# OXIDATION OF SULFIDE MINERALS. V. GALENA, SPHALERITE AND CHALCOCITE

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## ABSTRACT

Samples of galena, sphalerite and chalcocite were oxidized at 52°C and 68% of relative humidity in air for periods up to five weeks, and the products were analyzed for metal and sulfur-bearing species. Galena is. oxidized to $PbSO_4$, sphalerite to $ZnSO_4 + Fe_2O_3$ if iron-bearing, and chalcocite to CuO and CuS. The oxidation of galena and sphalerite proceeds according to a linear rate law; that of chalcocite leads to the formation of a coherent product layer impenetrable to $O_2$ and $H_2O$ vapor.

*Keywords*: air oxidation, oxidation products, sulfide minerals, galena, sphalerite, chalcocite.

## SOMMAIRE

Nous avons étudié l'oxydation dans l'air d'échantillons de galène, de sphalérite et de chalcocite à 52°C et 68% d'humidité relative, pour des périodes s'étalant sur cinq semaines. On a déterminé la concentration des métaux et des complexes du soufre dans les produits. La galène se transforme en $PbSO_4$, la sphalérite en $ZnSO_4$ (et $Fe_2O_3$ si l'échantillon est ferrifère), et la chalcocite en CuO et CuS. L'oxydation de la galène et de la sphalérite est une réaction du premier ordre. La chalcocite en s'oxydant forme une gaine cohérente imperméable à l'oxygène et à la vapeur d'eau.

(Traduit par la Rédaction)

*Mots-clés*: oxydation dans l'air, produits d'oxydation, sulfures, galène, sphalérite, chalcocite.

## INTRODUCTION

The Canadian Certified Reference Materials Project (CCRMP) offers ores and concentrates for sale to the analytical community for use as certified reference materials. Since many of these materials have a high sulfide content, they are potentially susceptible to air oxidation in storage, with the accompanying risk of rendering the certified element-values invalid. A study was therefore initiated to assess the

long-term stability of sulfide-bearing ores and concentrates. Part of this study was concerned with the nature of the products and kinetics of the oxidation of the commonly encountered sulfide minerals. The oxidation of pyrite, chalcopyrite and pyrrhotite at 52°C and 68% of relative humidity (RH) has already been investigated (Steger & Desjardins 1978). This report summarizes the results of the study of the oxidation of galena, sphalerite and chalcocite under the same conditions.

The air oxidation of galena at relatively low temperatures has been investigated without reaching a consensus on the nature of the oxidation product. Hagihara (1952), using a reflection electron-diffraction technique, and Kirkwood & Nutting (1965), using a transmission electron-diffraction technique, found this product to be $PbSO_4$, whereas Leja et al. (1963), using reflection infrared spectroscopy, concluded that it was $PbS_2O_3$. Using transmission infrared spectroscopy, however, Greenler (1962) identified $PbSO_4$, $PbSO_3$ and $PbCO_3$ in the oxidation products of galena. All these workers identified the oxidation product by comparing its electron-diffraction pattern or infrared spectrum with that of $PbSO_4$, $PbS_2O_3$, etc. A recently developed method (Steger & Desjardins 1977), whereby sulfate and thiosulfate in the oxidation products of sulfide minerals are separated chemically and their quantity is determined, gives a more direct identification.

The authors could not find any reference to a study of the air oxidation at low temperature of sphalerite. In several references (e.g., Khristoforov et al. 1969) that pertain to the oxidation of sphalerite ores during storage, the oxidation of sphalerite to $ZnSO_4$ is assumed to take place. A study to establish the nature of the oxidation at relatively low temperatures of such an economically important mineral as sphalerite was long overdue.

Chalcocite, $Cu_2S$, is a secondary copper sulfide mineral of minor commercial importance. A study of its oxidation was undertaken to compare a "metal-rich" mineral with "metal-

poor" minerals, *e.g.*, pyrrhotite, pyrite and minerals having approximately equal metal and sulfur, like chalcopyrite, galena and sphalerite. The oxidation of chalcocite at low temperatures has not been studied. Precipitated $Cu_2S$ was shown to oxidize at 240°C to CuO, CuS and $CuSO_4$ (Lefevre *et al.* 1957).

