VOLTZITE

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ABSTRACT

A seemingly homogeneous mineral from Sterling Hill, New Jersey, is found to be a mixture of ZnS (wurtzite) and an organometallic compound containing zinc. The bulk analysis shows Zn>S in atomic percent, and can be interpreted as of a zinc oxysulfide, but the Zn present over the requirements of the S is contained in the organic component. The original voltzite from Rosiers, France, was described as zinc oxysulfide, Zn_5S_4O, but is an apparently identical mixture. A number of probably similar occurrences have been reported in the literature. These include six localities for supposed zinc sulfocarbide, and five analyzed occurrences of so-called zinc oxysulfide.

The Sterling Hill material has the bulk composition Zn 60.63, Fe 0.32, Mn 0.016, S 27.23, C 3.38, H 0.69, N none, 0 [7.30], total 100.00 percent (average of three). The atomic ratio Zn/S is 1.09, corresponding to ZnS 82.19, ZnO 6.83. The mineral occurs as brownish black, submicrocrystalline botryoidal crusts. Small grains are transparent and faintly birefringent. The mean index of refraction is 2.08, and the specific gravity is 3.48. It is readily soluble in HCl with release of the organic component. The latter is a zinc salt of a highly oxidized organic acid. It carbonizes below 400°, turning the mineral black. X-ray, thermal, and infrared absorption data are given.

INTRODUCTION

Voltzite, a supposed oxysulfide of zinc, holds an unenviable place among minerals: authentic specimens can not be found, and present-day accounts of it are quite misleading. The original description by J. Fournet was published in 1833 in a relatively inaccessible journal, the *Annales Scientifiques Litteraires et Industrielles de l'Auvergne (Clermont-Ferrand, France)*. It indicated that voltzite was a mixture of an organometallic compound, termed zinc resinate by Fournet, and a sulfide of zinc. This was 16 years before the discovery of organometallic compounds by Frankland. The mineral was found at Rosiers, Puy-de-Dôme, France, as botryoidal crusts closely resembling sphalerite. Numerous other occurrences of botryoidal zinc sulfide containing carbon or a hydrocarbon were soon described, many under the name "leberblende". With passing years, in part as a consequence of critical remarks by Berzelius in 1840, mention of the organic component both of voltzite and of leberblende gradually dropped from reference works, the name leberblende disappeared into the synonymy, and voltzite took on a new life in the literature, if not in reality, as a problematic oxysulfide of zinc. A century and a third later, a new occurrence has been found of a substance that appears to be identical with the original voltzite of Fournet.

It is described here with a review of the occurrences of voltzite and leberblende earlier reported.

Voltzite from Rosiers, Puy-de-Dôme, France

This mineral, the original voltzite, occurred as botryoidal crusts composed of thin concentric shells or growth zones. The color is pink to yellow, but some growth zones are brownish and others, indicated to contain a minimum of an admixed organic component, are white. The surface of the crusts was said to be black through alteration, which Fournet thought probably involved only the organic material present. The luster is vitreous when fresh but turns resinous after a few days. The mineral is translucent to opaque, with a brownish white powder. The hardness is greater than 4, the specific gravity 3.66, and the cross-fracture is conchoidal.

The name was given by Fournet[1] after the chief engineer of the mine P. L. Voltz.[2] It appears as voltzine in the original description and as voltzit in a German résumé published by Fournet in 1834. The latter form has come into general use.

The mineral was found as a coating upon white quartz that lined an open fissure in a sulfide vein. It was associated with sulfates of Fe, Cu and Zn as products of oxidation and efflorescence, and is stated to be younger than the vein material (which contained cerussite and native copper). The voltzite thus seems to have formed in or near the zone of oxidation and to be supergene in origin.

The chemical behavior of voltzite is interesting, and offers the main criteria for identification. The mineral was described as dissolving with violence in HNO_3, yielding brown fumes of NO_2 and free sulfur. In HCl, dilute or concentrated, the mineral dissolves giving off H_2S, but not sulfur, and leaves a brown residue of organic matter. This has the form of sheets or flakes [that probably are pseudomorphous after fragments of the thin shells that compose the crust]. In hot HCl, the organic matter is in part dissolved to form a cloudy brown solution; on dilution with water the material is partially precipitated to give a turbid or milky appearance. Heated in a closed tube, water is given off very readily and this is followed by powerful decrepitation. The color of the sample changes on heating from yellow to black, which Fournet ascribes to decomposition of the organic material, and then through brownish green to

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[1] Joseph Jean Baptiste Xavier Fournet (1801–1869) of Strasbourg, mining engineer and director of mines at various places including Pont-Gibaud (1828–1833). Professor of Geology and Mineralogy at Lyon, and author of numerous scientific papers.

[2] Phillippe Louis Voltz (1785–1840) of Strasbourg, later Inspector General of Mines, and writer on paleontological and geological subjects.

yellow [oxidation to ZnO]. The organic material itself, when isolated by acid, is fusible, giving off first an aromatic odor which then becomes fetid and leaves a black coaly residue. On ignition in air, the black residue burns away leaving a residue of ZnO. Fournet here remarked that the Zn was present in combination as an insoluble resinate (" . . . *et laisse un résidue charbonneux noir, qui, par son incinération, met à découvert l'oxide de zinc, qu'elle retenait en combinaison sous forme de résinate insoluble.*"). No other comment on this matter, a key point in the interpretation of the composition of voltzite, is made in the paper.

