Mercury and Other Trace Elements In Sphalerite and Wallrocks From Central Kentucky, Tennessee And Appalachian Zinc Districts

GEOLOGICAL SURVEY BULLETIN 1252-F

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By JANICE L. JOLLY *and* ALLEN V. HEYL

CONTRIBUTIONS TO ECONOMIC GEOLOGY

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A discussion of the mercury, cadmium, germanium, gallium, and strontium content of sphalerite from ore deposits of the Central and Eastern United States

UNITED STATES GOVERNMENT PRINTING OFFICE, WASHINGTON : 1968

UNITED STATES DEPARTMENT OF THE INTERIOR

STEWART L. UDALL, *Secretary*

GEOLOGICAL SURVEY

William T. Pecora, *Director*

For sale by the Superintendent of Documents, U.S. Government Printing Office
Washington, D.C. 20402 - Price 25 cents (paper cover)

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MERCURY AND OTHER TRACE ELEMENTS IN SPHALERITE AND WALLROCKS FROM CENTRAL KENTUCKY, TENNESSEE, AND APPALACHIAN ZINC DISTRICTS

By JANICE L. JOLLY and ALLEN V. HEYL

Abstract

Sphalerite samples collected from the central Kentucky and central Tennessee districts and from a selection of other mineral deposits in the Central and Eastern United States contain anomalous amounts of mercury. Mercury is present as an integral part of sphalerite in amounts ranging from 100 to 300,000 parts per billion. Sphalerites from central Kentucky, central Tennessee, and from one locality in North Carolina contain the most mercury. Sphalerites from east Tennessee, other Appalachian Valley, and Upper Mississippi Valley zinc districts contain less mercury than those from central Kentucky, central Tennessee, and several eastern hydrothermal vein and massive sulfide deposits in metamorphic rocks.

The sphalerites of the central Kentucky and central Tennessee vein districts contain notable amounts of cadmium, germanium, and gallium, which along with mercury may possibly be recovered by smelters if sphalerites are mined in the future. These sphalerites also contain strontium, whereas this element is lacking in sphalerites analyzed from other districts. Sphalerites of the Appalachian Valley contain less germanium and cadmium than do those of the central Kentucky and central Tennessee veins. Even so, the cadmium content is relatively high in all sphalerites analyzed as compared with the content of those from other mineralized regions in the United States and Canada. Except for higher mercury content, sphalerites collected from Triassic border-zone deposits in Pennsylvania and Connecticut are similar in trace-element content to the Appalachian Valley sphalerites, whereas the higher temperature New England vein and massive sulfide sphalerites, which contain 5 to 10 percent iron, either completely lack or contain very little germanium or gallium.

Scattered preliminary analyses show that several minerals, soils, and wallrocks in mineral deposits in Central and Eastern United States also contain anomalous mercury. The mercury content of wallrock at the Faircloth vein in central Kentucky, at the Hoover vein in central Tennessee, and at a major ore body in the Mascot–Jefferson City belt of east Tennessee suggests the presence of detectable mercury leakage anomalies; such anomalies may be used effectively in prospecting for lead-zinc deposits.

INTRODUCTION

This paper describes in detail the first published occurrences of mercury in mineral deposits east of the Mississippi River. Until recently mercury was never considered a significant trace element in the lead and zinc deposits of the Central and Eastern United States. Preliminary observations on mercury in central Kentucky and central Tennessee sphalerites were presented by us (Jolly and Heyl, 1966) in a paper given at the 1964 Southeastern Section meeting of the Geological Society of America at Nashville, Tenn. The present paper is a product of research by members of the U.S. Geological Survey on the mineral deposits of the Central and Eastern United States from 1960 to 1967. The sphalerite and wallrock specimens analyzed were collected by Allen V. Heyl, Janice L. Jolly, and Maurice Brock in 1960, 1962, 1964, 1965, and 1966.

Only a few authentic natural occurrences of mercury east of the Mississippi River were known in 1964. Mercury was reported in a prospect adit near Vienna, Mo. (Roscoe Smith, oral commun., 1964), sampled by the U.S. Geological Survey and assayed by the U.S. Bureau of Mines. A channel sample of the face contained 0.01 to 0.005 percent mercury. W. S. White (oral commun., 1964), in checking a report of mercury associated with native silver in Michigan, had two samples analyzed from White Pine, Mich. The two samples of native silver contained 0.44 percent (98.5 percent silver) and 0.27 percent (68.5 percent silver) mercury.

Nearly all the other reported occurrences of mercury in the Central and Eastern United States are unsubstantiated, or the mercury in the occurrences is probably of artificial origin. There are a few unsubstantiated reports of metallic mercury placers in Michigan and along the Ohio River in the literature of the early 1800's (Cleaveland, 1822, p. 552). Free mercury in clay was reported by C. B. Strow in a freshly dug basement in Kanawha County, W. Va. Subsequent examination by the U.S. Bureau of Mines (written commun., 1942) revealed the presence of calomel(?) and cinnabar(?); one sample of clay assayed as much as 0.3 percent mercury. Samples 10 feet away, however, contained no mercury. The reason for this local accumulation of mercury is not known, and its presence here as a natural occurrence was subject to much debate. Native mercury also was reportedly found in a basement in Nashville, Tenn. (R. A. Laurence, oral commun., 1964). Probably both of these last two occurrences are

of recent human origin from some unexplained sources of waste mercury.

The absence of naturally occurring minerals such as cinnabar, metacinnabar, and calomel north and east of Arkansas may reflect the deep erosion of rocks and ore deposits and the greater age of the mineral deposits in this area than in those to the west. All mercury reported in this paper is in the form of trace amounts in minerals or in wallrocks of ore deposits.

Mercury has long been used as a geochemical prospecting tool (Hawkes and Webb, 1962; Saukov, 1946; Williston, 1964). Case histories of prospecting on the basis of anomalous trace concentrations of mercury have been published in the U.S.S.R. (Saukov, 1946; Vershkovskaya, 1956; Fursov, 1958; Ozerova, 1959) and recently in the Western United States where similar methods have been utilized (Brokaw and others, 1962; Friedrich and Hawkes, 1966). The recent development of more precise methods of measurement, accurate to 1 to 2 ppb (parts per billion) mercury, is certain to make mercury even more valuable as an indicator of base-metal ores.

Mercury is not commonly considered as a potential byproduct where it occurs as a minor element in lead-zinc deposits. At Langpele mine, Sweden, however, mercury is currently recovered from sphalerite that commonly contains 0.1 to 0.2 percent mercury. Chiefly a lead-zinc district, Langpele is nevertheless one of the largest sources of mercury in the world (Erland Grip, oral commun., 1966; Gavelin, 1955, p. 823).

ACKNOWLEDGMENTS

The assistance of many individuals in the preparation of this study is gratefully acknowledged. Members of the Kentucky Geological Survey and the Tennessee Division of Geology and R. A. Doyle, State Geologist of Maine, were of particular help. The assistance of Douglas Black, M. R. Brock, A. R. Taylor, Richard Lewis, W. E. Hall, R. A. Laurence, George Simmons, J. D'Agostino, D. Cox, and Helmuth Wedow of the U.S. Geological Survey, as well as many private company geologists, especially from the New Jersey Zinc Co., American Zinc Co., Dennison Mines, Ltd., Callahan Mining Co., Tri-State Zinc Co., Ozark-Mahoning Co., and Eagle Picher Co., was of great value. The special efforts of Joseph Dinnin and Helen Worthing of the U.S. Geological Survey in developing new and more accurate chemical and spectrographic methods of analysis were notably helpful in the success of the study.

METHODS OF ANALYSIS

Special refinements were made in each method of analysis used, which included wet chemical (Dinnin and Worthing, 1966), atomic absorption, and special spectrographic procedures. Agreement (table 1) between different methods of analysis on the same sample was good for some samples and poor for others. The reasons for this are the many difficulties encountered in handling mercury-bearing sulfides, as well as variable limits of sensitivity between methods. Although the technical aspects of analytical methods are not an objective of this paper, some problems inherent in mercury analysis should be mentioned.

