

THE SUBSTITUTION OF OXYGEN FOR SULFUR IN WURTZITE AND SPHALERITE*

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ABSTRACT

Small amounts of oxygen can substitute for sulfur in wurtzite and sphalerite. The maximum amount of oxygen found in synthetic sphalerite in this study is 0.7 weight per cent ZnO compared to a maximum of 1.0 weight per cent ZnO in wurtzite (Kroeger and Dikhoff, 1952). The addition of 0.7 weight per cent ZnO to sphalerite reduces the unit cell edge from $5.4093 \pm 0.0002 \text{ \AA}$ to $5.4065 \pm 0.0003 \text{ \AA}$. This decrease explains the discrepancy between unit cell measurements on "pure" sphalerite made by various workers.

Oxygen was found in ZnS precipitated by passing H_2S gas through an aqueous solution of ZnSO_4 at room temperature. Oxygen can be added to pure ZnS by heating ZnS with ZnO. The oxygen can be removed by heating the Zn(S, O) with excess sulfur or with an oxygen getter such as metallic magnesium.

X-ray analysis of a few natural sphalerites supports calculations that show that the amount of oxygen present in sphalerite under equilibrium conditions should be below the limits of analytical detection.

INTRODUCTION

Small amounts of oxygen can substitute for sulfur in wurtzite and sphalerite. Sphalerite with a ZnO content of 0.7 per cent by weight and wurtzite with a ZnO content of 1.0 per cent by weight can readily be synthesized. The presence of oxygen in solid solution in wurtzite or sphalerite causes a measurable change in some of the physical properties of both phases. A discussion of the effect of oxygen on the unit cell edges of the two ZnS polymorphs is worthwhile for three reasons.

First, in phase equilibrium studies the presence of oxygen in the ZnS possibly may have significant effects on the activity of ZnS and thus modify the stability relations, although this effect may very well prove to be below the limits of observation.

Second, the composition of sphalerite solid-solutions are frequently determined in the laboratory by unit cell edge measurement, and the undetected presence of oxygen can lead to serious errors in interpreting the results.

Third, oxygen has been found in both wurtzite and sphalerite synthesized by precipitation from aqueous solution at room temperatures. Because ZnO has the wurtzite structure, the presence of oxygen in solid solution in ZnS may possibly play a role in promoting the metastable precipitation of wurtzite or of ZnS polytypes in mineral deposits. One of the factors contributing to the metastable growth of wurtzite at low tem-

perature may be the availability of oxygen or other trace constituents.

Kroeger and Dikoff (1952) demonstrated that oxygen replaces sulfur in the wurtzite structure, causing a decrease in the unit cell edges. To the best of our knowledge, it has not previously been demonstrated that oxygen forms a measurable solid solution in sphalerite, though it would be surprising if oxygen entered one polymorph and not the other.

PREPARATION OF MATERIALS

Sphalerite and wurtzite were prepared by heating zinc filings and elemental sulfur in sealed, evacuated, silica-glass tubes. Zinc filings were prepared from rods of high purity zinc purchased from Central Research Laboratories, American Smelting and Refining Company. Elemental sulfur was obtained as clean lumps of high-purity, carbon-free sulfur, from the Freeport Sulfur Company. Analyses of these materials are presented by Skinner and others (1959).

Freshly prepared zinc filings and sulfur were weighed, loaded and sealed in evacuated silica-glass tubes. The sealed tubes were placed in a cold furnace and the temperature raised to 900° C. in approximately 5 hours and held at this level for 24 hours. A fine-grained white powder of sphalerite resulted. After the charge cooled any excess sulfur or excess zinc was clearly visible under the binocular microscope. Prolonged heating for a week or more at 900° C. produced recognizable single crystals of sphalerite up to 0.05 mm. in diameter. Pure wurtzite was produced in a comparable manner by heating the charge above 1020° C., the sphalerite-wurtzite transition temperature.