Fournet's analysis was effected by fusing a bulk sample in a mixture of KNO_3 and $NaHCO_3$. Total Zn, S, and Fe were determined in the re-

TABLE 1. COMPOSITION OF VOLTZITE FROM ROSIERS

	1		1a		2		2a
Zn	66.20	ZnS	72.98	Zn	66.10	ZnS	81.01
Fe	1.26	ZnO	21.45	Fe	1.26	ZnO	14.62
S	24.73	FeS	1.98	S	27.00	FeS	1.61
Rem.	[7.81]		[3.59]		[5.64]		[2.76]
Total	[100.00]		[100.00]		[100.00]		[100.00]

1. Composition calculated from the reported weights of the precipitates in Fournet's analysis using modern atomic weights (sample 5.00 grams, $BaSO_4$ 9.00 grams, ZnO 4.12 grams, Fe_2O_3 0.09 grams). Remainder is water, organic material, oxygen, etc. A duplicate determination of the Zn gave 64.56 percent.

1a. Same recast to show the distribution of the total Zn as ZnS and ZnO on the basis of an interpretation as an oxysulfide. Atomic ratio, ZnO:ZnS = 1:2.84.

2. Analysis as originally stated by Fournet (1933), recast in elemental form.

2a. Same recast as an oxysulfide. Atomic ratio, ZnO:ZnS = 1:4.63.

sulting solution. It is clear that any Zn associated with the admixed organic matter would appear above the requirements of the S found on analysis, leading to an interpretation as an oxysulfide. This was the interpretation made by Fournet.

The original analysis of Fournet (1833) as recalculated from the stated weights of his sample and precipitates using modern atomic weights is given in Table 1, column 1. The only considerable change is in the value for S, as seen by comparison with the composition as computed originally (Table 1, column 2). This has the effect of much increasing the amount of oxygen present in an interpretation as an oxysulfide, from O:S = 1:4.6 (Fournet rounded his derived formula off to $Zn_5S_.O$) to O:S = 1:2.8.

Authentic specimens of the voltzite from Rosiers apparently are not

extant. According to Gonnard (1876) the mineral was found only once. Fournet did not state the amount of material obtained by him, but it probably was small. Lacroix (1896) said that authentic specimens were not known in any French collection. Extended enquiries by the writer established that none of the leading reference collections of the world has specimens. Specimens labelled voltzite from localities other than Rosiers are common in collections, and have been made the basis of observations attributed to voltzite in the general sense, but a following summary indicates that they are ill-defined and their relevance to the matter is uncertain.

The treatment of voltzite in modern reference works has minimized or eliminated reference to the organic component. It is not mentioned at all in Hintze's *Handbuch der Mineralogie* (1904) or in Doelter's *Handbuch der Mineralchemie* (1926). In Dana's *System*, the second edition (1844) cites Fournet's analysis with no note of the organic material; the third (1844), fourth (1854) and fifth (1882) editions cite only "resinous matter, trace" under the analysis; the sixth (1892) edition and the seventh (1944) edition (where I failed to consult Fournet's paper) eliminated even this. Almost all accounts agree in calling the mineral an oxysulfide. Hey (1955) and Strunz (1957, 1966), however, give the composition of voltzite as $Zn(As,S)$ or (Zn,As) S on the basis of observations indicated beyond. Groth (1882) stated that voltzite was a mixture of ZnS and ZnO. Breithaupt's *leberblende* was put without description into the synonymy of sphalerite by Dana (1844), on the basis of remarks by Berzelius (1840), where it remained until 1882 when it was transferred to the synonymy of voltzite.

Voltzite from Sterling Hill, New Jersey

In 1935, miners working in the 2300 stope on the 1680-foot level of the Sterling Hill mine encountered a cavernous zone in which was found a stalactitic mass, likened to a wasp's nest, of an unfamiliar iridescent black mineral. Unmindful of company restrictions on the removal of salable specimen material, the foreman and the work crew divided up the find on the spot and took it home in lunch boxes. A specimen ultimately was brought to L. H. Bauer, then Chief Chemist of the mine laboratories, who identified it as botryoidal sphalerite. The matter would have rested here had not Mr. Bauer noticed that large grains when dissolved in HCl left a residue of organic material. A quantitative chemical analysis on a bulk sample was then made, that indicated an excess of Zn over the requirements of ZnS. Following the death of Mr. Bauer, most of the existing specimens were obtained and the investigation was taken up by the writer.