The literature is full of references to electrochemical, hydrometallurgical and geological investigations of the oxidation, electrochemical dissolution and oxidative dissolution of sulfide minerals. As important as these references may be for an understanding of certain phenomena, they are not relevant to this study, merely because a liquid aqueous phase, whether rain, water or acidic leach solution, is involved. In air oxidation, water in the vapor phase is involved. The presence of a liquid phase alters both the reaction mechanism and kinetics either by the dissolution of soluble reaction products or by allowing electrochemical oxidation mechanisms to occur (Bailey 1977).

## EXPERIMENTAL

*Minerals*

The 37-74 μm size fractions, prepared from crushed massive specimens of galena (Galena, Kansas), sphalerite (Ottawa Co., Oklahoma) and chalcocite (Superior, Arizona), were cleaned according to the procedure of Steger & Desjardins (1978). Another sample of sphalerite (Montauban, Québec) required further treatment with a Frantz separator to remove pyrrhotite. Microscopic examination indicated traces of chalcocite, digenite and gangue in the galena and approximately 2% gangue plus traces of pyrite and chalcopyrite in both samples of sphalerite. The chalcocite contained traces of chalcopyrite and pyrite and 2.5% bornite (mean of two determinations by quantitative image-analysis). The elemental analysis and suggested empirical formulae of the minerals are given in Table 1. The Cu:S ratio of

TABLE 1. RESULTS OF CHEMICAL ANALYSIS OF SULFIDE MINERALS

| Mineral | % Metal | % S | Empirical Formula |
|---|---|---|---|
| Galena | Pb, 85.71 | 13.39 | PbS |
| Sphalerite (high iron) | Zn, 56.67 Fe, 8.26 | 32.68 | $Zn_{0.834}Fe_{0.146}S$ |
| Sphalerite (low iron) | Zn, 65.31 Fe, 0.09 | 32.16 | $Zn_{0.999}Fe_{0.001}S$ |
| Chalcocite | Cu, 78.32 | 20.63 | $Cu_2S$ $Cu_5FeS_4$ |

1.92:1 is inconsistent with chalcocite, but electron-microprobe analysis and X-ray-diffraction studies confirmed that the mineral is chalcocite $Cu_2S$. The low Cu:S ratio is due to the bornite.

*Oxidation of mineral samples*

The procedure of Steger & Desjardins (1978) was followed. For each mineral, ∼ 16 g were weighed into a tared 90 x 50 cm crystallization dish, which was then placed in a controlled temperature–humidity chamber (Blue M. Electric Co., Blue Island, Illinois). The conditions of 52 ± 1°C and 68 ± 3% RH were monitored with a dry bulb – wet bulb thermometer combination. The samples were removed from this chamber after selected time intervals, put in a desiccator over Drierite® for 18–20 hours to remove adsorbed water, weighed to determine △ wt. (the change in weight due to oxidation), and then thoroughly mixed manually. After the removal of subsamples of ∼ 2 g, the mineral samples were reweighed and returned to the chamber. The value of △ wt. is reported only for chalcocite. Although the values of △ wt. for galena and sphalerite showed a tendency to increase with oxidation period, they were erratic, especially for the longer periods. This is attributable to the fact that the potential accumulative error, due to the multitude of weighings, is significant with respect to the low △ wt. resulting from the small extent of oxidation undergone by galena and sphalerite. These errors are estimated to be 0.04 g/mole and 0.02 g/mole for galena and sphalerite, respectively, for the 5-week oxidation period.

The oxidation conditions of 52°C and 68% RH are, of course, relatively extreme compared with ambient conditions, but are nevertheless necessary to promote oxidation to an extent sufficient for a study lasting months rather than years.