The sphalerite prepared from zinc filings and elemental sulfur was optically isotropic and the x -ray diffractometer tracings showed sharp, symmetrical reflections. The wurtzite prepared from zinc filings and elemental sulfur was optically anisotropic and the x -ray diffractometer tracings showed the sharp, symmetrical reflections characteristic of 2H wurtzite as opposed to the more complicated patterns characteristic of the other wurtzite polytypes (Hill, 1958).

A sphalerite-wurtzite mixture, prepared at room temperature by passing H₂S through a cold aqueous solution of ZnSO₄, was also used in the investigation. The precipitate is too fine grained for determination by optical observation whether the wurtzite and sphalerite occur as individual crystals, or as polytypic mixtures, but x -ray powder diffraction patterns indicate that they are discrete phases and that polytypic intergrowths are absent or so minor as to be below the limit of detection by the x -ray method. The ratio of sphalerite to wurtzite in the precipitate is approximately 4 to 1. The sphalerite content of the precipitated material was increased by recrystallizing the precipitate at temperatures from

900° to 1000° C. for 10 to 12 days in sealed, evacuated, silica-glass tubes. We could not, however, recrystallize such material entirely to sphalerite; a trace of wurtzite always remained. Even after 12 days at 1000° C., when the charge had completely recrystallized to crystals from 0.1 to 1.0 mm. in their longest dimension, approximately 3 per cent of the crystals were wurtzite, the remainder being sphalerite. Wurtzite, completely free from sphalerite, was readily prepared by recrystallizing the precipitate in sealed, evacuated, silica-glass tubes above 1020° C. for periods as short as 6 hours.

The x -ray diffractometer tracings of the recrystallized precipitate suggest that other polytypes besides the 2H wurtzite type have grown in the sphalerite-wurtzite mixture during recrystallization. These polytypes could not be individually characterized by powder diffraction methods. The wurtzite prepared by recrystallizing the precipitated ZnS above 1020° C. was largely the 2H polytype, but x -ray diffractometer tracings indicated that small amounts of other polytypes were also present.

MEASUREMENT OF UNIT CELL EDGES

The sphalerites and wurtzites used as starting materials were characterized by means of x -ray powder diffraction techniques, using powder photographs and (or) x -ray diffractometer tracings. The identification was made by reference to the powder diffraction data presented by Swanson and Fuyat (1953). The effect of dissolved oxygen on the unit cell of wurtzite has been quantitatively established by Kroeger and Dikhoff (1952). Their data show that oxygen causes both the a - and c -axes of wurtzite to contract. The (300) line of wurtzite gives an intense, conveniently located reflection with copper $K\alpha$ radiation and thus provides a good measure of the shrinkage of the a dimension.

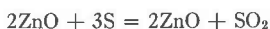
Measurements were made with a Norelco x -ray diffractometer. Analytical reagent NaCl was used as an internal standard, the NaCl (422) line being used for comparison. A value of $5.64028 \pm 0.00010 \text{ \AA}$ at 20° was taken for the unit cell edge of NaCl (Fron del, 1955). Fron del's original measurement is stated in kX units but has been converted to \AA by the $kX/\text{\AA}$ conversion factor (Bragg, 1947). The precisions of measurement for the a_0 of NaCl and for the Bragg conversion factor are an order of magnitude higher than those required to demonstrate the effects discussed in the present study. Thus, even if the stated precisions by Fron del and Bragg are proven too optimistic, it is unlikely that use of their data will introduce significant errors. All measurements were conducted at an average temperature of 25° C., and although the room temperature was variable, the variation did not exceed 4° C. and has been ignored. Differences in the cell edge of the NaCl standard caused by temperature variations were less than the precision of measurement.

Unit cell edge measurements of sphalerites were made in two ways. Most of the measurements were made in 114.59 mm. diameter x -ray powder cameras using the Straumanis film mounting technique, and copper $K\alpha$ radiation. Back reflection lines were measured and the measurements extrapolated to $2\theta = 180^\circ$ by the Nelson and Riley (1945) function. Samples were also measured on a Norelco x -ray diffractometer with copper $K\alpha$ radiation using NaCl as an internal standard. Measurement of the sphalerite (422) and (331) lines were made relative to the (422) and (420) lines of NaCl.