The mineral occurs as botryoidal crusts up to a few millimeters thick, and as stalactitic or drapery-like pendant sheets that appear as if they had hardened from a flowing, gel-like mass. Typical specimens are shown in Figure 1. The crusts and sheets show a concentric lamination on a fine scale, without distinct fibrosity, and are quite brittle. The color is black to dark brownish black. The luster is slightly resinous. The matrix is coarsely granular calcite containing altered grains of franklinite with, locally, pyrite and yellow-green crystalline sphalerite. The surface of the matrix was corroded and pitted by solution before the deposition of the voltzite crust. The association of the mineral and its properties indicate that it was formed at ordinary temperatures and pressures, probably by
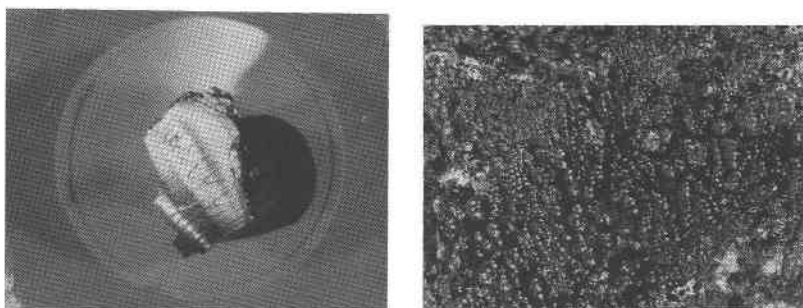

FIG. 1. Right: Botryoidal crust of zinc sulfide from Sterling Hill. Actual size about 3 inches across. Left: Fragment of pendant sheet. Actual size about 1 inch.

meteoric solutions. The watercourse in which the mineral was found is not located within the zone of Precambrian weathering present in the Sterling Hill orebody (Metsger, *et al*, 1958), but may be related thereto.

Chemical composition. Three closely agreeing quantitative chemical analyses of different samples are cited in Table 2. The main features of the composition are the presence of C, H and O, and the excess of Zn over S in atomic ratio, with $Zn/S = 1.09$ instead of 1. This corresponds to an empirical distribution of the total Zn as ZnS 82.19 weight percent and ZnO 6.83 percent. The small amounts of Si and Mg present are attributed to admixture and the Fe is assumed to be present in substitution for Zn. Spectrographic analyses showed Zn to be the only major cation, with Fe and Mn in strong traces.

In the averaged analysis, which will be employed hereafter in discussions of the composition, the atomic ratio H/C is 2.43. The analytical value for H is a direct determination, that includes the H present in both the organic component and in the nonessential water present. The contribution of H from the two sources is difficult to estimate. The weight

loss graph obtained by heating in air or He is essentially continuous from almost room temperature through the temperature, known to be below 350°, where the organic component decomposes. Direct H_2O determinations by both absorption and modified Penfield techniques, obtained by heating the sample at various temperatures in air and in He, indicate that the total yield up to 250° is about 4 percent. The weight loss by desiccation at room temperature is about 0.1 percent and the loss by heating at 60° and at 100° is 0.6 and 1.1 percent respectively (Fig. 2). If the latter figure is taken as representing the nonessential H_2O, and the cor-

TABLE 2. COMPOSITION OF VOLTZITE FROM STERLING HILL

	1	2	3	Average		4
Zn	60.76	60.67	60.44	60.63	ZnS	82.19
Fe	0.32	n.d.		0.32	ZnO	6.83
Mn	0.016	n.d.		0.016	FeS	0.50
MgO	0.30	0.25		0.28	MnS	0.03
SiO₂	0.15	n.d.		0.15		
S	27.29	27.17	27.22	27.23		
C	3.37	3.41	3.37	3.38		
H	0.74	0.68	0.65	0.69		
N	none	none	none			
O	[7.05]			[7.30]		
Total	[100.00]			[100.00]		

1. L. H. Bauer analysis, 1936. C, H and N determinations by S. M. Nagy, 1964.

2. F. A. Gonyer analysis, 1952. Fe present. C, H and N determinations by S. M. Nagy, 1964.

3. A. Bernhardt microchemical analysis, 1962. Fe present.

4. Average analysis recast to show interpretation as an oxysulfide. Atomic ratio, ZnO: ZnS = 1:10.76.

responding amount of H deducted from the total value of H = 0.69, the H/C ratio that can be attributed to the organic component approaches 2.

The innermost layer of the crusts has a more crystalline appearance, a relatively high index of refraction (>2.08), and gives a much sharper sphalerite X-ray pattern. It also contains less of the organic component, with C 2.58, H 0.51. The remainder of the zoned crust, used in the analysis, is rather uniform. Six supplementary C and H determinations, made on different specimens and on samples of slightly different color, gave extremes of C 3.02, H 0.59 and C 3.97, H 0.86 with most near the values of the bulk samples cited in Table 2.