Most important to any method is the recognition of the relation of the mercury to its host mineral. Fryklund and Fletcher (1956, p. 227), Stoiber (1940), and Friedrich and Hawkes (1966) have considered mercury as among the elements likely to substitute for part of the sphalerite lattice. Our information also indicates that the mercury in sphalerite of these districts is held in the lattice. It is probably incorporated by coprecipitation and does not occur as a separate included or intergrown mineral such as cinnabar or metacinnabar. Several reasons for this conclusion are as follows:

1. No mercury minerals are known in the districts.
2. X-ray diffraction traces showed the presence of not two but one mineral that has sphalerite structure.
3. No foreign mineral was observed in microscope examination of slides and polished sections.
4. Microchemical tests of the coarsely crushed but not powdered sphalerite did not free any mercury but were negative, as expected if the mercury was a part of the lattice.

Fryklund and Fletcher (1956) and Oftedal (1940) indicated that mercury as a component of natural sphalerite reacts differently to the spectroscopic arc as compared with mercury in the compound mercuric sulfide mixed into a synthetic standard. The mercury held in the sphalerite lattice is less volatile and burns longer, presenting a problem to accurate spectroscopic analysis.

Friedrich and Hawkes (1966) also recognized the inherent difficulties in analyzing sulfides and probably many rock-forming silicates for mercury. On this problem they stated: "* * * mercury substitutes for other elements and therefore can be extracted only after destruction of the lattice. The tightly bound mercury in these minerals is released much more slowly and at a variable rate." After destruction of the lattice, Friedrich and Hawkes used

a gold filter trap as an extra step in their method of analysis to avoid this problem.

Variant results for two separate handpicked parts of the same sample may also indicate that the mercury is not evenly distributed throughout the mineral. The amount of grinding in sample preparation and the conditions under which the sample is stored also might attribute to a variant assay. Mercury has been detected evaporating from recently ground sphalerite samples (F. N. Ward, oral commun., 1965). Such losses by leakage can be held at a minimum only if the sample is ground immediately prior to analysis. Without these special precautions, mercury analyses of sulfides such as sphalerite probably should be regarded as semiquantitative.

Mercury fulminate, used in blasting caps and certain other explosives, is another possible major source of contamination of samples from fairly recent mines (W. H. Callahan, oral commun., 1966) and from roadcuts in which the chemical is used for explosives. Unusual care should be taken to obtain unfractured clean samples with entirely fresh surfaces to minimize such contamination.

MERCURY IN SPHALERITE

Mercury has been reported in sphalerite from several sources, many of which were compiled by Fleischer (1955) in a paper on minor elements in some sulfide minerals. In Europe, mercury has been reported in sphalerite from Austria (Schroll, 1950–51; 1953); Bohemia (Kutina, 1953; Yak, 1951); France, the Mediterranean area, and northern Africa (De Launay and Urbain, 1910); Spain (Pina de Rubies and Lopez de Azcona, 1937); Norway (Oftedal, 1940); and Sweden (Gabrielson, 1945).

Sphalerite that contains mercury has also been reported from the Soviet Union (Saukov, 1946). Fursov (1958) described a mercury anomaly derived from oxidation of mercury-rich sphalerite and galena. The mercury was considered an "isomorphous admixture," in both ore and wallrock, as no mercury sulfides were known in the deposit. Ozerova (1959) in the Karatu district also reported mercury aureoles around lead-zinc deposits derived from mercury-bearing sphalerite, galena, tetrahedrite, and barite. Ozerova (1959, p. 799) concluded that mercury is present probably as a "diadochic substitute" in all minerals.

In the United States, mercury has been reported as a minor element in sphalerite from the Coeur d'Alene district of Idaho

(Fryklund, 1964; Fryklund and Fletcher, 1956); Leadville, Colo. (Bartlett, 1889); and Cripple Creek, Colo. (Eckel, 1961). In the Coeur d'Alene district, mercury substitutes for zinc in amounts from 0.005 to 0.02 percent and averages 0.0095 percent. Other than tetrahedrite, which contains less than 0.01 percent mercury, no other mercury-bearing mineral is known in that district (Fryklund and Fletcher, 1956, p. 227). At Cripple Creek, Colo.,

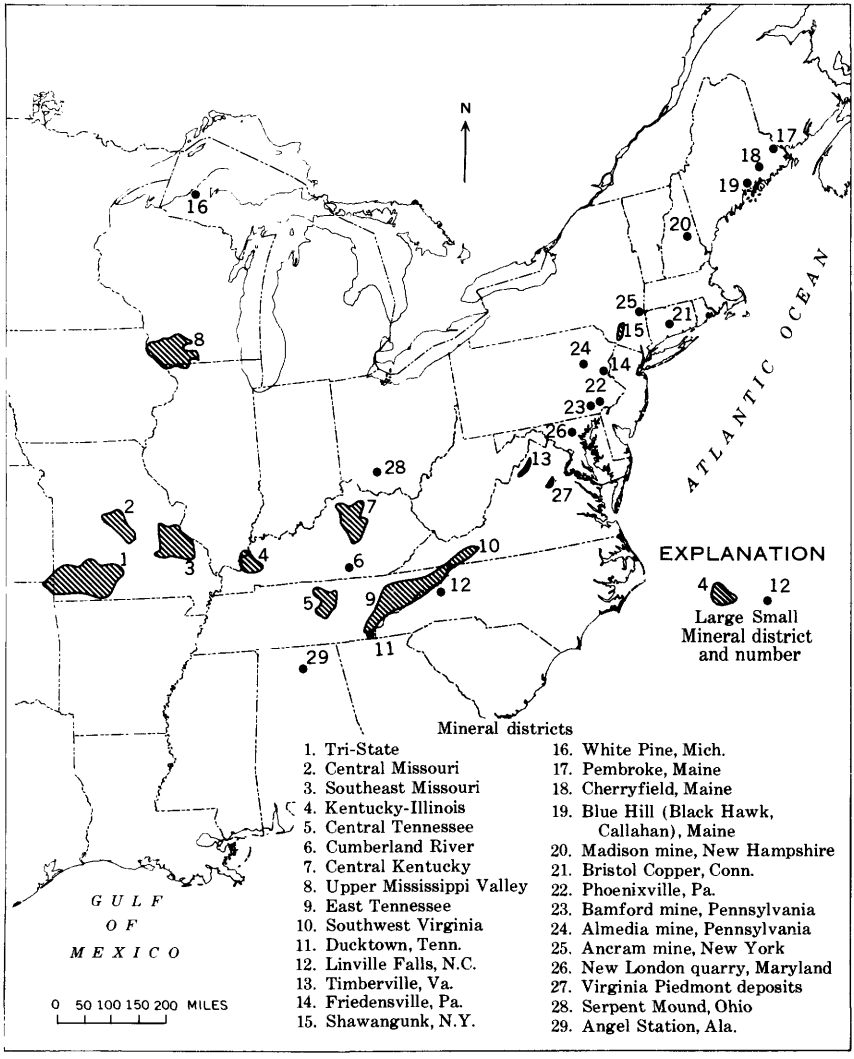

FIGURE 1.—Mineral districts in Central and Eastern United States from which mercury-bearing samples were obtained.

one small specimen suggests the complete replacement of a sphalerite crystal by cinnabar.