*Determination of parameters of oxidation*

The oxidation products were analyzed for lead for galena, zinc for both sphalerites, and copper for chalcocite by selective extraction with a 15% ammonium acetate, 3% acetic acid solution (Steger 1977). All subsamples were analyzed for elemental sulfur by the volatilization–spectrophotometric method of Steger (1976b). The entire suite of initial and oxidized samples of chalcocite was analyzed for sulfate and thiosulfate by the method of Steger & Desjardins (1977), in which the sulfur-bearing anions are separated from the sulfide minerals by ion exchange with sulfide ion. The sulfate is determined directly by precipitation with ex-

cess $Ba^{2+}$. Another portion of the sulfur–anion sample is oxidized and precipitated with $Ba^{2+}$ to give the sulfate above and the sulfate resulting from the oxidation of non-sulfate sulfur-bearing oxidation products, such as thiosulfate.

Because of the small extent of oxidation in galena and the two sphalerites, the quantities of sulfate and thiosulfate are approximately the same as those suggested by the reproducibility of this method; only the unoxidized and 5-week-oxidized samples were analyzed for sulfate and thiosulfate. Because no thiosulfate was found (see below), the sulfate in the oxidation product(s) in all samples was determined as follows. A 150-ml aliquot of the ammonium acetate – acetic acid extract, prepared to determine the metal in the oxidation product(s), was boiled to dryness and twice redissolved in 5 ml each of concentrated hydrochloric and nitric acid and then boiled to dryness to remove acetate. The residue was dissolved in approximately 20 ml water, the pH adjusted to $\sim$ 4 with hydrochloric acid and the resulting solution passed through a Dowex 50W–X8 column to remove the metal ions. Water was used as the eluant. After reduction of the sample volume to $\sim$ 25 ml, the sulfate was determined as $BaSO_4$ (Steger & Desjardins 1977). Even if present, thiosulfate is not determined in this method because it is decomposed to elemental sulfur and $SO_2$ by the acidic leachant. The sulfur is filtered off with the mineral and $SO_2$ is volatilized. The sulfate values therefore refer to sulfate in the oxidation products.

### Reflectance spectra of chalcocite

The diffuse reflectance-spectra of samples of chalcocite, covellite and CuO were obtained in the region 6800–3500 Å with a Cary 14 spectrophotometer equipped with an integrating sphere.

### DISCUSSION

The results of the determination of the parameters of the oxidation of galena, the two sphalerites and chalcocite are summarized in Tables 2–6. The numbers in brackets represent the estimated reproducibility of the results and apply to all samples of a given mineral. The agreement between the values of sulfate in the oxidized samples of galena and sphalerite (1) from the ammonium acetate – acetic acid extract (Tables 2–6) and (2) by the sulfate–thiosulfate method of Steger & Desjardins (1977) is to be noted.

TABLE 2. RESULTS OF ANALYSIS OF OXIDIZED GALENA

| Time (hr) | $10^{-3}$ moles/mole PbS | | |
|---|---|---|---|
| | Pb (II) | $SO_4^{2-}$ | S° |
| Unoxid. | 0.36 (0.07) | 1.12 (0.12) | 0.37 (0.15) |
| 72 | 0.44 | 1.37 | 0.30 |
| 168 | 0.58 | 1.57 | 0.37 |
| 240 | 0.64 | -- | 0.30 |
| 336 | 0.77 | 1.62 | 0.15 |
| 504 | 0.92 | 1.82 | 0.30 |
| 672 | 1.17 | 1.97 | 0.30 |
| 840 | 1.40 | 2.28 | 0.15 |

TABLE 3. RESULTS OF ANALYSIS OF OXIDIZED HIGH-IRON SPHALERITE

| Time (hr) | $10^{-3}$ moles/mole | | |
|---|---|---|---|
| | Zn(II) | $SO_4^{2-}$ | S° |
| Unoxid. | 0.44 (0.06) | 0.16 (0.12) | 0.06 (0.15) |
| 72 | 0.46 | 0.18 | 0.09 |
| 168 | 0.56 | 0.27 | 0.09 |
| 240 | 0.60 | -- | 0.06 |
| 336 | 0.62 | 0.35 | 0.09 |
| 504 | 0.73 | 0.41 | 0.06 |
| 672 | 0.85 | 0.53 | 0.06 |
| 840 | 1.01 | 0.73 | 0.06 |