Organic component. The mineral is quickly attacked by strong HCl or HNO_3, more rapidly when warmed, and the action is much more rapid than with powdered crystalline sphalerite. A faint unidentified organic odor was noticed against the background of H_2S when large samples were dissolved in a minimum of acid. Large grains when slowly dissolved in cold dilute acid leave fragile pseudomorphs of brown organic material. On close examination these may be seen to preserve the original growth banding. When the rate of solution is high the emitted bubbles of H_2S tend to disrupt and disperse the residue. If the grains are heated to 350°C or more before the acid treatment, the rapidity of the acid attack is in-
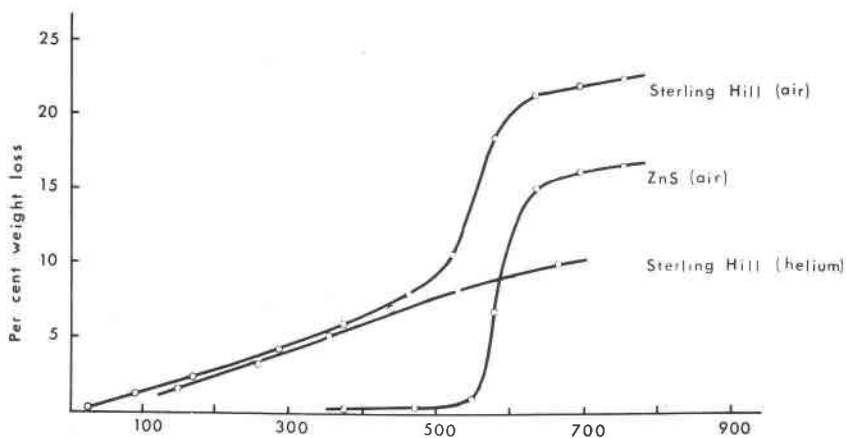

FIG. 2. Weight loss as a function of temperature on heating in air and in helium. Sterling Hill material.

creased. The color of the sample and of the residue then becomes darker, and at 500° is black (see Thermal Data).

The organic residue is insoluble in molecular solvents such as benzene, toluene, xylene and CCl_4, but is readily dissolved or dispersed by polar liquids such as alcohol, diethylene glycol and especially ammonia, There is a slight solubility in cold dilute HCl and a larger one in hot strong acid, giving a brown solution. When a strong solution is diluted with water a turbid brownish sol is formed which soon coagulates. No soluble matter is removed from the mineral by 24-hour treatment in alcohol in a Soxhlet extractor. The zonal structure, however, becomes accentuated when large grains are immersed in ammonia.

The organic residue when air dried is optically isotropic, with *n* about 1.64, and does not give an X-ray pattern.[1] When heated in air, it does

[1] One sample showed an indistinct line with *d* 3.84 Å.

not melt but chars and at red heat burns away to leave a white residue of ZnO. A direct quantitative determination of the amount of the organic component present is not possible because of the appreciable solubility in acid. Zn apparently is also extracted from the organic residue by the acid treatment. A residue obtained by dissolution of the mineral in 1:1 HCl at 8°C amounted to 4.0 percent, after drying at 60°, and contained 7.1 percent Zn as ZnO. In concentrated acid at 22° the yield was much smaller and the content of Zn was only 2.1 percent. The washed and dried residue when taken up by alcohol, filtered, and recovered by evaporation, also contains Zn. Assuming that the mineral is a mixture of stoichiometric ZnS with an organometallic compound of Zn, the amount of the latter plus the nonessential water is 16.8 percent. If the nonessential water is taken as 1.1 percent, as indicated earlier, the atomic ratio Zn:C:H:O in the organic component is roughly 1:3:6:4.

Infrared absorption spectra of the organic residue were unsatisfactory, apparently because the material mostly forms a colloidal dispersion rather than a true solution in polar solvents. The soluble (?) portion absorbs throughout the 2- to 25-micron region. The sharpest absorptions were identified as C–H, carboxylic and carboxylate bands. The material apparently is the Zn salt of a highly oxidized organic acid. An infrared absorption spectrum run on the fresh mineral, using KBr mounting and a NaCl prism, showed no significant differences from that of ordinary Santander sphalerite. A broad-line nuclear magnetic resonance spectrum of the fresh mineral showed a strong and sharp H line but no other obvious differences from ordinary sphalerite.

The remarkable similarity of the Sterling Hill material to the original voltzite from Rosiers is apparent. It includes not only the presence of organic material containing zinc, and the reactions of this material, but also the physical properties of the mineral insofar as a comparison can be made.

Physical and optical properties. The scratch hardness is 4 1/2. Measurements of the specific gravity on the Berman microbalance varied widely, from 3.1 to 3.49. The variation is probably largely or wholly owing to cracks in the quite brittle grains. No clear evidence could be obtained of a variation in different growth zones. A pycnometric determination on a 1-gram sample of the material of analysis 1, consisting of more or less flawed grains, gave 3.40. The best value is taken as 3.48.

Under the microscope crushed grains generally are clear and transparent. A very closely spaced zoning, distinct from but parallel to the gross color banding in the crusts, may be observed. The grains are faintly birefringent, with extinction parallel and perpendicular to the zoning.

Some zones are virtually isotropic. There is no convincing evidence of admixture. A very indistinct fibrosity is present perpendicular to the growth zones. It is much less apparent than in the fibrous crusts of ordinary wurtzite.

The index of refraction in Na light is slightly variable. All samples are between 2.008 and 2.155; most are between 2.04 and 2.13, and the average is approximately 2.08. The measured values are much less than those for sphalerite low in Fe (n 2.37) or for wurtzite (ω2.356, ϵ2.378) in Na light. The index of refraction is not markedly changed by heating at 250°C. Samples heated in He at 650° are turbid, isotropic, with n much over 2.16. The variation in n is most marked between bands differing in color, but a small difference also exists between adjacent microscopic zones. The variation may reflect differences in the content of nonessential water or in the organic component, or both. The substance is not fluorescent in either long- or short-wavelength ultraviolet radiation or in an X-ray beam.