Analyses of 76 sphalerite samples from mineral districts in the Central and Eastern United States show anomalous mercury content (table 1). Figure 1 shows the location of these mineral districts. Mercury occurs in amounts ranging from 100 to 300,000

TABLE 1.—*Mercury content of sphalerite from Central and Eastern U.S. mineral districts*

[Number in parentheses after mine or district name indicates index number shown in fig. 1. Letter in parentheses following the mercury analysis value indicates separate parts of hand-picked specimens; letter may be repeated under the separate analytical methods, indicating a split of the same part of a specimen. Spectrographic analyses: N.D., none detected (less than 5,000 ppb); <5,000, between 4,000 and 4,999 ppb]

Location and description	Mercury content, in parts per billion		
	Wet chemical analyses [1]	Spectrographic analyses [2]	Atomic absorption methods [3]
Appalachian Valley zinc districts			
Pennsylvania:			
Uberroth mine, Friedensville (14), Lehigh County, Beekmantown Group			
Massive gray sphalerite	----------	N.D.	----------
Bamford zinc mine (23), Lancaster County, Kinzers Formation			
Gray sphalerite	----------	15,000	----------
Almedia mine (24), Columbia County, in Devonian dolomite			
Brown sphalerite	----------	5,000	----------
Virginia:			
Bowers-Campbell mine (13), Rockingham County, Beekmantown Dolomite			
Dark sphalerite	----------	----------	100
Bowers-Campbell mine (13), Rockingham County, Beekmantown Dolomite			
Yellow sphalerite	----------	N.D.	----------
Old Timberville mine (13), Rockingham County, Beekmantown Dolomite			
Yellow sphalerite	----------	7,000	----------
Ivanhoe mine (10), Austinville district, Wythe County			
Brown sphalerite	1,100	----------	----------
Arcadia zinc mine (10), Scott County, Kingsport dolomite			
Black sphalerite	----------	5,000	----------
Myers prospect (10), Smyth County, Beekmantown Dolomite			
Yellow sphalerite	----------	<5,000	----------
East Tennessee:			
Mascot mine (9), Knox County, Kingsport Formation			
Dark-banded sphalerite	----------	N.D.	----------
Yellow sphalerite	----------	N.D.	----------
Young mine (9), Jefferson County, Kingsport Formation			
Yellow sphalerite	----------	N.D.	----------
New Jersey Zinc Jefferson City mine (9), Jefferson County, Kingsport Formation			
Yellow sphalerite			
Flat Gap mine (9), Hancock County, Kingsport Formation	----------	5,000	----------
Dark colloform sphalerite	----------	N.D.	----------
Yellow sphalerite	----------	N.D.	----------
Very pale yellow sphalerite	----------	N.D.	----------
New Prospect mine (9), Union County, Maynardville Limestone Member			
Colloform yellow—dark gray sphalerite	----------	N.D.	----------
Shiloh prospect (9), Hawkins County, Kingsport Formation			
Orange-yellow sphalerite	----------	5,000	----------

See footnotes at end of table.

TABLE 1.—*Mercury content of sphalerite from Central and Eastern U.S. mineral districts*—Continued

Location and description	Mercury content, in parts per billion		
	Wet chemical analyses [1]	Spectrographic analyses [2]	Atomic absorption methods [3]
Appalachian Valley zinc districts—Continued			
East Tennessee—Continued			
Ballard mine, Sweetwater (9) district, Monroe County, Kingsport Formation			
Pale-yellow sphalerite	----------	5,000	----------
Jackson mine, Embreeville (9) district, Washington County, Shady Dolomite			
Brown sphalerite	----------	5,000	----------
North Carolina:			
Linville Falls prospect (12), McDowell County, Shady Dolomite			
Bluish-gray sphalerite	----------	300,000	----------
Mississippi Valley mineral districts			
Central Tennessee:			
Hoover vein (5), Cannon County, Carters Limestone			
Dark sphalerite	390 (a)	----------	350 (b)
Red-orange sphalerite	700	----------	----------
Red-orange sphalerite	300	----------	----------
Oakley vein (5), Wilson County, Carters Limestone			
Dark sphalerite in second-stage barite	12,500 (a)	----------	----------
	3,500 (b)	----------	----------
Holt vein (5), Williamson County, Carters Limestone			
Dark sphalerite	----------	30,000	----------
Vickers vein (5), Dekalb County, Catheys Limestone			
Dark sphalerite	----------	300,000	----------
Central Kentucky:			
Zone 1: Allender vein (7), Woodford County			
First-stage dark sphalerite	300	N.D.	----------
First-stage dark sphalerite	300 (a)	----------	500 (b)
Second-stage yellow-black sphalerite	24,500 (a)	----------	----------
	28,000 (b)	----------	----------
	130,000 (c)	----------	----------
Second-stage yellow-black sphalerite	170,000	----------	----------
Zone 2: McChord vein (7), Fayette County			
Second-stage yellow-black sphalerite	500	----------	1,800
Zone 3: Camp Pleasant vein (7), Franklin County			
Yellow-black sphalerite	7,800 (a)	----------	----------
	8,100 (b)	30,000 (b)	----------
Georgetown quarry vein (7), Scott County			
Yellow-black sphalerite	17,800–18,000 (a)	----------	----------
	37,500 (b)	100,000 (b)	6,500 (c)
Gratz vein (7), Cox prospect, Henry County			
Second-stage yellow-black sphalerite	170,000	----------	----------
Gratz vein, Ohio shaft, Owen County			
Second-stage yellow-black sphalerite	180,000 (a)	200,000 (b)	----------
Gratz vein, Twin Valley mine, Owen County			
First-stage yellow-black sphalerite	1,000 (a)	----------	----------
	1,100 (b)	----------	425 (c)
Second-stage yellow-black sphalerite	120,000	----------	----------
Milner vein (7), Woodford County			
Second-stage yellow-black sphalerite	1,000	5,000	----------
Purdy vein (7), Bourbon County			
Second-stage yellow-black sphalerite	1,000 (a)	----------	250 (b)
Third-stage red-orange sphalerite	200 (a)	----------	450 (b)
Illinois-Kentucky fluorspar district			
Southern Illinois:			
Oxford mine (4), Cave-In-Rock, Hardin County			
Brown sphalerite	----------	----------	20,000
Deardorf mine (4), Cave-In-Rock, Hardin County			
Dark-brown sphalerite	----------	----------	100

TABLE 1.—*Mercury content of sphalerite from Central and Eastern U.S. mineral districts*—Continued

Location and description	Mercury content, in parts per billion		
	Wet chemical analyses [1]	Spectrographic analyses [2]	Atomic absorption methods [3]
Upper Mississippi Valley district			
Northern Illinois:			
Bautsch mine (8), main shaft-pitch, Galena, Jo Daviess County			
Brown sphalerite	----------	----------	250
Amelia mine (8), Galena, Jo Daviess County			
Reddish-brown sphalerite	----------	----------	150
Wisconsin:			
Old Dodgeville mine (8), Dodgeville, Iowa County			
Sphalerite	----------	----------	300
Hoskins mine (8), New Diggings, Lafayette County			
Sphalerite	----------	----------	425
Belmont Mound (8), Iowa County			
Sphalerite in Silurian limestone	----------	----------	1,000
Thompson-Temperly mine (8), New Diggings, Lafayette County			
Sphalerite	----------	----------	100
Piquette No. 2 mine (8), Tennyson, Grant County			
Sphalerite	----------	----------	700
Tri-State district			
Oklahoma:			
Blue Goose mine (1), Cardin, Ottawa County, 1,200 feet from trough			
Sphalerite	----------	----------	1,000
Webber mine (1), north of Picher, Okla., in Cherokee County, Kans.			
Sphalerite	----------	----------	650
Maine sulfate districts			
Maine:			
Dolsan Mines Ltd., Pembroke, Washington County, Ellsworth Schist			
Discovery pit (17), Pb–Zn veins in diabase			
Black sphalerite	----------	----------	40,000
Spanish pit (17), Pb–Zn veins in fractured diabase and agglomerate			
Black sphalerite	----------	----------	34,000
Big Hill pit (17), Zn–Pb–Ag veins in fractured volcanic agglomerate			
Black sphalerite	----------	----------	5,400
Cherryfield prospect (18) (Cu, Pb, Zn, Ag), Washington County, Ellsworth Schist			
Veins in sheared diabase			
Black sphalerite	----------	----------	5,400
Callahan mine (19) (Cu, Zn, Pb), Hancock County, Ellsworth Schist			
Massive red sphalerite and chalcopyrite in talc schist			
Red sphalerite	----------	----------	5,400
Black Hawk mine (19) (Cu, Zn, Pb, Ag, Au), Hancock County, Ellsworth Schist			
Massive sphalerite zone in fragmental quartzite			
Black sphalerite	----------	----------	32,000
New England–Pennsylvania veins			
New Hampshire:			
Madison mine (20) (Pb, Zn), Carroll County			
Mineralized fracture zone in granite of White Mountain Plutonic-Volcanic Series			
Dark-brown sphalerite	----------	----------	11,000
Connecticut:			
Bristol Copper mine (21), Hartford County, Triassic Newark Group			
Brown sphalerite	----------	----------	30,000
Pennsylvania:			
Wheatley mine (22), Phoenixville district, Chester County, Wissahickon Formation			
Pb–Zn veins in gneiss and pegmatite and Triassic shale			
Brown sphalerite	----------	20,000 (a)	17,000 (b)