Diffraction lines were measured by projecting the measured center-lines of the intensity profiles to background intensity, and measuring the intersection point. Replicate diffractometer tracings were made by oscillating back and forth over the peaks being measured, ensuring that relative errors were reduced to a minimum.

OXYGEN IN WURTZITE

Two methods of preparing oxygen-free wurtzite were used. First, zinc filings were heated with sulfur in slight excess of that necessary to form ZnS, to temperatures above 1020° C., in evacuated silica-glass tubes. Secondly, the precipitated wurtzite-sphalerite mixture was heated with free sulfur. In both cases the free sulfur reacts with any ZnO present in accordance with the equation



which goes virtually to completion since the amount of SO_2 generated is very small.

All oxygen detectable by unit cell measurements was removed from the precipitated ZnS in a single 2 hour heating at 1100° C. with excess sulfur. Repeated heatings did not measurably affect the unit cell edge.

The measured a_0 values of the two oxygen-free wurtzite samples prepared were 3.8232 \AA and 3.8237 \AA (Table 1). For pure ZnO a_0 is 3.2495 \AA (Heller and others, 1950). Following Kroeger and Dikhoff (1952) we have assumed that the composition of wurtzites containing oxygen can be obtained from a straight line joining the a_0 values of ZnS and ZnO on a plot of a_0 versus composition.

To determine the amount of oxygen that will enter the wurtzite structure, charges of approximately equal amounts of ZnO and ZnS were heated in sealed, evacuated silica-glass tubes. Some ZnO reacted with the silica-glass tube to form a thin skin of Zn_2SiO_4 , but this thin reaction shell effectively insulated the ZnS-ZnO mixture from the silica tube and prevented further reaction, ensuring that excess ZnO always remained at the end of the run and hence that the wurtzite was saturated with oxygen. At 1150° C. we found that wurtzite in equilibrium with ZnO contained

TABLE 1. THE EFFECT OF OXYGEN ON a_0 OF WURTZITE, AND THE SOLUBILITY OF OXYGEN IN WURTZITE (Oxygen content expressed as per cent ZnO)

Starting material	Heating conditions	Phase detected	a_0 , Å	Mole per cent ZnO in ZnS ¹
ZnS, precipitated (mixture of sphalerite and wurtzite)	1100° C., free S present, 12 hours	Wurtzite, S, SO ₂	3.8232	0
ZnS, from Zn and S (ZnS in form of sphalerite, a_0 5.4093 Å)	1200° C., free S present, 24 hours	Wurtzite, S	3.8237	0
ZnS, precipitated (mixture of sphalerite and wurtzite)	Not heated	Wurtzite sphalerite	3.8195	0.5
Do.	1100° C., 48 hours	Wurtzite	3.8195	0.85
ZnS and ZnO, equal weights (ZnS in form of sphalerite, a_0 5.4093 Å)	1060° C., 24 hours	Wurtzite, ZnO, SO ₂	3.8185	1.0
Do.	1150° C., 12 hours	Do.	3.8175	1.2

¹ Estimated from unit cell edge.

1.2 ± 0.1 mole per cent ZnO. The results of the runs are given in Table 1, and compare reasonably well with the one mole per cent ZnO solubility at 1200° C. found by Kroeger and Dikhoff (1952). We believe that equilibrium was established within the times stated in Table 1 at the given temperatures because longer heating periods at the same temperatures did not change the unit cell edges. We did not, however, establish that the reactions were reversible. A wurtzite crystallized at 1150° C. in the presence of excess ZnO, having a final a_0 value of 3.8175 Å, did not show an increase in a_0 when held at 1060° C. for 48 hours.

It is significant that the wurtzite in the ZnS precipitated at room temperature has an a_0 value of 3.8195 Å, indicating a ZnO content of 0.85 mole per cent ZnO. An attempt was made to verify the ZnO content by carefully igniting weighed charges of the precipitated wurtzite-sphalerite mixture to ZnO in air at 700° C. Care was taken to prevent any sublimation or vaporization of the ZnO so formed by keeping the crucible in which the firing was performed covered, except for a very small gap allowing air to enter. When a constant weight was reached after repeated heatings, it was assumed that all the ZnS had been converted to ZnO. Samples of approximately 3 grams treated in this way had a final weight several milligrams higher than would be expected if the precipitate had been pure ZnS. Four repetitions of this procedure gave differences corresponding to an average of 0.7 ± 0.2 weight per cent ZnO in the original sample.