TABLE 4. RESULTS OF ANALYSIS OF OXIDIZED LOW-IRON SPHALERITE

| Time (hr) | $10^{-3}$ moles/mole | | |
|---|---|---|---|
| | Zn(II) | $SO_4^{2-}$ | S° |
| Unoxid. | 0.22 (0.06) | 0.03 (0.12) | 0.04 (0.15) |
| 72 | 0.27 | 0.09 | 0.07 |
| 168 | 0.29 | 0.11 | 0.07 |
| 240 | 0.30 | -- | -- |
| 336 | 0.35 | 0.13 | 0.06 |
| 504 | 0.39 | 0.24 | 0.13 |
| 672 | 0.46 | 0.29 | 0.10 |
| 840 | 0.52 | 0.35 | 0.10 |

TABLE 5. SULFATE AND THIOSULFATE IN GALENA AND SPHALERITE

| Mineral | Time (hr) | $10^{-3}$ moles/mole mineral | |
|---|---|---|---|
| | | $SO_4^{2-}$ | $S_2O_3^{2-}$ |
| Galena | Unoxid. | 0.75 (0.40) | 0.0 (0.80) |
| | 5 wks | 2.50 | 0.0 |
| High-iron Sphalerite | Unoxid. | 0.14 | 0.0 |
| | 5 wks | 0.59 | 0.0 |
| Low-iron Sphalerite | Unoxid. | 0.12 | 0.0 |
| | 5 wks | 0.31 | 0.0 |

TABLE 6. RESULTS OF ANALYSIS OF
OXIDIZED CHALCOCITE

| Time (hr) | $10^{-3}$ moles/mole $Cu_2S$ | | | |
|---|---|---|---|---|
| | Cu(II) | $SO_4^{2-}$ | $S_2O_3^{2-}$ | $S°$ |
| Unoxid. | 2.36 (0.05) | 3.58 (0.40) | 0.0 (0.80) | 0.200 (0.15) |
| 72 | 24.71 | 3.97 | 0.0 | 0.200 |
| 168 | 31.68 | 3.27 | 0.0 | 0.200 |
| 240 | 33.82 | 2.97 | 0.0 | 0.250 |
| 336 | 36.24 | 2.33 | 0.0 | 0.100 |
| 504 | 39.20 | 3.43 | 0.0 | 0.100 |
| 674 | 40.98 | 4.02 | 0.0 | 0.274 |
| 840 | 42.55 | 3.81 | 0.0 | 0.140 |

The zero value for thiosulfate in Table 5 does not necessarily imply that thiosulfate or sulfite is not formed during the oxidation of galena and sphalerite. The method employed cannot determine thiosulfate at less than $\sim 3 \times 10^{-3}$ moles/mole of mineral. The possibility that an amount of thiosulfate equal to these limits could be formed during the 5-week oxidation period will be ruled out below. Similarly, the determination of sulfate and thiosulfate in the oxidation product(s) of chalcocite showed that thiosulfate or sulfite did not exceed the determination limit of $\sim 4 \times 10^{-3}$ moles/mole chalcocite.

## Oxidation reactions

All changes due to oxidation are those differences in Pb(II), Zn(II) or Cu(II), $SO_4^{2-}$, $S_2O_3^{2-}$ and S between the initial and oxidized samples, and are denoted by $\triangle Pb$, $\triangle Zn$, $\triangle Cu$, $\triangle SO_4^{2-}$, etc. The expected total oxidized sulfur, $\triangle S_T$, is given by $\triangle Pb$, $\triangle Zn$ or $\triangle Zn + \triangle Fe$ and $\triangle Cu$ times the ratio of sulfur to metal in the mineral.

## Galena and sphalerite

The results for the oxidized sulfur species for galena and the two sphalerites in Tables 2–5 indicate that only $SO_4^{2-}$ is formed during oxidation.

