THE GEOCHEMISTRY AND GEOTHERMOMETRY OF SPHALERITE IN THE LEAD-ZINC-SILVER LODES OF THE KENO HILL-GALENA HILL AREA, YUKON[1]

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ABSTRACT

The occurrence and geochemistry of sphalerite in the Keno Hill lead-zinc-silver lodes is discussed in detail. The iron content of the sphalerite ranges from 0.63 to 11.54 per cent, the cadmium content from 0.71 to 1.16 per cent, and the manganese content from 0.005 to 0.20 per cent. The principal trace elements are Sb, As, Ag, Cu, Pb, Sn, Si, and Al. The germanium and indium contents are low.

Precise cell edges for the sphalerite were determined and plotted against the mole per cent FeS. There is a linear relationship between these two quantities.

An attempt was made to determine the temperatures of crystallization of sphalerite using the mole per cent FeS present in ten representative samples. The conclusion reached is that the method is not applicable to the Keno Hill deposits.

INTRODUCTION

This paper summarizes the geochemistry and geothermometry of sphalerite in the lead-zinc-silver lodes of the Keno Hill-Galena Hill area, Yukon. It is part of an extensive investigation of zinc in these lodes and is dedicated to Professor J. E. Hawley of Queen's University, Kingston, an eminent geologist who has devoted a lifetime to the study of the geochemistry of ore minerals.

The Keno Hill-Galena Hill area is in Central Yukon, 35 miles northeast of Mayo and some 220 miles due north of Whitehorse. The area is particularly noted for its lead-zinc-silver-cadmium lodes which have been prolific producers since their initial discovery in 1913.

The principal producing mines in the area (See Fig. 1) are the Hector-Calumet and Elsa, both located on Galena Hill. Former producing mines were the Silver King, Bermingham, and Galkeno on Galena Hill; the Onek, Ladue-Sadie-Friendship, Lucky Queen, Shamrock, and No. 9 on Keno Hill; and the Bellekeno on Sourdough Hill.

GEOLOGY AND MINERALOGY OF THE LODES

The general geology of the Mayo District, of which the Keno Hill-Galena Hill area is a part, was described first by Keele (1905) and later

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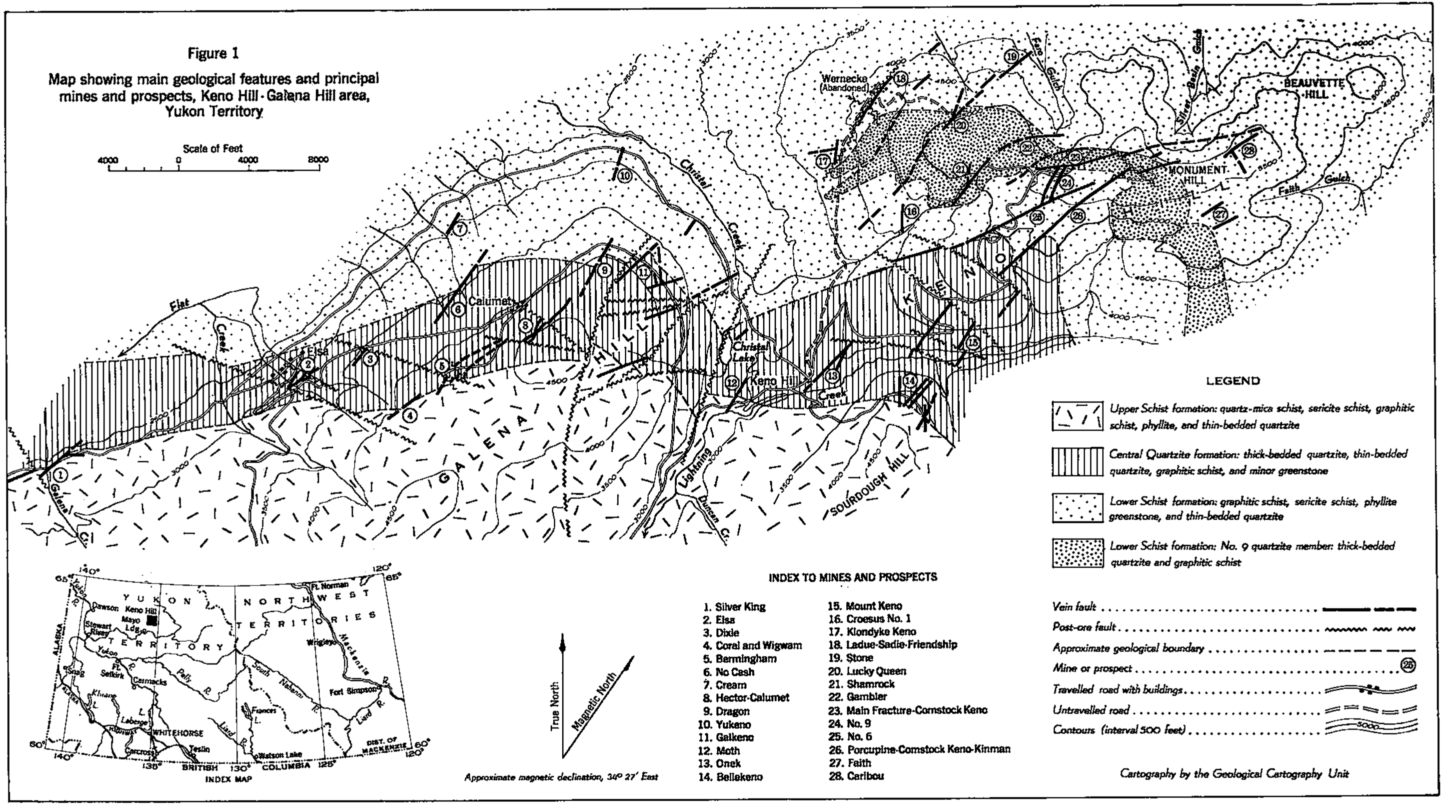