OXYGEN IN SPHALERITE

Because a great deal of significance is attached to the unit cell edge of pure sphalerite in phase equilibria studies, much effort has been expended in obtaining a satisfactory value for pure sphalerite (Skinner and others, 1959). Unit cell edge measurements revealed distinct differences between precipitated sphalerite and sphalerite formed by solid state reaction of zinc and sulfur in sealed, evacuated silica-glass tubes (Tables 2 and 3).

Oxygen-free sphalerites were synthesized directly from zinc and sulfur in the presence of either excess sulfur or excess zinc, in the absence of oxygen in evacuated silica-glass tubes. Although a small difference in unit cell edge was observed between the excess Zn and excess S samples, the difference is insignificant as it is of the same order as the measurement error. The precipitated ZnS, containing oxygen in solid solution, was converted completely to sphalerite by heating to 850° C. in the presence of free sulfur, or, alternatively, in the presence of metallic magnesium which acted as a preferential collector for the oxygen. The magnesium ribbon was separated from the ZnS by a small rod of silica glass which prevented the solids from coming into contact, but allowed gaseous transfer. The sphalerites so treated have virtually identical unit cell edges and are believed to be oxygen free. The results obtained from

TABLE 2. THE UNIT CELL EDGES OF PURE SPHALERITE

Starting material	Heating conditions	How measured	a_0 , Å
ZnS, from Zn and S (ZnS in form of sphalerite)	750° C., excess S, several days	Diffractometer, internal standard NaCl	5.4094
do.	do.	do.	5.4094
do.	do.	Film	5.4095
do.	900° C., excess S, 36 hours	do.	5.4095
do.	850° C., excess Zn, 90 hours	do.	5.4089
do.	850° C., excess S, 90 hours	do.	5.4093
do.	do.	Diffractometer, internal standard NaCl	5.4094
do.	850° C., excess S, Mg metal present, 90 hours	Film	5.4093
ZnS, from Zn and S (ZnS in form of sphalerite)	850° C., excess Zn, Mg metal present, 90 hours	Film	5.4090
ZnS, precipitated (mixture of sphalerite and wurtzite)	850° C., free S present, 90 hours	Diffractometer, internal standard NaCl	5.4093
do.	850° C., Mg metal present, 90 hours	Film	5.4094

TABLE 3. UNIT CELL EDGES OF SPHALERITES CONTAINING ZnO

Starting material	Heating conditions	How measured	a_0 , Å	Mole per cent ZnO in ZnS
ZnS, precipitated (mixture of sphalerite and wurtzite)	Not heated	Film and diffractometer, internal standard NaCl	5.4065	0.8
do.	950° C., vacuum, ¹ 12 days	Film (measured on 4 separate samples)	5.4070	0.8
do.	850° C., excess Zn, ¹ 90 hours	Film	5.4071	0.8
ZnS, from Zn and S, plus ZnO. Approximately equal weights (ZnS in form of sphalerite, a_0 5.4093 Å)	900° C., 48 hours	do.	5.4079	0.5 ²
do.	800° C., 96 hours	Film and diffractometer, internal standard NaCl	5.4081	0.4 ²

¹ Recrystallized product contained less than 5 per cent wurtzite.

² Estimated from unit cell edge.

these measurements are given in Table 2. The most satisfactory value fitting the data in Table 2 for the a_0 of sphalerite free from oxygen is 5.4093 ± 0.0002 Å.

It is significant that the precipitated ZnS containing oxygen recrystallized in the presence of free sulfur, or an oxygen collector such as magnesium ribbon, converted completely to sphalerite in a few hours at 850° C., whereas the same material could never be converted completely to sphalerite without introduction of magnesium ribbon or excess sulfur to remove most of the oxygen.