TABLE 1.—*Mercury content of sphalerite from Central and Eastern U.S. mineral districts*—Continued

Location and description	Mercury content, in parts per billion		
	Wet chemical analyses [1]	Spectrographic analyses [2]	Atomic absorption methods [3]
New England–Pennsylvania veins—Continued			
New York:			
Ancram Ag–Pb mine (25), Dutchess County			
Black sphalerite	----------	70,000	----------
Otisville Pb mine (15), Orange County, Shawangunk Conglomerate			
Brown sphalerite	----------	50,000	----------
Virginia–Maryland Piedmont deposits			
Maryland:			
New London marble quarry (26), Frederick County, Wakefield Marble			
Gray sphalerite	----------	10,000	----------
Virginia:			
Dumfries mine (27), Louisa County, Wissahickon Formation			
Black sphalerite	----------	15,000	----------
Valzinco mine (27), Spotsylvania County, Wissahickon Formation			
Black sphalerite	----------	<5,000	----------
Armenius mine (27), Louisa County, Wissahickon Formation			
Black sphalerite	----------	30,000	----------
Serpent Mound and other Ohio deposits			
Ohio:			
Serpent Mound (28), Adams County, Silurian and Devonian dolomite			
Yellow sphalerite	----------	N.D.	----------
Smith quarry, Highland County, Greenfield Dolomite Member of Silurian age			
Pale-brown sphalerite	----------	<5,000	----------

[1] By special procedures (Dinnin and Worthing, 1966); U.S. Geol. Survey analyst, J. I. Dinnin, 1964, 1965, and 1966.
[2] By special procedure (Dinnin and Worthing, 1966); U.S. Geol. Survey analyst, H. W. Worthing, 1965.
[3] U.S. Geol. Survey analyst, J. H. McCarthy, 1964; W. W. Janes, 1967.

ppb in the sphalerites of these districts. Most of the samples given in table 1 contain mercury well above the average background values for limestone and sandstone wallrock. A few of the samples are listed as mercury not detected, below 5,000 ppb mercury, which is the lower limit of detection for the specially adapted spectrographic method used. The central Kentucky, central Tennessee, and McDowell County, N.C., sphalerites contain the highest amounts detected. The sphalerites of the Wisconsin lead-zinc district and those collected in the east Tennessee, Virginia, and Pennsylvania Appalachian Valley zinc-mineral districts contain the lowest amounts detected. Although the Linville Falls, N.C., deposit is normally considered part of the Appalachian Valley zinc deposit group, the large amount of mercury in the sphalerite may be an indication that the deposit is anomalous to the group and that it may not have the same genesis. Likewise,

the lack of significant mercury in the Serpent Mound structure, Ohio, sphalerites indicates they are not related to the nearby central Kentucky mineralization.

In the central Kentucky district, where the mineral paragenesis and zoning (fig. 2) is well established (Jolly and Heyl, 1964), it was possible to collect a few specimens to represent each stage and zone. The ore deposits of the central Kentucky district have a districtwide lateral zoning in a concentric pattern. Within each zone three or four stages of mineral deposition occur. Near the middle of the district, two centers of fluorite-calcite dark sphalerite veins are designated Zone 1. Surrounding these centers is a much larger Zone 2, in which nearly all the veins contain fluorite, barite, calcite, and yellow-black sphalerite. Galena is absent or present in only minute quantities in both Zones 1 and 2. In Zone 3, barite, galena, and sphalerite are the principal minerals; fluorite is absent, or present only in traces. Textures of the mineral veins change from bands of course comb crystals in Zone 1 to mostly colloform bands in the outer zones. The mineral paragenesis (fig. 2) throughout the district is constant and traceable, although the relative abundance of minerals varies from vein to vein.

Fourteen sphalerite samples collected from the central Kentucky mineral district contain 200 to 200,000 ppb mercury. More than half the samples contain amounts greater than 8,000 ppb, and five contain more than 100,000 ppb (0.01 percent). This preliminary selection indicates that the highest values of mercury are in the second-stage yellow-black sphalerites of all zones. In contrast, the mercury values of the first and third stage dark and red sphalerites are much lower.

Sphalerites from the mineralized areas of eastern Tennessee all contain 5,000 ppb mercury or less. Sphalerites collected from the Jefferson City mine, Ballard mine, and Jackson mine contain 5,000 ppb mercury, but less is indicated for the yellow and dark sphalerites from the Mascot, Flat Gap, and New Prospect mines. The analyzed sphalerites from the Appalachian Valley zinc deposits of Virginia also contain less than 5,000 ppb mercury. Black sphalerite from the Arcadia mine, Scott County, Va., contains 5,000 ppb mercury. The five samples from the Wisconsin mineral district contain 1,000 ppb mercury or less.

Preliminary analyses of sphalerite-bearing ores from other Appalachian Valley zinc districts and a few nearby districts

	Pre-mineral	Primary minerals				Secondary minerals
		Stage 1	Stage 2	Stage 3	Stage 4	
Shearing	××	×××	×××	×××		
Barite		Gray or white White ?-?	White Gray and pink Chalky	Chalky crusts and crystals		
Fluorite		White-buff	Bluish Clear	Purple		
Sphalerite		Black	Yellow-black	Yellow and red-orange		
Calcite		Stubby crystals, white	Pale lavender Pink or white	Sharp crystals, clear, pink, or white		
Galena						
Ferroan dolomite or ankerite						
Chalcopyrite						
Pyrite				?—?		
Marcasite						
Celestite						
Quartz and jasperoid				?—?		
Gypsum				?—?		?—?
Strontianite				?—?		
Malachite						
Cerussite						
Smithsonite						

FIGURE 2.—Mineral paragenesis in the central Kentucky mineral district. The lines indicate sequence of mineral deposition. Descriptions of some of the more distinctive mineral varieties are given.

suggest that mercury is rather abundant in some of the sphalerite. The districts in which mercury was detected include:

Faber mine, Albemarle County, Va.
Roanoke, Roanoke County, Va.
Osborn mine, Cresswell, Russell County, Va.
Ducktown, Polk County, Tenn.
Angel Station, Calhoun County, Ala.
Shawangunk mine, Sullivan County, N.Y.
Guymard mine, Orange County, N.Y.

For comparison, sphalerites from several higher temperature mineral deposits were also analyzed. These included (see table 1) sphalerites from the massive sulfide deposits of eastern Maine and Virginia and the hydrothermal mineralized veins of New Hampshire, Connecticut, Pennsylvania, New York, and Maryland. The amount of mercury detected in these sphalerites ranges from 5,000 to 70,000 ppb. It would appear that most sphalerites of hydrothermal origin in the Central and Eastern United States contain anomalous mercury as a trace element and that deposition need not have been at low temperature. Deposits that are generally presumed to have magmatic affiliations have sphalerites that contain between 1 and 10 percent Fe (see table 2).

That sphalerites in central Kentucky, Tennessee, and other Appalachian Valley zinc districts—as well as sphalerites in massive sulfide and other known high-temperature hydrothermal deposits—contain mercury in any amount greater than normal background is of general significance to geochemical prospecting. These analyses are presented here to illustrate the strong possibilities of finding mercury anomalies in overlying soils and wallrock, which can be useful in locating blind ore deposits in most of the Eastern United States lead-zinc districts. Further sampling may also show that some districts, such as in central Kentucky and North Carolina, contain sufficient mercury in sphalerites to warrant its recovery as a byproduct.

The presence of mercury as an integral part of sphalerite precludes the supposition that it is the result of a more recent addition by replacement or by pore-space filling. Mercury was probably deposited from the original ore solution, coprecipitating with zinc in the cubic zinc sulfide lattice. In this way, the precipitating mineral "scavenges" (Hawkes, 1957) traces of certain elements from solutions and incorporates them into the crystal lattice. In central Kentucky and central Tennessee, the zinc sulfide that contains the mercury is sphalerite, as established by X-ray, and not wurtzite.

