2 + 3\,O_2 \rightarrow 2\,FeS_2O_3$$
$$2\,FeS_2 + 3\,O_2 \rightarrow 2\,FeSO_3 + 2\,S^0 \text{ (or possibly } SO_2 \uparrow)$$

Theoretically, these two products could be distinguished on the basis of the small amounts of $S^0$ formed, but this is impossible as will be seen below.

The parameters of the linear relationships, $\Delta SO_4^{2-} = m\Delta Fe + b$, are $m = 1.50$, $\Delta m = \pm 0.16$ and $r = 0.997$ where $\Delta m$ is the 95%-confidence interval of the slope and $r$ is the correlation coefficient. The value of 1.5 for $m$ suggests strongly that the Fe(III) product of oxidation is $Fe_2(SO_4)_3$. The value of the intercept, $b$, is not reported because no use is made of it. In all relationships $b \neq 0$ but the value of $\Delta b$, the 95%-confidence interval of the intercept, was such that no statistical significance could be attributed to the value of $b$ other than a result of the scatter in the data.

A comparison of the total expected oxidized sulfur, $\Delta S_T$, which is given by $2\Delta Fe$ for pyrite[*], with the experimentally found oxidized sulfur, $\Delta SO_4^{2-} + \Delta S^0$, indicates the loss of some oxidized sulfur during the course of the experiment. This also applies to chalcopyrite and pyrrhotite. The nature of this lost sulfur was not determinable with the available equipment but the

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[*]It is stressed here that $\Delta Q$ is the difference between the quantity $Q$ of any oxidized sample and the oxidized sample of the initial oxidation period. $\Delta_0 Q$ is the difference between $Q$ of any oxidized sample and the initial sample.

following evidence suggests that it is $S^0$ which is volatized or oxidized to $SO_2$. The $S^0$ data for chalcopyrite in Table II illustrates a loss of $S^0$. Also, samples of 5, 10 and 100 mg $S^0$ which were kept at 52°C and 68% RH for 4 weeks showed a loss of 3, 3.4 and 9.4 mg $S^0$, respectively. It is this loss of S which makes the distinction between $FeS_2O_3$ and $2FeSO_3$ impossible.

This loss of S also results in somewhat low values of $\Delta_0$ wt for the oxidized samples. The corrected values of $\Delta_0$ wt are given by the observed value of $\Delta_0$ wt plus the weight of sulfur corresponding to $\Delta S_T - \Delta SO_4{}^{2-} - \Delta S^0$ and are given in Table IV. Because as will be seen below, it is necessary to correlate the weight gain with the oxidized metal to establish the degree of hydration, it is also necessary to arbitrarily set $\Delta_0$ wt of the oxidized sample after the initial oxidation period equal to zero in order to determine the values of $\Delta$ wt which can be appropriately correlated with $\Delta$ Fe. These values of $\Delta$ wt are also shown in Table IV.

The expected change in weight, $\Delta wt_E$, for the oxidized pyrite samples is given by the weight of oxygen corresponding to $4\Delta SO_4{}^{2-}$. It must be noted that the oxygen uptake due to $\Delta S_2O_3{}^{2-}$ need not be considered because it is constant within experimental error for all oxidized samples. The difference between $\Delta$ wt and $\Delta wt_E$ is due to water of hydration. The relationship between $\Delta$ Fe and $(\Delta wt - \Delta wt_E)$ has $m = 44$ and $\Delta m = \pm 13$ which suggests that each $Fe_2(SO_4)_3$ is associated with $5 \pm 1.4\ H_2O$ of hydration.

*Chalcopyrite.* Attempts to determine the oxidized Cu in this mineral with 10 $M\ H_3PO_4$ (Steger, 1977a) or 15% ammonium acetate, 3% acetic acid (Steger, 1977b) failed; the values determined were very dependent on the extraction
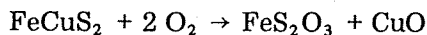
TABLE IV