TABLE 7. LINEAR RELATIONSHIP PARAMETERS

| Mineral | a | ± $\triangle a$ | b | ± $\triangle b$ | r |
|---|---|---|---|---|---|
| | | | $10^{-5}$ moles/mole | | |
| Galena | 0.97 | 0.19 | 11.3 | 12.7 | 0.979 |
| High-iron Sphalerite | 0.96 | 0.11 | −0.35 | 3.0 | 0.996 |
| Low-iron Sphalerite | 1.07 | 0.21 | −0.051 | 3.5 | 0.985 |

The parameters of the linear relationship $\triangle SO_4^{2-} = a \triangle M + b$, where $\triangle M$ represents $\triangle Pb$ and $\triangle Zn$ for galena and sphalerite, respectively, are reported in Table 7; $\triangle a$ and $\triangle b$ are the 95% confidence interval of the slope $a$ and intercept $b$, and $r$ is the correlation coefficient. That $\triangle b$ is greater than $b$ implies that no statistical significance can be attributed to the nonzero value found for $b$ other than as a result of the scatter in the data.

The relatively wide 95% confidence interval of the slope and the intercept is due to the fact that (1) only a small fraction of the sulfide specimens is oxidized and (2) the analytical methods used to determine the parameters of oxidation are subject to the error commonly associated with chemical phase-analysis (Steger 1976a).

The calculated value of the slope for the relationship $\triangle SO_4^{2-} = a \triangle M + b$ suggests that the oxidation reaction for galena is PbS + $2O_2 \rightarrow PbSO_4$. Because $\triangle M$ is also $\triangle S_T$ for galena, all the oxidized sulfur is accounted for as sulfate; the "zero" value for thiosulfate for galena in Table 5 is therefore valid. This present study is in agreement with those of Hagihara (1952) and Kirkwood & Nutting (1965), who found $PbSO_4$ to be the oxidation product of galena.

The values of $a$ 0.96 and 1.07 suggest that the oxidation of sphalerite is described by ZnS + $2O_2 \rightarrow ZnSO_4$; note that $ZnSO_4$ is likely hydrated. This reaction does not take into account the oxidation of the iron in the sphalerite, which is important for the high-iron specimen ($\sim$ 8.3% Fe). The good agreement between the oxidized zinc and sulfate indicates that the sulfur associated with the oxidized iron has been oxidized either to $SO_2$ or to $S°$, elemental sulfur, and lost by subsequent sublimation. The loss of much larger quantities of $S°$ than those formed in the oxidation of the high-iron sphalerite was demonstrated in the oxidation of pyrrhotite (Steger & Desjardins 1978). The oxidation of iron-bearing sphalerite can therefore be described as $Zn(Fe)S + O_2 + H_2O \rightarrow ZnSO_4 + (Fe_2O_3 \cdot nH_2O) + S°$ or $SO_2$. It has been assumed that the iron is oxidized to Fe(III), and no attempt to balance the equation has been made.
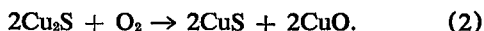
## Chalcocite

The image analysis of the unoxidized chalcocite and that oxidized for 5 weeks indicated 2.2 and 2.8% bornite, respectively. It is evident that there is no difference in the bornite con-

tents to account for the extent of oxidation observed; it can be concluded that the determined parameters pertain to the oxidation of chalcocite.

Table 6 illustrates that the sulfide component of chalcocite either must be lost as $SO_2$ on complete oxidation to copper oxide according to

$$Cu_2S + 2O_2 \rightarrow 2CuO + SO_2 \qquad (1)$$

or remains unoxidized according to

$$2Cu_2S + O_2 \rightarrow 2CuS + 2CuO. \qquad (2)$$

The oxidation of chalcocite to digenite, $Cu_{1.8}S$, and copper oxide according to $Cu_2S + 0.1\ O_2 \rightarrow Cu_{1.8}S + 0.2\ CuO$ can be ruled out. The formation of $40.2 \times 10^{-3}$ moles CuO during the 840-hour period would be accompanied by the formation of $40.2 \times 10^{-3}/0.2 = 0.2$ moles $Cu_{1.8}S$; *i.e.*, 20% of the chalcocite would have been altered to digenite. Neither the X-ray-diffraction nor image-analysis studies detected this digenite.