The presence of mercury as an integral trace element in sphalerite suggests that the deposits are hydrothermal (warm water) in origin. Mercury may be transported in ore solutions as a complex ion in slightly alkaline sulfide solutions, as the volatile chloride, or as a mercury vapor (Krauskopf, 1951). The solubility of mercuric sulfide in pure water (pH 7) at 25°C is 1×10^{-17} grams per liter and at 400°C is 3×10^{-15} (Verhoogen, 1938). It also has been reported (Hawkes and Webb, 1962) that when mercury vapor comes in contact with cool ground water, it condenses and cannot move through permeable material that is saturated with water. This fact indicates that pure cool water is incapable of carrying much mercury in solution.

Most workers (Tunell, 1964; Krauskopf, 1951) agree that the temperature of alkaline ore solutions depositing mercuric sulfide must be low, not as low as 80°C, nor as high as 250°C. Krauskopf (1951) stated that mercuric sulfide cannot exist in any system above 250°C that includes moving vapors without high concentrations of mercury or sulfur. It is also doubtful that mercury can exist as a complex sulfide ion in solutions at such temperatures. At temperatures where other sulfides precipitate, mercuric sulfide is unstable, so that its components are forced to travel to a cooler region before the compound can form. Even so, in deposits where mercuric sulfide is not a predominant constituent, it seems evident that mercury can be incorporated or scavenged by other precipitating sulfides (such as tetrahedrite and sphalerite) at a much higher temperature. With further study on the geochemistry of mercury as a minor component of minerals such as sphalerite, mercury may prove useful as a low-temperature geothermometer. Mercury is an element with normally limited physicochemical and temperature capacities, and it seems likely that the reasons for its presence, as well as amount present, as a minor element in other minerals will also show definable limitations.

The available geologic and geochemical data suggest (Jolly and Heyl, 1964) that the central Kentucky veins were deposited at temperatures less than 120°C. Edwin Roedder (written commun., 1967) has studied fluid inclusions in seven samples of fluorite and sphalerite from five mines of the central Kentucky district. They were found to be very similar to the fluid inclusions in most other deposits of the Mississippi Valley type. All 125 inclusions believed to be primary had freezing temperatures below −10°C (as low as −25°C), indicating concentrated brines containing approximately 15 to 35 weight percent salts. A small

group of primary inclusions in the outermost zone of several of the fluorite crystals contained considerably less concentrated brines, in the range of 5 to 10 weight percent salts. Although no homogenization experiments were run, all the inclusions contained small bubbles, indicating low temperatures of formation.

The geochemical data recently provided by Hall and Friedman (1963) from minerals in the Kentucky-Illinois district suggest by analogy that the ore-bearing solutions in central Kentucky and in central Tennessee were heated connate brines, probably mixed with minor quantities of magmatic brines. Districtwide zoning of minerals in a concentric pattern of three established zones (Jolly and Heyl, 1964) also affords critical evidence of heat that was supplied from a possible magmatic source centered deep beneath the Lexington and the Nashville domes. Higher temperatures of deposition in the central Kentucky district are indicated by the abundance of fluorite, dark sphalerite, and comb textures of veins (which are characteristic of epithermal ore deposits) in the central Zone 1 and by their absence in the outer two zones.

CADMIUM, GERMANIUM, AND GALLIUM IN SPHALERITE

The sphalerites of the central Kentucky and central Tennessee lead-zinc-barite-fluorite veins also contain notable amounts of cadmium, germanium, and gallium (table 2), which along with mercury should be considered as potential byproducts at the smelters, should these veins be mined in the future. In 37 semiquantitative spectrographic analyses representing a complete range of sphalerite from all zones in central Kentucky, the average cadmium content is 1.34 percent, the average gallium is 0.009 percent, and the average germanium is 0.028 percent. The average cadmium content of six sphalerite specimens from central Tennessee is 1.3 percent, average gallium is 0.015 percent, and average germanium is 0.02 percent.

According to Warren and Thompson (1945), the average cadmium content of sphalerites of eastern Canada, Newfoundland, Greenland, and the Eastern United States is less than 0.30 percent; that of sphalerites of the Western United States and Mexico is 0.43 percent. The maximum cadmium content in sphalerite reported (Campbell, 1959) is 2.1 percent in Sardinia. Stoiber (1940) stated that the 0.01 to 0.1 percent gallium, which is typical of many of the central Kentucky sphalerites, is higher than any European analyses and most other sphalerites of the Mississippi Valley type. The principal domestic source of ger-

TABLE 2.—*Complete semiquantitative spectrographic analyses of selected mineral*

[Analyses by J. Harris and H. Worthing,

	Sample	Si	Al	Fe	Mg	Ca	Ti	Mn	Ag	Ba
	Central Kentucky									
1	CK-323A	0.01	0.002	0.3	0.002	0.2	0.0003	0.002	0.0003	0.1
2	A1-106A	.001	.001	.3	.001	.1	0	.0003	.0001	1.5
3	TL-94B	.007	.003	.2	.0015	.03	.0005	.0002	.00005	.15
4	Cumb 210	.7	.001	.2	.02	.07	.003	.0005	.0002	.3
5	Boyle-1	.01	0	.1	.005	.003	0	0	0	.0005
	Central Tennessee									
6	Hoov-64-1	.01	.001	.5	.001	.001	0	.0001	0	.015
7	Oak-64-100	.001	.001	.5	.001	.1	0	.0007	0	.5
8	K-64-100A	.7	.001	.15	.02	.3	.003	.0002	0	.015
	Kentucky-Illinois									
9	WH-59-74A	0	0	4.2	0	0	0	.002	.0002	.0002
10	WH-59-53	0	0	1.2	0	0	0	.002	.0002	.0002
	East Tennessee									
11	FG-10	.07	.001	.3	.015	.1	0	0	.0002	.0003
12	T-12	.1	.001	.3	.001	.01	0	0	.007	.0003
	North Carolina									
13	LF-60-1	.03	.001	1	.07	.1	0	.001	.0015	.0003
	Maine									
14	BLK-106-66	2	.02	10	1	.05	.007	.2	.0007	.0003
15	BH-206-66	2	<.001	10	.01	.1	0	.3	.07	.0005
16	IP-106A-66	.3	<.001	7	.02	.07	0	.3	.02	.0003
17	Sul-200-66	1	.01	5	.007	.005	.007	.02	.1	.001
	New England and Pennsylvania veins									
18	Mad-100-66	.15	<.001	1.5	.002	.002	0	.15	.0002	.0005
19	Bris-100-66	.15	<.001	.7	.003	.003	0	.01	.0001	.0003
20	W-201-66	.02	<.001	1	.0015	.001	0	0	.0002	.0003

[1] Mercury analyses are excessive owing to procedures used.
[2] Mercury was detected in these samples by other methods of analysis. See table 1.

1. Faircloth vein ; Stage 1, Zone 1, dark sphalerite.
2. Allender vein ; Stage 2, Zone 1, dark sphalerite.
3. Gratz vein ; yellow-black sphalerite, Stage 2, Zone 3.
4. Cumberland River vein ; Stage 3, Zone 3, red sphalerite.
5. Diagenetic light-colored ZnS, Boyle Dolomite, Panola quadrangle, Kentucky.
6. Hoover vein, dark sphalerite.
7. Oakley vein, dark sphalerite.
8. Knight vein, red-yellow sphalerite.
9. Hutson mine, Kentucky, dark sphalerite.
10. Deardorff mine, Illinois, sphalerite.
11. Flat Gap mine, Hancock County, yellow sphalerite.
12. Jefferson City mine, Jefferson County, yellow sphalerite.

sphalerites from the central Kentucky, central Tennessee, and other districts

U.S. Geol. Survey. Values are in percent]