Corrected values of $\Delta_0$ wt and $\Delta$ wt

| Time (h) | Pyrite | | Chalcopyrite | | Pyrrhotite | |
|---|---|---|---|---|---|---|
| | $\Delta_0$ wt | $\Delta$ wt | $\Delta_0$ wt | $\Delta$ wt | $\Delta_0$ wt | $\Delta$ wt |
| Un-oxidized | 0.0 | — | 0.0 | — | 0.0 | — |
| 5 | | | | | 0.73 | 0.0 |
| 12 | | | | | 1.74 | 1.01 |
| 24 | | | | | 3.09 | 2.36 |
| 48 | | | | | 3.66 | 2.93 |
| 72 | 0.44 | 0.0 | 0.16 | 0.0 | | |
| 96 | | | | | 4.36 | 3.63 |
| 168 | 0.66 | 0.22 | 0.26 | 0.10 | | |
| 185 | | | | | 5.40 | 4.67 |
| 240 | 0.93 | 0.49 | 0.35 | 0.19 | | |
| 336 | 1.09 | 0.65 | 0.48 | 0.32 | 5.90 | 5.17 |
| 504 | 1.36 | 0.92 | 0.67 | 0.51 | 6.59 | 5.86 |
| 672 | 1.67 | 1.23 | 0.72 | 0.56 | 7.45 | 6.72 |

time. No explanation can be given and it is necessary, therefore, to assume that the quantity of oxidized Cu is essentially the same as the quantity of oxidized Fe so that the total oxidized metal is $2 \Delta Fe$.

As was stated for pyrite, the oxidation product represented by $S_2O_3^{2-}$ can be either thiosulfate or sulfite and it may be associated with both $Fe(II)$ and $Cu(I)$ in the case of chalcopyrite as in:

$$FeCuS_2 + 2 O_2 \rightarrow FeS_2O_3 + CuO$$

or

$$4 FeCuS_2 + 7.5 O_2 \rightarrow 2 FeS_2O_3 + 2 Cu_2S_2O_3 + Fe_2O_3$$

The parameters of the relationship, $\Delta SO_4^{2-} = m (2 \Delta Fe) + b$ are $m = 0.85$, $\Delta m = \pm 0.11$ and $r = 0.995$. The value of $m$ because $2 \Delta Fe$ is also $\Delta S_T$, suggests that 15% or ~1/8 of the oxidized sulfur does not form sulfate; this is consistent with the reaction:

$$4 FeCuS_2 + 15.5 O_2 \rightarrow Fe_2(SO_4)_3 + Fe_2O_3 + 4 CuSO_4 + S^0$$

There is a loss of oxidized sulfur during the course of the oxidation of chalcopyrite to yield slightly low values of $\Delta_0 wt$. As was explained for pyrite, it is difficult to determine accurately the appropriate correction to $\Delta_0 wt$ and, therefore, the $\Delta wt$ values for chalcopyrite are corrected as was done for pyrite and they are reported in Table IV. The value of $\Delta wt_E$ is also calculated as explained for pyrite but the formation of $Fe_2O_3$ must be taken into account for chalcopyrite. The relationship between $2 \Delta Fe$ and $\Delta wt - \Delta wt_E$ has $m = 94$ and $\Delta m = \pm 40$, i.e., $5 \pm 2 H_2O$ of hydration per oxidized metal.

*Pyrrhotite*. The oxidation of pyrrhotite proceded to such an extent that after 12h at 52°C and 68% RH goethite, $FeO(OH)$, and $S^0$ were identified as the major products by X-ray diffraction. The minor amounts of $Fe(III)$-$SO_4^{2-}$ and $Fe(II)$-$S_2O_3^{2-}$ products that may have formed were not detected. If it is assumed that $Fe(III)$-$SO_4^{2-}$ is in fact $Fe_2(SO_4)_3$, the relationship between $2/3 SO_4^{2-}$ and $Fe(III)$ points out that the $Fe(III)$ in $Fe_2(SO_4)_3$ comprises only $2.2 \pm 0.1\%$ of the total $Fe(III)$. The predominant oxidation reaction is:

$$2 Fe_7S_8 + 10.5 O_2 + 7 H_2O \approx 14 FeO(OH) + 16 S^0$$
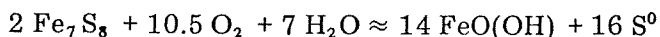
The goethite may be further hydrated (Palacho et al., 1963). Indeed, by following the procedures described for pyrite for calculating the loss of S and correcting the values of $\Delta wt$ (reported in Table IV) and also for calculating the expected gain in weight, $\Delta wt_E$, for the oxidized pyrrhotite samples, the linear relationship between $\Delta Fe$ and $(\Delta wt - \Delta wt_E)$ has $m = 7.9$ and $\Delta m = \pm 1.7$ which corresponds to approximately ½ O per oxidized iron or to the compound $2 FeO(OH) \cdot H_2O$.