The gain in weight, $\triangle$wt., due to the oxidation of chalcocite is shown in Table 8. If chalcocite oxidized to CuO and CuS, $\triangle$wt. would correspond to the weight of oxygen uptake. The parameters of the linear relationship, $\triangle$ wt. $= a\triangle$Cu $+ b$, are $a = 18$, $\triangle a = \pm 2$ g/mole Cu(II) and $r = 0.995$. A gain in weight of $18\pm 2$ g/mole Cu(II) agrees with the formation of CuO.

If, however, chalcocite oxidized to CuO only, the true gain in weight, $\triangle$wt.$_c$, would be given by $\triangle$wt. plus a correction for the weight of sulfur lost. This correction of $\triangle$wt.$_s$ corresponds to 0.5 $\triangle$Cu moles/mole $Cu_2S$. Both $\triangle$wt.$_c$ and $\triangle$wt.$_s$ are given in Table 8. The parameters of the relationship, $\triangle$wt.$_c = a\triangle$Cu $+ b$, are

TABLE 8. GAIN IN WEIGHT ON OXIDATION
OF CHALCOCITE

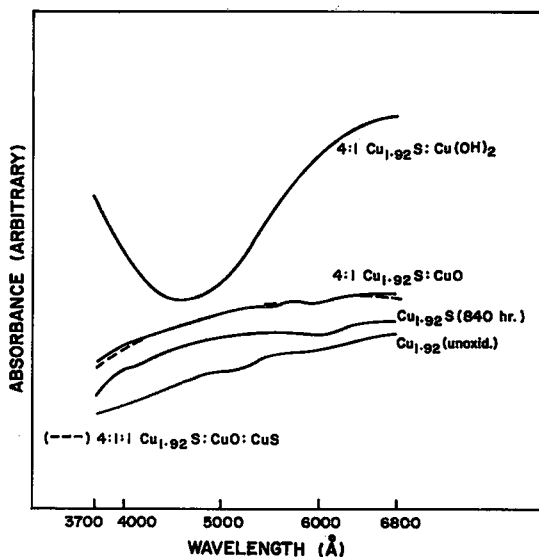| Time (hr) | g/mole $Cu_{1.92}S$ | | |
|---|---|---|---|
| | $\triangle$wt. | $\triangle$wt.$_s$ | $\triangle$wt.$_c$ |
| Unoxid. | 0.0 | 0.0 | 0.0 |
| 72 | 0.388 | 0.359 | 0.747 |
| 168 | 0.555 | 0.470 | 1.025 |
| 240 | 0.600 | 0.505 | 1.105 |
| 336 | 0.614 | 0.544 | 1.158 |
| 504 | 0.680 | 0.591 | 1.271 |
| 672 | 0.684 | 0.613 | 1.297 |
| 840 | 0.684 | 0.645 | 1.329 |



FIG. 1. The diffuse reflectance spectra of chalcocite, CuS and CuO.

$a = 35$, $\triangle a = 1$ $\pm$ g/mole Cu(II) and $r = 0.9997$. A gain in weight of 35 g/mole Cu(II) implies the formation of $Cu(OH)_2$.

The two possible oxidation reactions of chalcocite can be distinguished by the product(s) formed, *i.e.*, CuO, CuS or $Cu(OH)_2$. Figure 1 shows (1) the diffuse reflectance spectra of unoxidized chalcocite, (2) the sample of chalcocite oxidized for 840 hours and (3) 4:1 mixtures of unoxidized chalcocite–CuO and unoxidized chalcocite–$Cu(OH)_2$. The unoxidized chalcocite was added to the CuO and $Cu(OH)_2$ to approximate roughly the chalcocite oxidized for 840 hours.

Oxidized chalcocite distinctly shows increased absorbance in the region $5500 - 3700$ Å, compared with unoxidized chalcocite. A comparison of the spectra in Figure 1 clearly shows that CuO is the oxidation product and that the oxidation of chalcocite proceeds according to reaction 2.