X-ray data. The untreated substance gives a distinct but rather diffuse X-ray pattern corresponding to that of sphalerite. No additional lines were observed. The unit-cell dimension was approximately determined as $5.39 \pm .01$Å; this is close to that of ordinary sphalerite low in Fe, with $a \sim 5.406$ Å. After heating in the range 150°–300° the pattern becomes sharper and weak additional lines corresponding to wurtzite-2H appear. The two most prominent wurtzite lines are ($10\bar{1}1$) and ($10\bar{1}0$), appearing as shoulders on the broad (111) (0002) sphalerite peak. Samples that have been heated to temperatures of 600° and over in inert atmospheres, with accompanying carbonization of the organic component, also gave a definite but poor pattern of wurtzite-2H. The approximate cell dimensions are a 3.82, c 6.24 Å, which are close to those of ordinary wurtzite. No graphite or other lines were observed.

Thermal data. A weight-loss graph obtained by heating duplicate powdered samples in air to constant weight at various temperatures up to 750°C is given in Figure 2. The inflection at about 550°–600°C represents oxidation to ZnO, as shown by X-ray study. A sample of Santander sphalerite converted to ZnO in the same range. The total weight loss of two samples heated in air directly to 1000° amounted to 23.58 and 23.70 weight percent. These values correspond well with the value 23.24 percent calculated on the basis of total oxidation of the Zn with accompanying loss of S, H_2O and organic material.

The response of the substance when heated in helium or nitrogen is different from that in air. On heating, samples begin to darken in color

at about 350°C, become black at about 500°C and stay black at higher temperatures. A residue of finely divided carbon is left on dissolution in acid. Separate samples heated in He at 670°, 745°, 870° and 900°C gave relatively sharp X-ray powder patterns of wurtzite. Quantitative analyses of these samples, cited in Table 3, showed a lower atomic ratio of Zn/S, between 1.0 and 1.04, than in the unheated material, with Zn/S 1.09. Evidently the excess of Zn over the requirements of the S present is more or less lost on heating. The mechanism of this and the accompanying weight changes are not well defined. Zinc freed during the decomposition of the organic component may be present as metallic Zn, which melts at 419° and boils at 907°C at one atmosphere and hence might be lost. The Zn evidently is not volatilized as an organometallic compound since the carbon is very largely or entirely retained in the heated sample.

The weight loss measurements in He below about 500°C are essentially

TABLE 3. ANALYSIS AND ATOMIC RATIOS OF SAMPLES HEATED IN He

	670°		870°		900°	
Zn	65.12	1.04	66.2	1.00	64.8	1.03
S	30.71	1	32.4	1	31.10	1
C	3–4		present		3	

Analyses by Dr. Jun Ito. Fe present.

duplicable, as seen in Figure 2. Very erratic measurements were obtained in both He and N at higher temperatures. In part these were caused by a very slight sublimate of unidentified colorless lathlike crystals on and near the sample boat that formed at 600°–700°C and possibly below. Samples heated in He to 745°C or over and then heated in air at 900°C all lost weight over the value 23.24 percent calculated on the basis of conversion of total Zn to ZnO, to a total of 26.33 percent in one instance. This supports the belief that Zn is somehow lost in part during heating in He.

A differential thermal analysis curve in air showed a broad endothermal dip extending from about 80° to 250°C, representing loss of water, with a uniform exothermal drift thereafter up to about 550°C when oxidation began.

Zn organometallic compounds. Many organometallic compounds of zinc and also chelating agents for this element are known. Most of them do not come into consideration in the present connection because of their low thermal stability and high chemical reactivity. The most likely class

of substances are the zinc salts of the polyoxymethylene glycols and their sulfuretted analogues. Numerous more or less well established compounds of this nature have been synthesized, such as by reacting methanal with metal hydroxides, metal sulfides, or metal polysulfides, and some are stable to over 200°C. The best known of these substances is zinc formaldehyde sulfoxylate; it forms orthorhombic crystals when heated at 245° that break down to a mixture of ZnO and ZnS.

A product surprisingly similar to the natural material was obtained by reacting crystalline $Zn_2(CH_2)O_2(OH)_2$ made by the method of Franzen and Hauck (1915) with Na_2S solution. The yellowish precipitate was repeatedly washed with water and with alcohol and then gave the analysis cited in Table 4, column 1. The Zn/S atomic ratio is 1.13, corre-

TABLE 4. ANALYSES OF SYNTHETIC MATERIALS

	1	2
Zn	57.6	65.7
S	24.9	24.5
C	4.79	0.82
H	1.21	0.41
O	[11.50]	[8.57]
Total	[100.00]	[100.00]

Analyses: Zn and S by Dr. Jun Ito, 1964; C and H by Dr. S. M. Nagy, 1964.

sponding to ZnS 75.68, ZnO 8.49. The material gave a diffuse ZnS X-ray pattern and blackened on heating. It probably is a mixture or adsorption complex of ZnS with an organometallic compound of zinc. A similar product was obtained by reacting Zn acetate, Na_2S, and methanol in water. The well-washed precipitate dried to a translucent horn-like mass and gave the analysis of Table 4, column 2. This material gave a diffuse ZnS X-ray pattern. The Zn/S atomic ratio is 1.32, corresponding to ZnS 74.47, ZnO 19.59. Both samples contain much nonessential H_2O.