*Water of hydration.* The values reported for the water of hydration of the oxidation products of pyrite, chalcopyrite and pyrrhotite, have no significance other than to indicate that there is water of hydration. It should be noted that the term $(\Delta wt - \Delta wt_E)$ is a difference between two values which are themselves differences between experimental quantities, so that errors could play an important role in determining the magnitude of $(\Delta wt - \Delta wt_E)$. Moreover, as oxidation proceeds and the product layer thickens, the possibility of different degrees of hydration throughout this layer must be considered so that the products could, in fact, be associated with a range of hydration. A change in hydration due to overnight drying over Drierite® in the desiccator was also contemplated. However, a sample of $Fe_2(SO_4)_3 \cdot x H_2O$ where $x = 6.8$ (BDH Analytical Reagent) showed no significant loss of $H_2O$ even after 2 weeks in the desiccator.

## Speculation on mechanism

The manner in which the oxidation of pyrite, chalcopyrite and pyrrhotite was carried out is, in general, not recommended for kinetic studies because the removal of samples from the oxidation chamber and subsequent drying in the desiccator likely gives an oxidation rate that differs from that which would be found if the oxidation were allowed to continue uninterrupted. A detailed kinetic analysis of the data was not undertaken for this reason. This somewhat unusual procedure was followed because it is more consistent with what is, in effect, encountered in the use of certified reference materials which are subjected to more favorable oxidation conditions when the bottle in which they were kept is opened. After tight re-sealing, it seems reasonable to expect decreasing oxidation as the oxygen and water vapor in the bottle are consumed.

A linear relationship between $\Delta Z$ and $t/\Delta Z$ where $Z$ is the thickness of a product layer at time $t$, is often used as a test for behavior according to the parabolic rate law (Galwey, 1967). $\Delta Z$ is often reported as the quantity of product (in grams or moles) per unit of surface area. For a series of oxidized samples of a mineral specimen, however, the value of $\Delta Fe$, $\Delta SO_4^{2-}$, etc., can be used as a measure of $\Delta Z$ because the original surface areas are nearly constant. If the reaction rates of several minerals are compared, the effect of different surface areas must be considered.

Fig. 1 illustrates the plots of $\Delta Z$ vs. $t/\Delta Z$ for $\Delta Z = \Delta_0 SO_4^{2-}$, $\Delta SO_4^{2-}$ and $(2/3 \, \Delta_0 SO_4^{2-} + \Delta_0 S_2O_3^{2-})$ for pyrite, chalcopyrite and pyrrhotite. The values of $\Delta_0 SO_4^{2-}$ and $\Delta SO_4^{2-}$ for the sample of pyrrhotite oxidized for 96 h were not plotted because the value of $SO_4^{2-}$ is clearly outlying with respect to those for the other pyrrhotite samples. The break observed in these plots for pyrrhotite may not be real. Fig. 2 illustrates the plot of $\Delta Z$ vs. $t/\Delta Z$ for $\Delta Z = (\Delta Fe - 2/3 \, \Delta SO_4^{2-})$ which is the Fe(III) in FeO(OH). It is apparent that this system does not behave according to the parabolic law at low oxidation periods. The correspondence between the breaks in the curves for pyr-
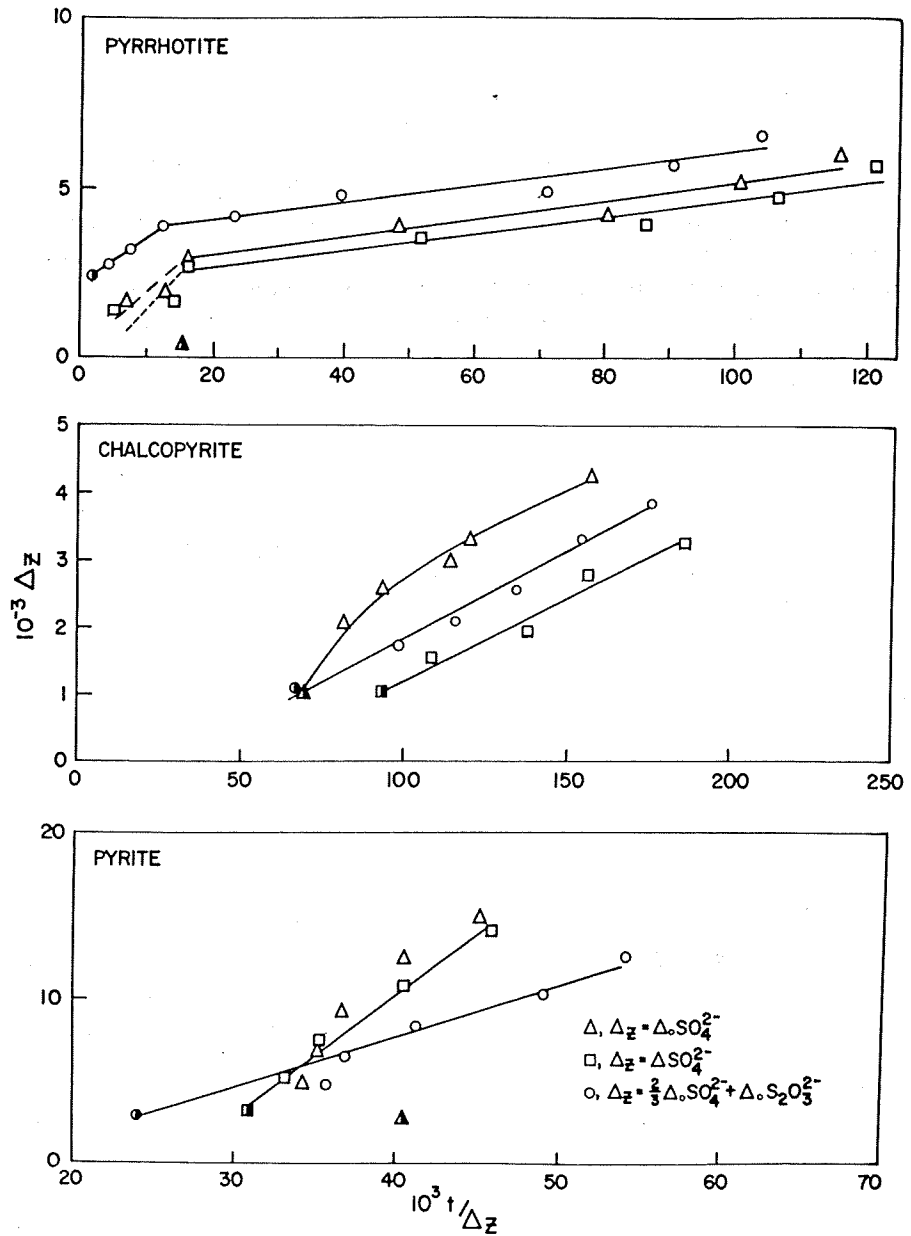
Fig. 1. Plots of $\Delta Z$ vs. $t/\Delta Z$ for pyrite, chalcopyrite and pyrrhotite.