Cd	Cu	Ge	Hg [1]	Ni	Pb	Sr	Ga	Co	Mo	Sn	In
Central Kentucky											
0.5	0.5	0.03	0	0	0.2	0.01	0.02	0	0	0	0
2.0	.3	.05	.3	.0015	.2	.05	.01	0	0	0	0
2.0	.5	.03	1	0	.07	.02	.03	0	0	0	0
2.0	.3	.1	0	0	.1	.007	.02	0	0	0	0
.2	.05	0	0	0	0	.001	.002	0	0	0	0
Central Tennessee											
2.0	.15	.02	[2] 0	0	.007	0	.01	0	0	0	0
2.0	.1	.01	.3	0	.2	.01	.005	0	0	0	0
.7	.2	.05	0	0	.007	.0007	.02	0	0	0	0
Kentucky–Illinois											
.64	0	.004	0	.0009	.17	0	.012	.0024	0	0	0
.38	0	.039	0	.0004	.002	0	.004	<.0004	0	0	0
East Tennessee											
.7	.02	.002	0	0	0	0	.0007	0	0	0	0
1	.05	.002	[2] 0	0	.01	0	.007	0	0	0	0
North Carolina											
.7	.03	0	[2] 0	0	0	0	.0015	.002	0	0	0
Maine											
1	.02	.0007	[2] 0	0	.05	0	.0007	0	.0015	0	0
1	1	0	[2] 0	0	.1	0	0	.01	0	0	0
1	.07	0	[2] 0	0	.02	0	0	.02	0	0	0
2	.3	0	0	0	.5	0	.0002	0	0	----	----
New England and Pennsylvania veins											
1	.015	0	[2] 0	0	.003	0	.015	0	0	0	.0015
2	.07	.005	[2] 0	0	.01	0	.007	.02	0	0	0
1	.03	.01	[2] 0	0	.02	0	.0015	.001	0	0	0

13. Linville Falls, McDowell County, sphalerite.
14. Black Hawk mine, Hancock County, massive sphalerite zone in fragmental quartzite, black sphalerite.
15. Big Hill pit, Pembroke, Washington County, veins in fractured volcanic agglomerate, black sphalerite.
16. Spanish pit, Pembroke, Washington County, veins in fractured diabase, black sphalerite.
17. Sullivan mine, Hancock County, veins in micaceous schist, dark sphalerite.
18. Madison mine, Carroll County, N.H., mineralized fracture zone in granite of White Mountain Plutonic-Volcanic Series, dark-brown sphalerite.
19. Bristol copper mine, Hartford County, Conn., minor sphalerite with copper ore in Newark Group along Triassic fault zone, brown sphalerite.
20. Wheatley mine, Phoenixville, Chester County, Pa., veins in fractured gneiss and pegmatite of Wissahickon Formation along Triassic border zone, brown sphalerite.

manium is the Tri-State zinc-lead district of Missouri, Kansas, and Oklahoma, where germanium is extracted from sphalerite concentrates containing 0.01 to 0.015 percent germanium, less than half the average germanium content of the central Kentucky and central Tennessee sphalerites.

Ivanov (1964) reported that high-temperature skarn-type lead-zinc deposits and low-temperature silver deposits have the most cadmium-rich sphalerites. Next are low-temperature lead-zinc deposits; intermediate-temperature sulfide deposits have the least. His data confirm, however, that the behavior of cadmium in ore formation is much more complex than one of simple temperature relationship. Cadmium in sphalerite at low temperatures, for instance, has an inverse relation to the concentration of chloride ions in solution, which explains the cadmium-lean ores associated with hydrothermal solutions derived from mafic magmas that are rich in chlorine. Cadmium may be enriched in ores deposited in carbonate rocks and in the presence of fluorite. Ivanov concluded that both the temperature of crystallization of sphalerite and the degree of concentration of cadmium in the hydrothermal ores determine the concentration of cadmium in ores; the effect of metallogenetic provinces on the concentration of cadmium in ores is considerable. Other workers, such as Badalov and Enikeev (1959), Warren and Thompson (1945), and Graton and Harcourt (1935), have indicated that cadmium in sphalerite increases as the temperature of ore formation decreases, so that its maximum content results in the lowest temperature sphalerites.

Our information (see examples in table 2), gathered from many analyses in a variety of mineral districts, indicates that most sphalerite from the Central and Eastern United States has a relatively high cadmium content as compared with other United States and Canadian districts, regardless of the temperature of deposition. High cadmium content in the epigenetic central Kentucky and central Tennessee sphalerites is most probably a result of its availability in a metallogenic province comparatively high in cadmium rather than a result of temperature as the principal controlling factor. The difference between the cadmium content of central Tennessee and central Kentucky sphalerites and the comparatively lower cadmium content of east Tennessee sphalerites may also be a reflection of temperature, but it is difficult to carry this type of comparison further.

The average cadmium content of eight sphalerites from Zone 1, Stage 1, of central Kentucky is 1.2 percent, slightly lower than

the district average (37 specimens) of 1.34 percent cadmium. Diagenetic sphalerites (example in table 2), however, collected from concretions and sedimentary fractures in the southern part of the central Kentucky district contain very small amounts of cadmium and gallium and are virtually free of germanium. The low values for these three elements in the diagenetic sphalerite refute the hypothesis of high cadmium in all low-temperature sphalerites and provide useful tools to distinguish these diagenetic sphalerites from the more common epigenetic sphalerites in the veins of the same district.

Germanium is generally supposed (Stoiber, 1940, p. 518; Fleischer, 1955, p. 993) to be most concentrated in sphalerites where the temperatures of formation are lowest. Graton and Harcourt (1935), Stoiber (1940), and Warren and Thompson (1945) also agree that gallium is a common minor constituent in low-temperature varieties of sphalerite.

As mentioned above, the cold-water diagenetic sphalerites of central Kentucky are virtually free of germanium (seven samples analyzed contained none) and low in gallium (seven samples contained an average of 0.001 percent). Table 3 shows preliminary germanium and gallium data for the epigenetic sphalerites in central Kentucky. Although the conclusions should be regarded as prelininary because of the small number of samples, the data in this table suggest that the vein black and yellow sphalerites are highest in both gallium and germanium in Zone 1, where the temperatures at the time of deposition were highest. This relation is indicated in table 3 by a comparison of the black and yellow sphalerites of Stages 1, 2, and 3 from Zone 1 to Zone 3.

TABLE 3.—*Average germanium and gallium content of sphalerites from the central Kentucky mineral district showing distribution by zone and stage of mineral distribution*

[Values are in percent. Numbers in parentheses indicate number of analyses. Analysis by semiquantitative spectrograph; U.S. Geol. Survey analyst, J. Harris, 1963, 1964]

	Color of sphalerite	Element	Zone 1	Zone 2	Zone 3
Stage 1	Black	Ge	0.04 (8)	0.01 (1)	0.01 (3)
	------ do ------	Ga	.01 (8)	.007 (1)	.008 (3)
Stage 2	Black and yellow	Ge	.03 (4)	.02 (6)	.01 (9)
	------ do ------	Ga	.009 (4)	.006 (6)	.008 (9)
Stage 3	Yellow and black	Ge	.03 (1)	0 (1)	.007 (1)
	------ do ------	Ga	.006 (1)	.005 (1)	.004 (1)
	Red and orange	Ge			.08 (3)
	------ do ------	Ga			.01 (3)

The late-stage red-orange sphalerites of both central Kentucky and central Tennessee (examples in table 2) contain on the average more germanium than other types. Red sphalerite from the Cumberland River veins in south-central Kentucky contains 0.07 to 0.1 percent germanium. Red sphalerite is most abundant in some veins of Zone 3, where the temperatures of formation are lowest. Although representative samples are not shown for all zones in table 3, red sphalerite is present as a late mineral in minor amounts in a few veins in every zone of the central Kentucky district, where it occurs as an overgrowth on earlier sphalerites, or in crosscutting veinlets with purple fluorite, and commonly replaces wallrock.

Several second-stage black and yellow sphalerites from the central Kentucky veins were separated by hand into black and yellow parts. For each sample, it was found that the yellow part was one order higher in both germanium and gallium than the black part. At the Purdy vein in Bourbon County, Ky., where black sphalerite forms the core to the sample analyzed, it was found that the germanium and gallium content increases from the black interior through outer rims of first yellow and last reddish orange. The cadmium content remains rather constant in all specimens analyzed. Although the dark-yellow sphalerite that is intergrown with the black is high in these elements, such is not true of a late very pale yellow sphalerite of the same district. In contrast to this pattern is a late (Stage 3) pale-yellow sphalerite collected in a roadcut vein near Danville, Ky.; it contains no germanium and is moderately lean in gallium, but is rich in cadmium.