The unit cell edge of the precipitated sphalerite in the sphalerite-wurtzite mixture containing 0.8 mole per cent ZnO was found to be 5.4065 Å which is significantly lower than 5.4093 Å of pure ZnS. After recrystallization of the precipitate, to convert most of the precipitated wurtzite to sphalerite and to retain the oxygen in solid solution, the unit cell edge of the sphalerite was 5.4070 Å. This figure was obtained regardless of the temperature of recrystallization (Table 3). It is not felt that any significance can be placed on the unit cell edge difference of the precipitated (5.4065 Å) and recrystallized (5.4070 Å) sphalerites as the difference is small and the measurement of the x-ray powder lines of the precipitated material is hindered somewhat by the presence of

wurtzite lines. It has been previously noted that recrystallization of the precipitated ZnS did not convert the entire charge to sphalerite, and that approximately 3 per cent of the wurtzite remained in the charge. Although the small percentage of wurtzite makes accurate unit cell measurements of the wurtzite in the mixture very difficult, we were able to ascertain that the wurtzite had an a_0 value of 3.8195 Å corresponding to a ZnO content of 0.85 mole per cent ZnO and hence that the wurtzite did not act as a strongly preferential collector for the oxygen in the charge. This indicates that the sphalerite in the recrystallized ZnS contained approximately 0.8 mole per cent ZnO.

There are few good unit cell edge measurements of pure sphalerite in the literature. Kullerud (1953) carefully measured sphalerite formed by heating zinc and sulfur in an evacuated silica-glass tube. This sphalerite, which we believe to be oxygen free, had a reported cell edge of 5.3985 ± 0.0001 Å. The unit cell edge of the NaCl used by Kullerud as an internal standard in his x -ray measurements was given by Wyckoff (1948) as 5.62869 Å. This introduces an error because the a_0 of NaCl used is actually in kX units, and hence the measurements are incorrectly stated in Å. If we use the kX/Å conversion factor of 1.00202 (Bragg, 1947), we obtain 5.4094 ± 0.0001 Å for the corrected value of Kullerud's measurement, which is in excellent agreement with the present figure for pure sphalerite.

Swanson and Fuyat (1953) reported 5.4060 Å as the unit cell edge of a sphalerite "prepared at 940° C. by the Radio Corporation of America Laboratories." It is not stated whether the sample was initially precipitated and subsequently recrystallized or whether it was formed by solid state reaction at 940° C. It is believed, however, that the sample contained significant amounts of oxygen, which accounts for its low unit cell edge.

We have previously noted that the precipitated ZnS containing approximately 0.85 mole per cent ZnO is a mixture of sphalerite and wurtzite. This mixture could not be recrystallized entirely to sphalerite unless the oxygen was removed by some means. This suggests either that the oxygen is promoting the metastable growth of wurtzite below the sphalerite-wurtzite transition temperature, or that the transition temperature itself (1020° C. for pure ZnS) is drastically lowered by the addition of a little oxygen. To check the hypothesis that the transition temperature is lowered, we recrystallized precipitated ZnS charges in evacuated silica-glass tubes at different temperatures from 700° to 1000° C. for periods up to 2 weeks. Regardless of the temperature and the heating time we could not remove all the wurtzite, and the unit cell edges of the sphalerites and wurtzites in the different runs were un-

changed within the limits of measurement error. These results indicate that although the sphalerite-wurtzite transition temperature may be lowered from 1020° C. by the addition of oxygen to ZnS, it is still above 1000° C. for ZnS containing 0.85 mole per cent ZnO.

To test the hypothesis that oxygen promotes the metastable growth of wurtzite below the sphalerite-wurtzite transition temperature, we prepared a series of charges of differing composition and crystallized them at 1000° C. for 1 week. The charges prepared were:

- A. Oxygen-free ZnS, prepared from zinc filings and sulfur.
- B. Oxygen-free ZnS to which an excess of sulfur was added.
- C. Oxygen-free ZnS to which 1.5 weight per cent ZnO was added.
- D. Precipitated ZnS containing approximately 0.7 weight per cent ZnO.
- E. Precipitated ZnS containing approximately 0.7 weight per cent ZnO, to which excess sulfur was added.