In the figure legend (Pyrite plot):

$\triangle, \Delta_{\bar{z}} = \Delta_\circ SO_4^{2-}$

$\square, \Delta_{\bar{z}} = \Delta SO_4^{2-}$

$\circ, \Delta_{\bar{z}} = \frac{2}{3}\Delta_\circ SO_4^{2-} + \Delta_\circ S_2O_3^{2-}$

Axis labels: PYRRHOTITE, CHALCOPYRITE ($10^{-3}\Delta_{\bar{z}}$), PYRITE, $10^3 t/\Delta_{\bar{z}}$
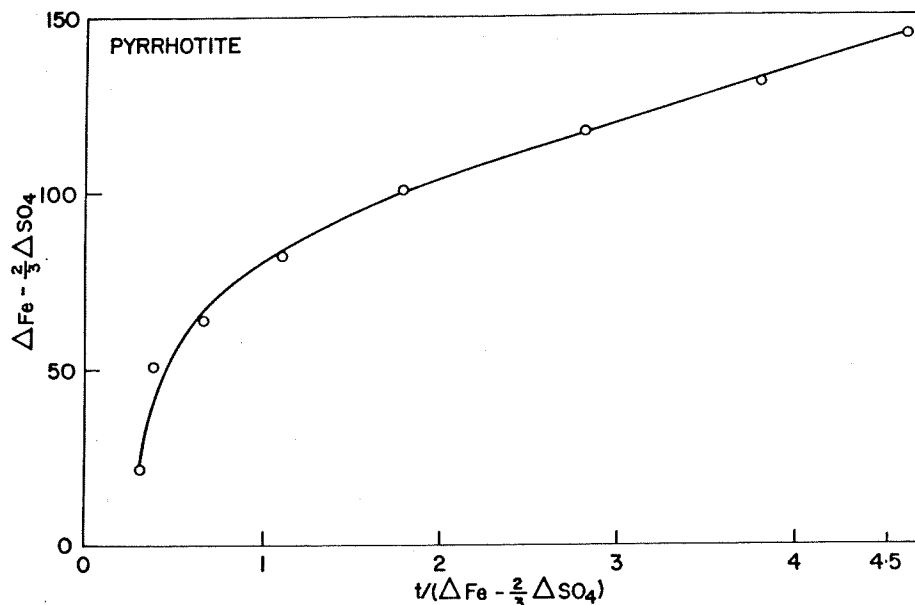
$\Delta Fe - \frac{2}{3}\Delta SO_4$