The presence of CuS could not be verified. A 4:1:1 mixture of unoxidized chalcocite–CuO–CuS gives a spectrum (broken line in Fig. 1) that differs only slightly from that of the 4:1 mixture of unoxidized chalcocite–CuO.

*Reaction kinetics*

The change in the oxidized metal, $M_{ox}$, is shown in Figure 2 as a function of the time of oxidation for galena and the two sphalerites. The oxidation proceeds according to a linear
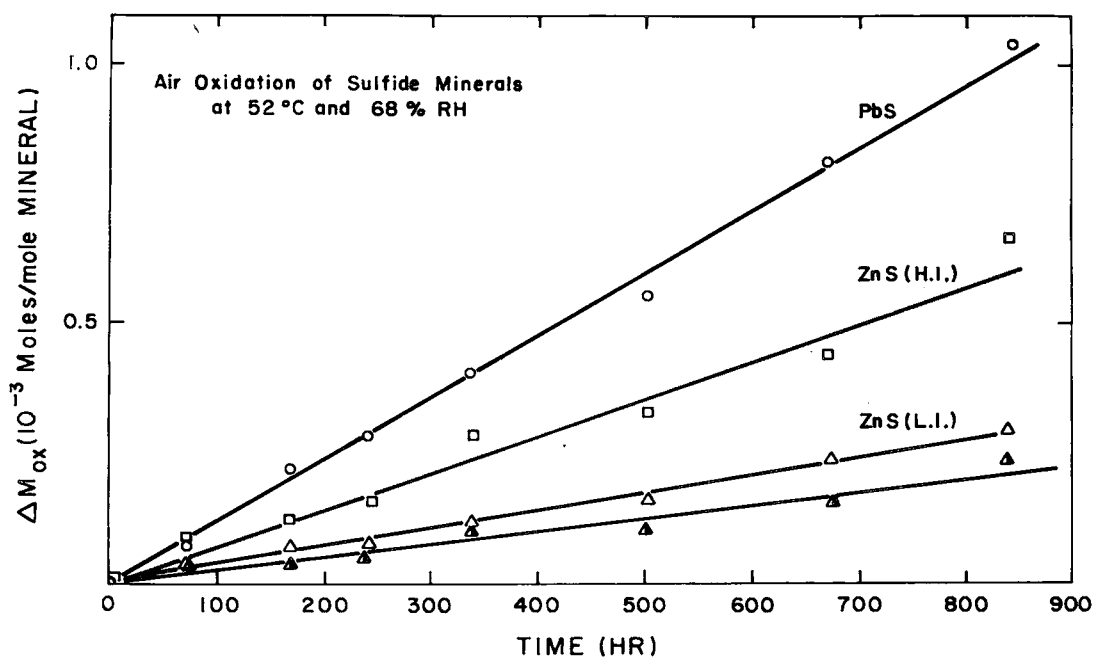
FIG. 2. The change in the oxidized metal content of samples of galena (circles) and sphalerite (squares, triangles) on oxidation at 52°C and 68% RH and dried in a desiccator after each oxidation period, and that of low-iron sphalerite (half-filled triangles) on oxidation at 50°C and 75% RH and maintained in the humidity chamber.

rate law $\triangle M_{ox} = kt$, which indicates a continued access of reactant gas(es) to the unreacted sulfide mineral through disruptions in the oxidation product (Galwey 1967).

The oxidation of chalcocite (Fig. 3) does not obey the accepted rate laws, i.e., linear, parabolic or logarithmic. The possibility of disruption of the rate law by the periodic drying of the sample in a desiccator had to be considered. Shown in Figure 3 are the results for another sample of chalcocite oxidized at 50°C and 75% RH and kept in the humidity chamber at all times. Subsamples were removed at the appropriate times. The chalcocite dried after each oxidation period continued to oxidize even after 5 weeks, whereas the sample retained in the humidity chamber ceased to oxidize at approximately 3 weeks. This arrest in oxidation suggests the formation of a coherent product layer through which $O_2$ and $H_2O$ vapor cannot pass (Galwey 1967). The continued oxidation of the chalcocite dried after each oxidation period indicates a breakdown in the impermeability of the product layer, so that oxidation can recommence with the insertion of the chalcocite into the humidity chamber.