The charges were individually loaded in evacuated silica-glass tubes and placed in the same furnace. The crystallization products were examined by x-ray diffraction, the results of which are shown in Fig. 1. It is apparent that in each run where oxygen was present in the system without free sulfur (C and D), a hexagonal wurtzite phase developed in addition to the predominant sphalerite. In those runs where oxygen was absent, or was combined as SO₂, only cubic sphalerite developed. It was further noted that runs C and D, in which wurtzite developed, were entirely crystallized to crystals from 0.2 mm. to 0.5 mm in their maximum dimension, whereas runs A, B, and E consisted entirely of crystals less than 0.05 mm. in their maximum dimension.

These results suggest that oxygen not only promotes the metastable growth of wurtzite, but that it also increases crystal growth rates.

OXYGEN IN NATURAL ZINC SULFIDES

It is of interest to consider the possibility of detectable amounts of oxygen in natural zinc sulfides.* We shall discuss this possibility first on the basis of theory and then on the basis of observation.

We have shown above that the maximum ZnO content is about 1.0 per cent. At low temperatures this will decrease, possibly to as low as 0.1 per cent or less, so that, as a crude measure, we can estimate that ZnS saturated with ZnO at geologically reasonable temperatures will contain between 0.1 to 1.0 mole per cent ZnO. For this purpose we can also make

* The mineral voltzite has been reported to have the composition Zn₅S₄O which would fall between the fields of ZnS and ZnO; Moss (1955), however, has shown that voltzite is actually a zinc arsenic sulfide containing no oxygen. No new phases intermediate between ZnS and ZnO were found in any of our studies.

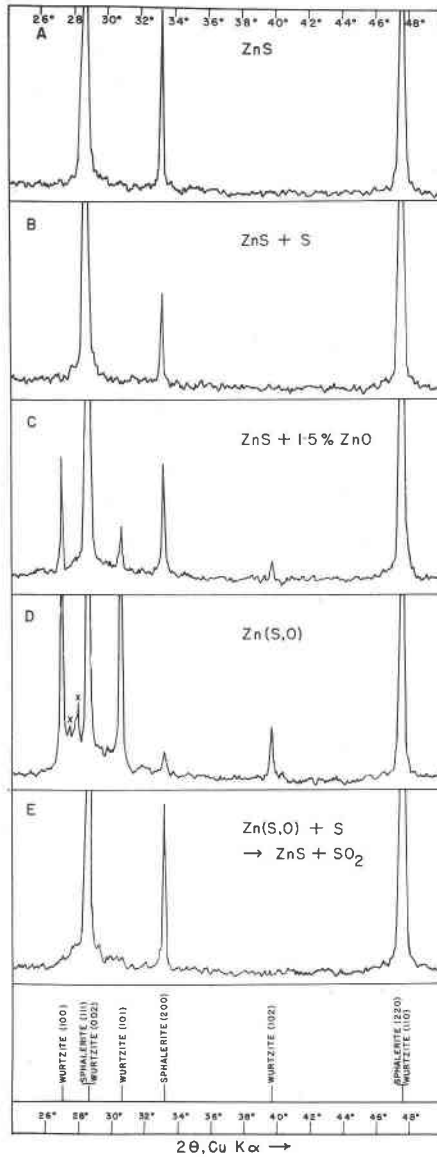


FIG. 1. X-ray diffractometer tracings of crystallization products from different starting materials, crystallized at 1000° C. for 1 week, (A) oxygen-free ZnS, (B) oxygen-free ZnS plus free sulfur, (C) oxygen-free ZnS plus 1.5 weight per cent ZnO, (D) precipitated ZnS containing 0.7 weight per cent ZnO in solid solution, (E) same as (D) but with free sulfur present. Peaks marked (X) in (D) are from wurtzite polytypes, c axis repeat distance not determined.