Fig. 2. Plot of $\Delta Z$ vs. $t/\Delta Z$ for $\Delta Z = (\Delta\text{Fe} - 2/3\,\Delta\text{SO}_4{}^{2-})$ which is the Fe(III) in FeO(OH).

rhotite in Fig. 1 and the region of low curvature in Fig. 2 is evident. The absence of such curvature in Fig. 1 may be a result of the uncertainty in the values of $\text{SO}_4{}^{2-}$ and $\text{S}_2\text{O}_3{}^{2-}$ which cannot be determined with the same reliability as the Fe(III) values. Moreover, $\Delta\text{Fe}$ is approximately 20 times $\Delta\text{SO}_4{}^{2-}$ so that the former may be a better indication of the chemical changes in pyrrhotite due to oxidation.

It is apparent from Fig. 1 that the use of $\Delta_0\text{SO}_4{}^{2-}$, the difference in $\text{SO}_4{}^{2-}$ between the oxidized and the initial samples, does not give a linear plot of $\Delta Z$ vs. $t/\Delta Z$ but that the use of $\Delta\text{SO}_4{}^{2-}$, the difference in $\text{SO}_4{}^{2-}$ between the oxidized samples and the oxidized sample of the initial oxidation period, does so. Clearly, the $\text{SO}_4{}^{2-}$ content must be affected during the initial oxidation period by some phenomenon which breaks down the linear relationship between $\Delta_0\text{SO}_4{}^{2-}$ and $t/\Delta_0\text{SO}_4{}^{2-}$. One possible explanation is that sulfate is not a direct oxidation product of these minerals but is instead an oxidation product of $\text{S}_2\text{O}_3{}^{2-}$. In this manner, the rate of formation of $\text{SO}_4{}^{2-}$ during the initial period depends on both the formation of $\text{S}_2\text{O}_3{}^{2-}$ as well as on its oxidation to $\text{SO}_4{}^{2-}$, only the former of which should be expected to give a linear $\Delta Z$ vs. $t/\Delta Z$ plot. After the $\text{S}_2\text{O}_3{}^{2-}$ value has become essentially constant, i.e., the rate of oxidation to $\text{SO}_4{}^{2-}$ equals the rate of formation, $\Delta\text{SO}_4{}^{2-}$ should also give a linear plot of $\Delta Z$ vs. $t/\Delta Z$, as is observed.

The oxidation of the possible moieties designated by $S_2O_3^{2-}$ to $Fe_2(SO_4)_3$ is:

$$2 FeS_2O_3 + 3 O_2 \rightarrow Fe_2(SO_4)_3 + S^0$$

and

$$6 FeSO_3 + 4.5 O_2 \rightarrow 2 Fe_2(SO_4)_3 + Fe_2O_3$$
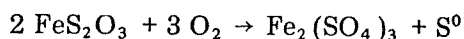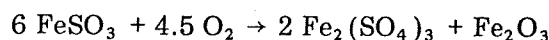
The latter reaction clearly does not yield the $Fe(III)/SO_4^{2-}$ ratio of 2/3 that is observed and it can be concluded, therefore, that the product designated by $S_2O_3^{2-}$ is, indeed, thiosulfate — either $Fe(II)$ or $Cu(I)$. The rate of formation of thiosulfate, given by $(2/3\ \Delta_0 SO_4^{2-} + \Delta_0 S_2O_3^{2-})$ does indeed give a linear $\Delta Z$ vs. $t/\Delta Z$ plot (Fig. 1).

Unfortunately, the data for pyrrhotite cannot be treated in the same manner as that for pyrite and chalcopyrite. One possible explanation is that because the oxidation of pyrrhotite proceeds to a much greater extent, it is also affected much more greatly by the repeated removal of the sample from the oxidation chamber and subsequent drying desiccator so that the $\Delta Z$ vs. $t/\Delta Z$ relationship is completely broken down.

## CONCLUSIONS

The oxidation of pyrite and chalcopyrite proceeds to give the metal sulfate(s) as the predominant product. Some metal thiosulfate is also formed but there is some evidence that this is the immediate oxidation product of the mineral and undergoes oxidation to sulfate. The predominant oxidation products of pyrrhotite are $FeO(OH)$ and $S^0$. An appreciably smaller amount of ferric sulfate is also formed. The presence of thiosulfate would suggest that the formation of sulfate also proceeds through the intermediate thiosulfate as has been suggested for pyrite and chalcopyrite.

## ACKNOWLEDGEMENTS

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