VOLTZITE FROM OTHER REPORTED LOCALITIES

Reference could be made here to occurrences of botryoidal sphalerite and wurtzite in general, since all such material now becomes of interest, but the citations will be limited to occurrences already reported to contain carbon or to be an oxysulfide.

A botryoidal zinc sulfide from Cornwall was analyzed by Kidd[1] in

[1] John Kidd (1780–1851), Professor of Chemistry and Medicine at Oxford.

1806, and a colored lithograph of the specimen was given by Sowerby in 1839, in his *British Mineralogy*, under the name of Oxy-Sulfide of Zinc. The picture is reproduced in Figure 3 and can be taken as representative of voltzite in general. The designation of Kidd's mineral as an oxysulfide reflects an earlier chemical terminology and is today a misnomer. The four S and Zn determinations by Kidd, S 31, 32, 32, 38 percent, and Zn [ZnO was stated] 66, 69, 66 and 63 percent, center around ZnS (with S 32.9 and Zn 67.1). The locality was given by Kidd only as one of the Gwennap mines, Cornwall. Sowerby stated that it was " . . . said to occur at Huel Unity and one or two other mines . . . " in Cornwall. This
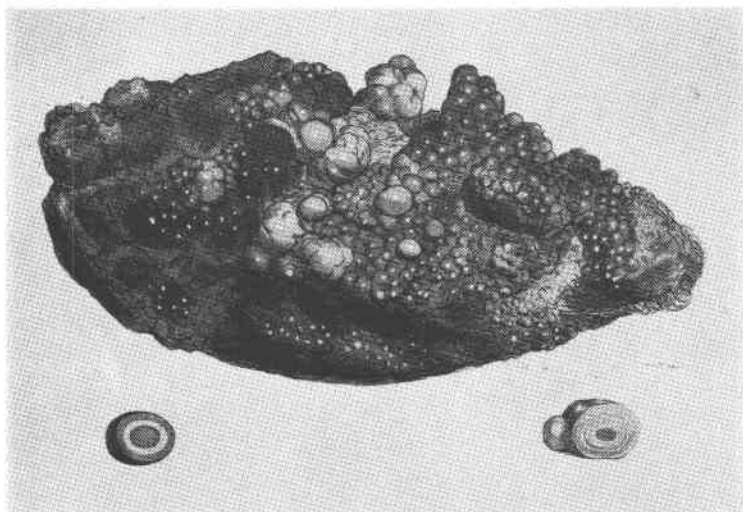

Fig. 3. Reproduction of the colored drawing of Oxy-Sulfide of Zinc from Cornwall given by Sowerby (1839). Scale not given; actual size probably 3 or 4 inches across.

or a similar specimen from Cornwall was later reported by Breithaupt (1838) to contain carbon, lending interest to some of the details of Kidd's description. The mineral forms light to dark brown botryoidal crusts with concentric layering, and is very brittle. The luster is waxy to silky, and sometimes iridescent. It is violently soluble in HNO_3; also soluble in HCl leaving a small residue (called S by Kidd, but presumably something else). The mineral loses about 1 percent H_2O on heating. Specimens of this or a similar material evidently were well known at the time. Levy (1837) mentions numerous examples in his catalogue of the Heuland collection. Greg and Lettson (1858) said that a white mammillated, fibrous type of sphalerite occurred at Huel Unity and Fowey Consols, Cornwall.

In 1838, A. Breithaupt described three occurrences of botryoidal zinc sulfide that contained a hydrocarbon. He was unaware of the work of Fournet and proposed the name leberblende, in allusion to the liver-like color, for the mineral. On heating in a closed tube, his material turned dark gray in color and afforded an odor likened to that of coal-tar. The intensity of the odor varied in specimens from the cited localities: Marienberg, the Hochmuth mine in Geier, and England. The heated, dark colored material was shown qualitatively by K. F. Plattner to contain carbon. The behavior of the fresh mineral in acids was not described, but it was noted that the heated material dissolved in HNO_3 to leave a residue consisting of free sulfur and carbon. Breithaupt did not describe the blackening as the result of the carbonization of a hydrocarbon and considered the mineral to be a zinc sulfocarbide. Berzelius in commenting on this work in his Jahresbericht of 1840 thought that the substances were mixtures of ZnS with Erdpech-bitumen or a similar carbonaceous substance. No quantitative chemical analyses were made. Qualitative tests showed the presence of Zn, S, a little Fe and a small amount of H_2O. The specimens from the three localities consisted of botryoidal and reniform crusts, wax yellow to chestnut brown in color and translucent, that had concentric growth bands. Breithaupt said the substance was of a porodic (amorphous) nature. Samples are brittle, with specific gravity 3.68–3.78.