Table 2 shows several complete semiquantitative spectrographic analyses of representative sphalerite samples from central Kentucky and central Tennessee as well as from several other districts. The sphalerite samples in table 2 from central Kentucky are selected sphalerites representing three mineral stages that range from Stage 1 in Zone 1 to Stage 3 in Zone 3. There is a close similarity between the minor elements of the central Kentucky sphalerites and those of central Tennessee, except for a general lack of silver in the sphalerites of central Tennessee. Sphalerites from central Kentucky and some from central Tennessee also contain strontium, which is notably lacking in all other sphalerites analyzed to date. One specimen each from the Sweetwater district, Tennessee, Dyer Hill, western Kentucky and Flat River, Mo., contain strontium and are exceptions in more than 100 analyses. The diagenetic sphalerites of central Kentucky are also lacking in strontium.

Semiquantitative spectrographic analyses of sphalerites collected from the hydrothermal veins and massive sulfide deposits of Maine, New England, and Pennsylvania indicate that the presence of gallium and germanium may well be a function of temperature as well as availability in a metallogenic province. Selected samples are shown in table 2 for comparison. Sphalerite from veins along the Triassic border zone at Bristol, Conn., and at Phoenixville, Pa., are similar to the Appalachian Valley zinc sphalerites in cadmium, germanium, gallium, and iron content. The sphalerites from Hancock and Washington Counties, Maine, and Carroll County, N.H., either lack or contain very low amounts of germanium and gallium. These sphalerites contain 5 to 10 percent iron and are thought to have been deposited at higher temperatures than those from either the Appalachian Valley zinc districts or the Bristol, Conn., deposits. Molybdenum, indium, and tin are elements found in the northeastern sphalerites that do not occur in most Appalachian and Mississippi Valley sphalerites. Indium was reported (Herbert and Young, 1956, p. 16, table 3) in sphalerites of the Timberville district, Virginia, and is known to occur in sphalerites of the southeast Missouri district. Indium was also reported by Stoiber (1940) as occurring in a single specimen from central Kentucky. In the many samples analyzed since, however, no indium has been detected, and it probably does not exist as a significant trace element that is typical of these sphalerites. Many of the sphalerites from Hancock and Washington Counties, Maine, have high silver values.

MERCURY IN OTHER ORES

On the basis of a study of mercury halos derived from lead-zinc deposits in Carboniferous limestone and dolomites in the Achisai district of the U.S.S.R., Fursov (1958) concludes that:

1. Mercury halos at the surface represent epicenters of blind ore bodies 25 to 300 meters below the surface.
2. Mercury dispersion halos within boundaries of the Achisai ore field should be regarded as an indirect indication of lead-zinc ores.
3. Mercury halos exist in areas where halos of lead and zinc are entirely absent.
4. Mercury is in sulfide and oxidized ores and in galena, sphalerite, pyrite, cerussite, and smithsonite. In general, cerussite from the oxidized zone contains the most mercury. (The mercury apparently accumulated in the cerussite by migration from the original adjacent host sphalerite, which was removed by

leaching. The more mobile element zinc was redeposited further out in the wallrock as smithsonite.)

5. Mercury has a very low mobility in unheated ground water, as does lead, but it is highly mobile as a vapor.

Ozerova (1959) concludes that mercury dispersion halos have a considerable advantage over lead halos because they are more extensive, a circumstance important in locating major areas for more detailed prospecting.

MERCURY IN OTHER MINERALS

Saukov (1946) and Ozerova (1959) also indicate that Hg^{+2} may replace Ca^{+2} or Ba^{+2}. Barite, calcite, and galena occur with sphalerite in many of the eastern and central mineral deposits. A few analyses for mercury were made on scattered samples of these minerals, as well as on oxidized ore, from Virginia, Kentucky, and Tennessee. All samples contain greater than background mercury. Barite from the Gratz vein, Owen County, Ky., which was analyzed by wet chemical methods, contains less than 300 ppb mercury. The amount of mercury detected in five galena samples from Kentucky and Virginia is 270 to 720 ppb. Preliminary analyses suggest that galena-bearing limestone from the Gordon-Wine prospect in the Timberville district of Virginia and from the Osborn mine in Russell County, Va., contains 200 to 700 ppb mercury.

Smithsonite from the Timberville mine in Rockingham County, Va., contains 15,000 ppb mercury, as indicated by a spectrographic analysis (U.S. Geol. Survey analyst, H. Worthing, 1967). Samples of oxidized ore, principally smithsonite, from the Hoover vein and the nearby Pascal vein of Cannon County, Tenn., contain less than 100 ppb mercury by wet chemical analysis (U.S. Geol. Survey analyst, J. Dinnin, 1965).

MERCURY IN WALLROCK

In permeable rock such as sandstone, limestone, or dolomite, mercury moves rather great distances from the source as a vapor or soluble mercuric chloride (Hawkes and Webb, 1962). It would be reasonable to expect, therefore, a broad hypogene halo of mercury dispersion in host rocks of lead and zinc ores. The shape of the resulting mercury anomaly depends upon the shape of the fractures and physical characteristics of the wallrock.

Mercury anomalies have most commonly been detected by analysis of bedrock rather than soil. According to Williston (1964), however, even analysis of mercury in air may be utilized in the future. Friedrich and Hawkes (1966) have suggested that the mercury content of residual soil, but not of the unweathered

rock, may be used as a guide to blind ore deposits in the Pachuca–Real del Monte district, Mexico.

Limestone wallrock suites from the main Faircloth vein in central Kentucky, the Mascot–Jefferson City belt of east Tennessee, and the Hoover vein in central Tennessee were analyzed for mercury by refined vapor absorption methods. The results shown in figure 3 and tables 4, 5, and 6 are well above the accuracy limit (1 to 2 ppb) of the method used.

A very narrow mercury leakage anomaly is indicated by the analyses. At the Faircloth vein, sample 3 was collected from the wallrock breccia at the center of the vein (see fig. 3); as might be expected, it contains the most (170 ppb) mercury. The specimen with the least amount of mercury (10 ppb) was collected 30 feet west of the vein. All samples were collected from a single limestone bed in the Tyrone Limestone of Middle Ordovician age, except the one in the vein center.

At the Hoover vein (table 5), sample 1, collected from the center of the vein, contains the most mercury (560 ppb). All samples were collected from a single limestone bed in the Carters Lime-

TABLE 4.—*Variance of mercury content in a suite of limestone samples from the Faircloth vein, Woodford County, Ky.*

[Vapor absorption analyses, U.S. Geol. Survey analyst, J. H. McCarthy, 1964]

Specimen	Location and description	Mercury (ppb)
3	Center of vein, altered, silicified limestone	170
5	West wall of vein, slightly silicified limestone	80
6	6 ft. west of vein, unaltered limestone	20
7	10 ft. west of vein, unaltered limestone	20
8	20 ft. west of vein, unaltered limestone	50
9	30 ft. west of vein, unaltered limestone	10
10	100 ft. west of vein, slightly silicified limestone	30
11	150 ft. west of vein, silicified limestone	70

TABLE 5.—*Mercury content of limestone wallrock from the Hoover vein, shaft 1, Cannon County, Tenn.*

[Atomic absorption analyses, U.S. Geol. Survey analyst, James Frisken, Dec. 12, 1966]

Specimen	Location and description	Mercury (ppb)
1	Center of vein, altered, silicified limestone	560
2	East wall, altered, silicified limestone	70
3	1 ft. east of vein, altered, silicified limestone	70
4	4 ft. east of vein, unaltered limestone	30
5	84 ft. southeast of vein, unaltered limestone	40
6	119 ft. southeast of vein, unaltered limestone	40
7	199 ft. southeast of vein, unaltered limestone	60
8	244 ft. southeast of vein, unaltered limestone	70
9	Soil above smithsonite cap on vein	2,200