the reasonable assumption that the activity of ZnO in ZnS (a_{ZnO}) is a simple linear function of the degree of saturation of the sphalerite in ZnO. (That is, if a sphalerite saturated with ZnO contains 1.0 mole per cent ZnO, then a sphalerite in an environment where $a_{\text{ZnO}}=0.1$ would contain 0.1×1.0 mole per cent or 0.1 mole per cent ZnO, and so on.) Now let us consider a natural hydrothermal solution at an arbitrary temperature, in this case 125° C., from which sphalerite is precipitating. Previously published calculations (Barton, 1957, 1959) enable us to estimate crudely the variation of the ratio $a_{\text{S}}=/a_{\text{OH}^-}^2$ in the ore-forming fluids. At 125° C. the $a_{\text{S}}=/a_{\text{OH}^-}^2$ ratio is about 10^{-1} to 10^3 . A solution in equilibrium with sphalerite saturated with ZnO at this temperature would have a ratio of about 10^{-8} , well beyond the limits of the usual type of hydrothermal environment. From these data we readily calculate that a_{ZnO} in sphalerite under typical hydrothermal conditions is approximately 10^{-4} to 10^{-8} times its saturation value, and this indicates that the amount of ZnO in the sphalerite would be somewhere between 10^{-4} and 10^{-9} mole per cent, an amount far too low to be detected by present techniques. Very large changes in the assumptions of temperature and composition of the solution used to make this calculation can be made without altering the conclusion that only very minute amounts of oxygen should be found in hydrothermal zinc sulfides.

The above thermodynamic argument is based on the assumption of equilibrium, but we know that there are frequently departures from equilibrium in low-temperature, sulfide-forming systems as is shown by the metastable development of marcasite and wurtzite. Hence the possibility exists that larger than equilibrium amounts of oxygen may become metastably incorporated into the zinc sulfide structure. This is demonstrated by the unheated, precipitated zinc sulfide, which contains about the same amount of ZnO as could be introduced at high temperature when free ZnO was present.* Indeed, it is possible that minor impurities such as oxygen, chlorine, cadmium, and manganese may contribute significantly to the kinetic factors responsible for the metastable precipitation (at low temperatures) of wurtzite and wurtzite-sphalerite polytypes instead of the stable sphalerite.

To test the above theoretical considerations we have looked for oxygen in natural zinc sulfides. Bulk analysis of the sample for oxygen would be unsatisfactory because of the problem in contamination by traces of atmospheric oxygen, by adsorbed water, and especially by water in nu-

* In fact, the precipitated ZnS was produced by bubbling H_2S (1 atm) through a Zn^{++} -bearing solution at room temperature. Under these conditions the $a_{\text{S}}=/a_{\text{OH}^-}^2$ ratio is about 10^{+6} which would give an extremely low a_{ZnO} and therefore an extremely low amount of oxygen in sphalerite under equilibrium conditions.

TABLE 4. SPECTROGRAPHIC ANALYSES OF NATURAL SPHALERITES
(Analyses by Janet D. Fletcher, U. S. Geological Survey)

Element ¹	"Robertsonite" USNM R575	"Brunckite" USNM R8328	"Cleiothane" USNM C432
Zn	Major	Major	Major
Cd	0.03 ²	1.1	0.36
Mn	0.016	0.13	0.12
Fe	0.28	0.056	0.017
Cu	0.00X	0.X	0.0X
Ge	0.00X	0	0
Sn	0	0	0
Pb	0.0X	0.0X	0.0X
Co	0.00X	0	0
Ni	0.00X	0	0
Ti	0.00X	0.00X	0.000X
Mg	0.00X	0.00X	0.00X
Ca	0.00X	0.00X	0.00X
Ba	0	0	0.000X
$a_0, \text{Å}$	5.4089 ± 0.0004	5.4126 ± 0.0005	5.4100 ± 0.0004

¹ Looked for but not found: Ag, Au, Hg, Pd, Ir, Pt, Mo, W, As, Sb, Bi, Se, Te, Tl, In, Cr, V, Ga, Sc, Y, Yb, La, Zr, Th, Nb, Ta, U, Be, Sr, P, B.