In 1863, Breithaupt drew attention to three additional occurrences of leberblende, and commented there was no doubt that this substance was one and the same with voltzite. He was undecided whether the carbon was an essential or an admixed constituent. The new occurrences included the Vereinigte Feld mine at Johanngeorgenstadt, the Eliaszeche at Joachimsthal, and Bernkastel on the Moselle. No quantitative chemical analyses were made.

Stibnite crystals from Felsöbanya sometimes are encrusted with a zinc sulfide, called wurtzite by Laspeyres (1884), that forms botryoidal and spherulitic aggregates. The material is honey yellow to orange yellow in color. On heating in a closed tube it loses water and decrepitates, darkens in color, blackens, and finally turns yellow [ZnO]. It is readily soluble in cold concentrated HCl. G. T. Prior (1890) analyzed some of this material and found Zn 59.22, S 27.85, Sb 2.2 (present as admixed oxide), total 89.27. This gives the Zn/S atomic ratio as 1.04, corresponding to the empirical composition ZnS 84.65, ZnO 3.02. The blackening of the substance by heat is suggestive of the presence of organic matter.

Cesàro (1883) briefly described under the name voltzite an orange-yellow waxy and translucent zinc sulfide, possibly pseudomorphous after stibnite, from an unstated locality. His approximate analysis, made on

a very small sample, gave Zn 67, S 28, rem. 5, total 100. This gives the Zn/S ratio as 1.17 with ZnS 85, ZnO 12.

Under the name schalenblende, F. Becke (1884) described botryoidal and stalactitic crusts of zinc sulfide from Mies, Bohemia. The mineral is yellow brown in color; specific gravity 3.672. An analysis by Heinisch gave Zn 65.84, Cd 1.02, Fe 0.45, S 30.23, gangue 1.11, total 98.65. The (Zn, Cd, Fe)/S atomic ratio is 1.085 corresponding to ZnO 6.60, ZnS 90.23, CdS 1.31 and FeS 0.71. Becke thought that the substance could be a mixture of ZnS and Zn_5S_4O, but no evidence of admixture was detected under the microscope. The material consisted of birefringent, optically positive fibers with parallel extinction. No observations were stated by Becke that bear on the possible admixture of an organic compound. Gerstendörfer (1890) gave further details of the occurrence and association. The color was noted to vary from black to dark brown, yellow brown, yellow and light to dark green. The material is translucent to opaque, with an iridescent tarnish, and is easily soluble in cold acid.

The occurrence of supposed voltzite at the Elias mine, Joachimsthal, was first described by J. Lindacker in 1853. The mineral formed botryoidal and reniform crusts of straw yellow, brownish red and greenish white colors. It has a fatty luster and is translucent. The specific gravity is 3.5–3.8. On heating, the mineral decrepitates violently. A chemical analysis gave Zn 69.08, S 27.47, total 96.55. The Zn/S atomic ratio is 1.23, corresponding to ZnS 83.5, ZnO 16.3. Lindacker's description does not afford evidence bearing on the presence of organic matter, but Breithaupt (1863) placed the occurrence at Joachimsthal with his leberblende. Zepharovich (1859) said that voltzite occurred in the Elias mine as half-spheroidal, small-reniform and stalactitic masses, often coated with pyrite, and was associated with leberblende. E. Bertrand (1881) found on optical study that a specimen consisted of microscopic hexagonal prisms, with cleavage angles of 120°; birefringent and optically positive. This corresponds to wurtzite. A. A. Moss[1] found material from the Elias mine to have a Zn/S atomic ratio of 0.97; the remainder was largely made up of As. Hey (1955) cites Moss and gives the composition of voltzite in the general sense as $(Zn,As)S$ or $Zn(As,S)$.[2] E. S. Larsen (1921) found a specimen from the Elias mine to consist of fibers with rather strong birefringence, uniaxial positive, with n about 2.03. This value is below those of ordinary sphalerite and wurtzite low in Fe. The mineral was said to alter in index liquids containing methylene iodide, sulfur and arsenic trisulfide, with accompanying decrease in birefringence and in-

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[1] Personal communication, October, 1958. See also Moss (1955).

[2] Schroll (1953) has shown that As is a common minor element in wurtzite (including schalenblende) and sphalerite, ranging over 1 percent.

crease in index of refraction (to above 2.20 in one instance). It seems that several different substances from Joachimsthal have been referred to as voltzite.

A dense type of zinc sulfide containing organic matter occurs at Wiesloch, Baden, as stalactites and banded crusts of yellow, gray, and brown color. It is in part interlayered with marcasite and galena. Schmidt (1881) observed that small fragments when heated over 400° gave both an aromatic and a grease-like organic odor and bleached in color. Analyses are lacking.

Sandberger (1889) described greenish brown fibrous crusts of supposed zinc oxysulfide from Brilon, Westphalia. The specific gravity is 4.05. An analysis by Petersen gave Zn 65.09, Cd tr., Cu 0.32, Fe 0.56 (Li,Na,Ca, Mg) 0.70, S 30.04, SO_3 0.10, "oxygen" 3.19, total 100.00 percent. Some goslarite and other impurities are present. After deducting Zn for the SO_3, the analysis corresponds to (Zn,Fe,Cu)S 91.4, ZnO 6.6. Sandberger noted in this connection that Li generally is present in the botryoidal, layered types of zinc sulfide.