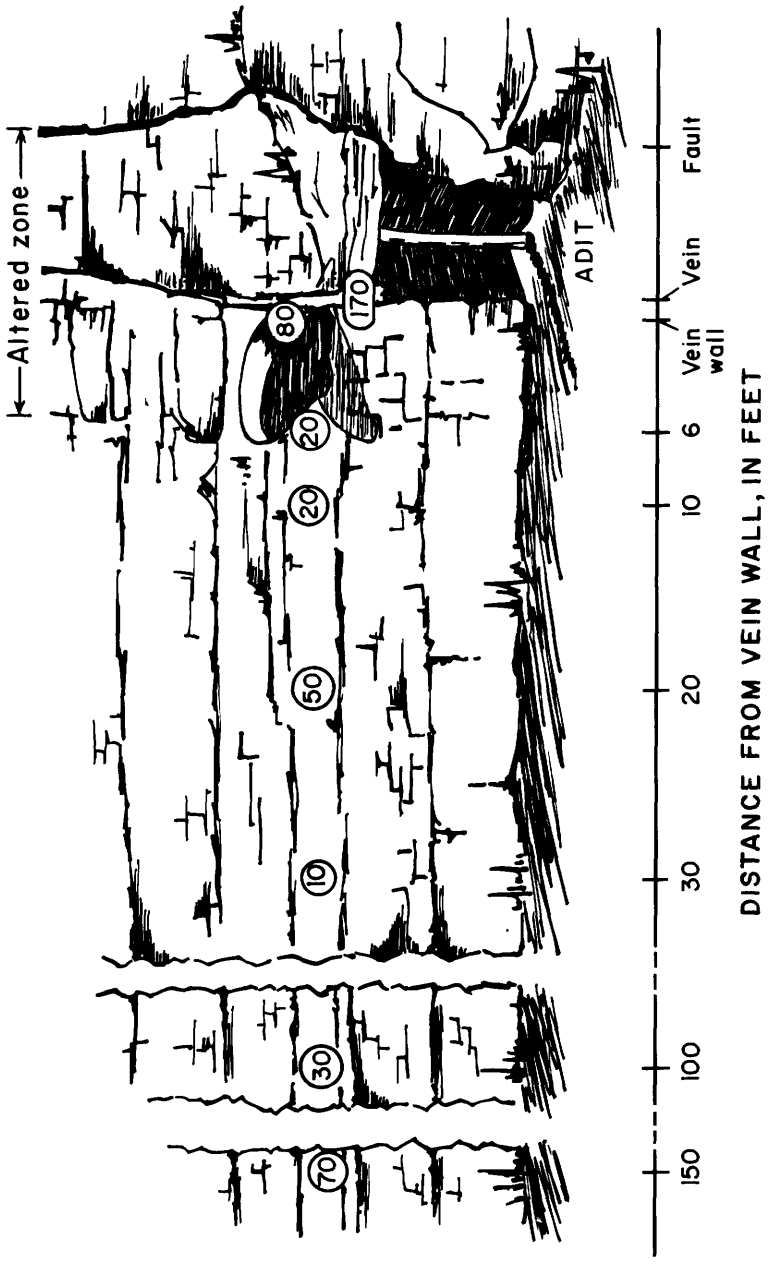

FIGURE 3.—Sketch of Faircloth mine adit showing location of limestone samples and amount of mercury, in parts per billion.

TABLE 6.—*Mercury content of a wallrock suite along a thinned, altered, and silicified limestone bed of a major ore body in the Mascot-Jefferson City belt, east Tennessee*

[Atomic absorption analyses, U.S. Geol. Survey analyst, James Frisken, Dec. 12, 1966]

Specimen	Location and description	Mercury (ppb)
1	Founder breccia, near edge of main ore, thinned, altered, and silicified chert; 3 in. thick	170
2	37 ft. west of sample 1, thinned, altered, and silicified chert	40
3	41 ft. west of sample 1 next to shear, thinned, altered, and silicified chert	10
4	42 ft. west of sample 1, just west of shear, much thinned, altered, and silicified chert	10
5	58 ft. west of sample 1, thinned, altered, and silicified chert	40
6	86 ft. west of sample 1, thinned, altered, and silicified chert	20
7	140 ft. west of sample 1, thinned, altered, and silicified limy chert; 6 in. thick	30
8	205 ft. west of sample 1, thinned, altered, and silicified limy chert; 10 in. thick	20
9	280 ft. west of sample 1, thinned, slightly altered limestone; 1.5 ft. thick	20

stone of Middle Ordovician age, except sample 1, from the center of the vein, and sample 9, from the soil above the vein. Sample 4 contains the least (30 ppb) mercury and is 4 feet east of the vein, indicating a very narrow anomaly. Soil directly over the vein contains even higher amounts (2,200 ppb mercury), suggesting that analysis of residual soils might provide a more pronounced anomaly. Sphalerite from the Hoover contains 300 to 700 ppb mercury (table 1).

Sample 1 from the east Tennessee suite (table 6), which also contains anomalous mercury (170 ppb), was collected from the edge of a main ore body where the siliceous limestone unit of the Kingsport Formation, locally known as the 46 chert, has been much altered and thinned to a chert bed only 3 inches thick. Where it is unaltered, the 46 chert is nearly 3 feet thick and is composed of limestone. Samples 3 and 4, which contain the least (10 ppb) amount of mercury, are within 1 foot of a shear zone along which postore hydrothermal alteration has occurred, as suggested by chemical and mineralogical studies now in progress. The sharp drop from 40 to 10 ppb at this point in the wallrock suite may be the result of removal or leaching of the original mercury by these late warm waters. The lowest mercury content might otherwise be expected in the least altered samples, 8 and 9, which contain 20 ppb.

Low mercury content is characteristic of limestone. The average mercury content of limestone, according to Rankama and Sahama (1950), is 33 ppb. Ozerova (1959) reported that the average limestone and sandstone of the Fergana Karatu Range,

U.S.S.R., contains 2×10^{-6} percent (20 ppb) mercury. The average shale contains 400 ppb mercury (Hawkes and Webb, 1962, p. 369), and the average igneous rock (Saukov, 1946) contains 77 ppb.

The limestone in the visibly unaltered wallrock of the Faircloth, Hoover, and the east Tennessee deposits (see tables 4, 5, and 6) ranges from 10 to 70 ppb mercury, whereas the more silicified samples nearest the deposits contain 70 to 560 ppb mercury. All analyses above 30 ppb, however, should be considered anomalous. Accordingly, samples 8, 10, and 11 of the Faircloth and samples 7 and 8 of the Hoover suites are thought to be near other veins as yet undiscovered.

Quartz, as disseminated replacement crystals and jasperoid, and dolomite commonly form alteration aureoles near veins in these and other lead-zinc districts (Hosterman and others, 1964) of the Central United States. At the Faircloth and Hoover veins, where silicification is most pronounced in the altered wallrock nearest the vein (see fig. 3 and table 5), mercury content is also highest. However, silicification does not seem to bear any relationship to the amount of mercury present in the deposit from east Tennessee or to the anomalous samples some distance removed from the known veins.

CONCLUSIONS

Mercury has been reported as a trace element in sphalerite and other minerals from the Western United States and other parts of the world, but this is the first notation of such an occurrence in the lead-zinc deposits of the Central and Eastern United States. Mercury has been detected in amounts greater than background in nearly every sphalerite analyzed, indicating that it is a very common and widespread trace element in most zinc deposits of Central and Eastern United States. The presence of mercury as an integral part of sphalerite suggests that these deposits are hydrothermal in origin—that is, they were deposited by heated aqueous solutions, which in the deposition of sphalerite of the Mississippi Valley type were probably largely heated connate brines. The presence of mercury anomalies associated with the central Kentucky, central Tennessee, and east Tennessee deposits suggests that other districts containing base metals in the Central and Eastern United States also have mercury wallrock halos associated with them. It is hoped that the knowledge of mercury association with these ore bodies will be of help in prospecting for

other low- to moderate-temperature deposits in the Central and Eastern United States, especially in the Mississippi Valley and Appalachian Valley zinc districts.

Trace elements such as mercury, cadmium, germanium, and gallium should not be overlooked when considering the total value of the zinc concentrates. These elements, especially mercury, cadmium, and germanium, may occur in sufficient quantities in some sphalerites, such as those of the central Kentucky and central Tennessee districts, to warrant consideration as worthwile byproducts at the smelters if new commercial ore bodies are found and mined. The unusual concentrations of these elements in the sphalerite of these two districts is a feature that distinguishes the deposits from those in many other districts. The east Tennessee and other Appalachian Valley sphalerites are notably leaner in germanium and mercury than those of central Tennessee and central Kentucky. The central Kentucky diagenetic sphalerites are very lean in cadmium, germanium, and gallium as compared with those in nearby veins. Comparison of central Kentucky and northeastern hydrothermal vein and massive sulfide sphalerites indicates that the amount of cadmium present is most likely a result of abundance in a metallogenic province high in cadmium, whereas germanium, gallium, and mercury contents may be related to temperature of deposition as well as to source.

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