² Results have an accuracy of ± 15 per cent except near limits of detection, where only one digit is reported.

merous fluid inclusions known to occur in most natural crystals. The ignition technique described previously would also be unsatisfactory because of elements other than zinc, sulfur, and oxygen present in natural zinc sulfides. Therefore the *x*-ray method was used. Because of the minor impurities known to be present in the zinc sulfides (see Table 4) the absolute unit cell size has little significance. What we are looking for is an *increase* in the unit cell size after the material has been heated with sulfur, thereby reflecting the effect of possible exchange of sulfur for oxygen.

A sphalerite (var. cleiothane, USNM C432) from Franklin, N. J., where zincite is abundant and where a_{ZnO} should be far higher than for typical hydrothermal ores, was studied by the *x*-ray method. The cleiothane sample was entirely sphalerite, but unfortunately was not associated with zincite. It had a unit cell edge of $5.4100 \pm 0.004 \text{ Å}$. This figure was not changed by recrystallizing the material in a vacuum at 900° C . for 1 day nor by recrystallizing it in the presence of excess sulfur at 900° C for 1 day. Spectrographic analysis (Table 4) of the sample showed that it was remarkably pure for a natural sphalerite, the major

additional element being 0.36 per cent cadmium, which is believed to be in solid solution in the sphalerite. Thus it appears that no measurable amount of ZnO is present in the cleiophane.

As ZnS is a comparatively soluble ore sulfide it commonly does not appear in the supergene zone, yet there are a few occurrences of secondary zinc sulfide. In supergene environments the $a_s = /a^2_{\text{OH}^-}$ ratio may fall to much lower values than is normal under hydrothermal conditions as is indicated by the formation of such minerals as cuprite, tenorite, and montroydite only in the oxidized zone. Were this the only factor controlling a_{ZnO} , we might expect to find an occasional secondary sphalerite or wurtzite containing measurable amounts of ZnO, but we must also deal with CO₂ and silica in the system. The pressure of CO₂ (or, expressed another way, the $a_{\text{CO}_2} = /a^2_{\text{OH}^-}$ ratio) is usually sufficiently high so that smithsonite and hydrozincite and not zincite are the stable secondary zinc minerals. An additional factor limiting a_{ZnO} is that reactive silica is frequently available and thus the zinc silicates hemimorphite, sauconite, and (rarely) willemite may form. Thus we expect that a_{ZnO} will seldom, if ever, become large enough to permit the entrance at equilibrium of measurable amounts of ZnO into ZnS in the supergene zone.

Two samples of zinc sulfide of probable supergene origin were examined by x-ray methods, the "robertsonite" (USNM R575) from Cherokee County, Kansas (Robertson, 1890), and the "brunckite" (USNM R8328) from Cercapuquio, Peru. X-ray powder diffraction patterns of the "robertsonite" showed that sphalerite was the only crystalline phase present. The sphalerite has a unit cell edge of 5.4089 ± 0.0004 Å. A spectrographic analysis of the sample showed that it is remarkably pure for a natural sphalerite, 0.28 per cent iron being the major additional element (Table 4). Recrystallizing the sample in a sealed evacuated silica-glass tube at 900° C. for 4 days did not change the unit cell edge. Recrystallizing the sample in the presence of free sulfur at 900° C. for 1 day increased the unit cell edge to 5.4095 ± 0.0003 Å. This increase cannot be taken as significant as it is just within the uncertainty of measurement.

X-ray powder diffraction patterns of the "brunckite" showed that sphalerite was the predominant phase present, but that about 5 per cent wurtzite was also present. The sphalerite in the "brunckite" had a unit cell edge of 5.4126 ± 0.0005 Å. Spectrographic analysis of the material indicated that it contained 1.1 per cent cadmium by weight (Table 4), and it is believed that the large unit cell edge indicates that cadmium is in solid solution in the sphalerite. Recrystallizing the material in evacuated silica-glass tubes at 900° C. for 4 days did not change the unit cell edge, and material recrystallized in the presence of free sulfur

at 900° C. for 1 day had a unit cell edge of $5.4129 \pm 0.0005 \text{ \AA}$, an insignificant increase.

No suitable samples of wurtzite could be obtained in sufficient quantities to examine them for their possible oxygen content.

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