Stache (1876) reported voltzite from Djebel Recas, Tunisia, but gave no description.

Summary and Conclusions

The occurrence of sphalerite and wurtzite as botryoidal, mammillary and reniform aggregates is well known. In cross-section the crusts typically show a concentric banding or growth-zoning, in which both the color and particle size may vary. The color zoning may be related to both particle size and the substitution of Fe for Zn; admixed foreign material may be a further factor. In fibrous crusts, the fibers are perpendicular to the growth bands. When the radius of curvature is small, the fiber orientation is radial and gives a spherulitic appearance in section. The particle size ranges from grains of fibers visible to the unaided eye, as in most of the so-called schalenblende,[1] through microscopic to submicroscopic dimensions. Decrease in particle size is in general accompanied by a decrease in the specific gravity and the index of refraction, as compared to coarsely crystallized sphalerite and wurtzite, and by an increase in the content of nonessential water. The observations of Prior (1890) and of many others also indicate that the rate of attack by HNO_3 and HCl is greater than in ordinary sphalerite and wurtzite. These types of zinc sulfide in general occur in near-surface deposits, where they have formed under essentially ordinary conditions of temperature and pressure. In some instances they occur in the deeper part of the zone of oxidation and are supergene in origin.

[1] For a detailed description of typical material see Ehrenberg (1931).

The material from both Rosiers and Sterling Hill is similar to the microcrystalline types of zinc sulfide mentioned above. It is distinguished from them by the presence of an organic component. The organic component is present in an extremely fine state of subdivision, as is indicated by the coherent pseudomorphous nature of the residue left by acid. For this reason there is no obvious evidence of admixture, aside from the variation in the content of organic material in different zones, especially in the Rosiers material. The observed variation in index of refraction and other characters of the zones is shown also by ordinary botryoidal crusts of sphalerite and wurtzite and is primarily a function of particle size and water content. It is unlikely on crystallochemical grounds that a substance of the bulk composition observed would form a homogeneous phase crystallizing with the structure and cell dimensions of wurtzite or sphalerite. The substance is believed to be a mixture, probably representing a coprecipitated gel. The distinguishing qualitative reactions are primarily the carbonization that takes place when it is heated with limited access of air and the production of an organic odor on heating. The unusual vigor of the attack by concentrated HNO_3 probably reflects the presence of oxidizable organic material in addition to the small particle size.

The admixed component in the Sterling Hill material is an organometallic compound of zinc, which probably accounts for the excess of Zn over S in atomic ratio of the bulk analysis. This also appears to be the case with the material from Rosiers, judging from observations made by Fournet, but confirmation is desirable. It is also possible in a general sense that organic material not containing zinc can occur in admixture. A review of the literature reveals numerous occurrences of botryoidal sulfide in which the presence of organic material has been established directly or is indicated by qualitative reactions.[1] In none of these instances, however, is there analytical evidence to establish the Zn/S atomic ratio. In other instances, analyses indicate an excess of Zn over S in atomic ratio, but in none has an organic component been sought experimentally.

It is known that small amounts of O can substitute for S in synthetic zinc sulfide, from the work of Kroeger and Dikhoff (1952), Bundel (1956), Skinner and Barton (1960) and others. The substitution increases the unit-cell dimensions. The maximum solubility is about 0.7 weight per-

[1] Analyses of sphalerite and wurtzite crusts from 19 localities, using standard gas absorption techniques (by S. M. Nagy, Microchemical Laboratory, Massachusetts Institute of Technology), showed carbon to be present in amounts significantly greater than the experimental error only in the powdery "brunckite" from Cercapuquio, Bolivia, with 0.51 percent C, and in botryoidal wurtzite from Welkeroth, Nassau, Germany, with 0.50 percent C. Hüttner (1905) found sphalerite to lose CO and H on heating at 800°–850°C.

cent ZnO in synthetic sphalerite and 1.0 weight percent in synthetic wurtzite. These values were obtained by equilibrating ZnS and ZnO at 800°–1150°C. Thermodynamic calculations indicate that the solubility under equilibrium conditions at ordinary temperatures and pressures should be extremely small. Analyses by Skinner and Barton (1960) of three natural sphalerite specimens, two of supergene and one of hydrothermal origin, support this finding. The very small solubility of O in ZnS casts further doubt on the natural occurrences of supposed zinc oxysulfide for which analyses are available. Aside from Sterling Hill (ZnO 6.83) and Rosiers (ZnO 21.45), which have been explained as mixtures, these include Mies (ZnO 6.60), Felsöbanya (ZnO 3.02), Brilon (ZnO 6.6), Joachimsthal (ZnO 16.3) and Cesàro's unstated locality (ZnO 12). Further study of this material is desirable, particularly with regard to the presence of organic material.

Zinc oxysulfides containing 25 atomic percent or more of ZnO have been reported as smelter products and as synthetic preparations by Arfvedson (1824), Fournet (1833), Kersten (1829, 1845) and Berthier (1839). Crystals of the supposed oxysulfide of Kersten (1829) were described by Breithaupt (1839). The existence of these substances is very doubtful, as was indicated by Rammelsberg (1845), and at least some represent mixtures.

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