The possibility that the drying in a desiccator

also affected the oxidation kinetics of galena and sphalerite was considered. Unfortunately, owing to a shortage of unoxidized material, this could be tested only for the low-iron sphalerite. It will have to be assumed, as seems reasonable, that the observed behavior is also applicable to galena and high-iron sphalerite. The results of the oxidation at 50°C and 75% RH of the low-iron sphalerite maintained in the humidity chamber for 5 weeks are shown in Figure 2. Clearly, a linear rate law is obeyed.

CONCLUSIONS

The present study suggests that the air oxidation of galena and sphalerite proceeds according to a linear rate law to give lead and zinc sulfate, respectively. Chalcocite oxidizes to form a coherent product layer of CuO and CuS. The rate at which these sulfide minerals oxidize will vary with temperature and relative humidity, but it is reasonable to assume that the oxidation products will remain the same, especially under less severe conditions.

The applicability of the results of this study to the long-term oxidation under ambient conditions of a zinc–lead reference ore, MP–1,
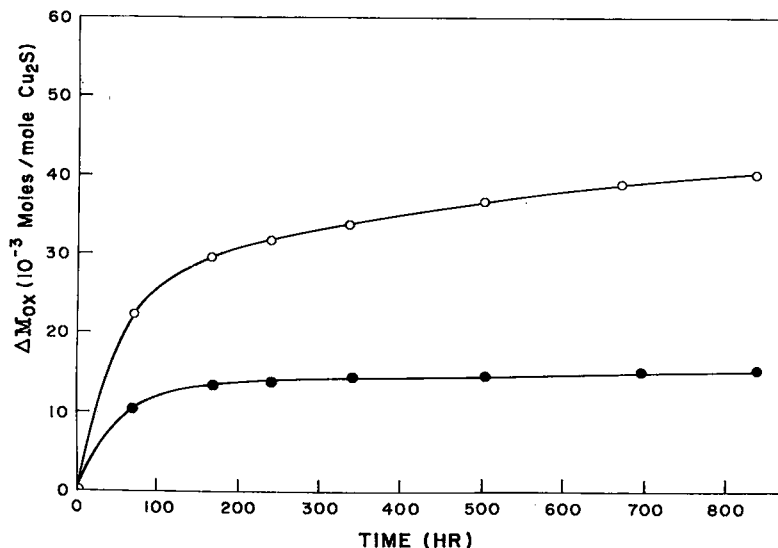
FIG. 3. The change in the oxidized copper content of two samples of chalcocite as a function of time (circles) of drying in the desiccator after each oxidation interval, and (filled circles) maintained in the humidity chamber.

which contains 25% sphalerite, 2.2% galena and 3.8% chalcopyrite, was documented by Faye & Steger (1979). MP–1 had undergone sufficient oxidation while in storage in sealed bottles to lower the concentrations of the certified elements below the lower 95% confidence limits of the 1972 certification program. In addition, eight bottles of MP–1 in use in three different laboratories had a zinc content varying from 15.53 to 16.14%, all lower than the certified value of 16.33%. The values of the oxidized zinc, lead and copper also varied from bottle to bottle in a manner corresponding inversely to that of the total zinc value. On the basis of the oxidized metal value and the findings of the present study that (1) sphalerite and galena oxidize to zinc and lead sulfate, respectively, and that (2) chalcopyrite oxidizes to copper and ferric sulfates plus iron oxide (Steger & Desjardins 1978), the gain in weight due to oxidation of each bottle of MP–1 was calculated. The calculated new total zinc concentrations due to the gain in weight were in good agreement with the analytically determined zinc concentrations for the eight bottles.

Finally, it should also be mentioned that the results of this study and those for the iron sulfide minerals could prove useful in understanding the oxidation reactions and resulting compositional changes of sulfide-bearing museum specimens or material dumps under dry conditions.

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