Figure 1

Map showing main geological features and principal mines and prospects, Keno Hill-Galena Hill area, Yukon Territory

Geological Survey of Canada

FIG. 1.

by Bostock (1947). The geology of Keno Hill was described by Cockfield (1924) and that of Galena Hill by Stockwell (1926). McTaggart (1960) has published a report on the detailed geology of both Galena and Keno Hills, and Kindle (1955) has summarized the principal features of the geology of the Mayo Lake-Galena Hill-Keno Hill district. Carmichael (1957) has described the geology of the deposits being exploited by United Keno Hill Mines, Limited. Boyle (1956, 1957) commenced a detailed investigation of the lead-zinc-silver deposits in 1953 and has published preliminary papers dealing with the geology and geochemistry of the lodes on Galena, Keno, and Sourdough Hills. All of these publications cover the geological setting of the lodes from various aspects and can be consulted by those interested in the details. The following summary is brief and covers only the salient points pertinent to the description and discussion in the present paper.

The consolidated rocks underlying the Keno Hill-Galena Hill area are mainly sedimentary in origin and include schists, phyllites, slates, and quartzites, probably of Precambrian or Palaeozoic age. Conformable greenstone lenses and sills occur in profusion in places in the sedimentary strata, and a few lamprophyre and quartz-feldspar dykes and sills are present locally. The rocks dip gently south and are cut by numerous early and late brecciated fault zones. The early fault zones strike northeast, generally dip southeast, and contain the lead-zinc-silver lodes. The majority of the late fault zones strike northwest, dip southwest, offset the early fault zones and lodes, and are essentially unmineralized. The age of the faults is uncertain; they were probably formed during Cretaceous time.

The principal lodes occur in the competent thick-bedded quartzites and greenstones at three structural sites; at the junction of two or more faults; at the junction of a fault and subsidiary fracture; and in greenstones or thick-bedded quartzites at or near the sites where the faults pass upward from these rocks into incompetent schists and thin-bedded quartzites.

Two types of lodes are present in the early faults; one contains essentially quartz with pyrite, arsenopyrite, and small amounts of boulangerite, bournonite, meneghinite, galena, and sphalerite; the other is mineralized with manganiferous siderite, galena, sphalerite, pyrite, argentian tetrahedrite, and other sulphosalts. Although both types may occur separately, it is more common to find hybrid lodes consisting of the quartz type which have been fractured and cemented with minerals characteristic of the siderite type. The age of the lodes is not known with certainty. They cut quartz-feldspar porphyry dykes and sills thought to be of Cretaceous age or younger.

The upper parts of most lodes are highly oxidized to depths varying from 25 to 500 feet or more. Two zones can generally be recognized in most lodes, an intensely oxidized upper zone and a lower zone of reduction. The latter tends to telescope the lower part of the oxidized zone and upper part of the primary zone in most lodes and presumably formed in the vicinity of a former fluctuating water table. The oxidized zones are porous and cavernous and contain a veritable host of minerals, among which limonite, wad, anglesite, cerussite, silver-bearing beudantite and plumbojarosite, bindheimite, gypsum, native sulphur, malachite, azurite, smithsonite, quartz, scorodite, and native silver are predominant. The minerals in the zones of reduction include those commonly present in both the primary and oxidized zones, augmented by characteristic developments of pyrargyrite, native silver, acanthite, and small amounts of supergene calcite, siderite, sphalerite, galena, pyrite, hawleyite, and greenockite.

As a whole the lodes exhibit a marked enrichment of silver and lead and a depletion of zinc in the oxidized zones, compared with the primary zones (Table 1). This is due to the great mobility of zinc and relatively restricted mobility of lead and silver under oxidizing conditions.

TABLE 1. LEAD, ZINC, AND SILVER CONTENTS OF OXIDIZED AND UNOXIDIZED ORES, KENO HILL-GALENA HILL AREA

Location	Description	Pb%	Zn%	Ag oz/ton
Silver King mine, Galena Hill	Oxidized ore near surface	61.4	1.7	374.2
"	Unoxidized ore 80 feet below surface	22.3	6.8	156.8
"	Unoxidized ore 100 feet below surface	3.9	8.7	38.5
Hector-Calumet mine, Galena Hill	Average assay of oxidized ore	9.87	4.29	51.18
"	Average assay of unoxidized ore	9.2	8.4	38.4
Lucky Queen mine Keno Hill	Average assay of upper 50 feet of vein. Sorted ore	42.0	4.5	485.3
"	Average assay of ore below 50 foot level	6.0	8.0	77.0
Onek mine, Keno Hill	Average assay of ore—surface to 50 foot level	42.0	0.67	88.1
"	Average assay of ore on 400 foot level	6.97	17.4	17.2

NOTE: Assays and analyses of Silver King, Hector-Calumet, and Lucky Queen ores from various private company reports. Assays and analyses of Onek ores by Mines Branch, Ottawa.

OCCURRENCE OF SPHALERITE

Sphalerite is an abundant ore mineral in all of the lodes of the Keno Hill-Galena Hill area. It belongs principally to the siderite stage of mineralization, but in a few places it appears with galena in the early quartz-pyrite-arsenopyrite lodes. Most of the sphalerite is of hypogene origin, but in the zones of reduction of some lodes small quantities of supergene sphalerite are present in porous zones and along fractures.

In unbrecciated lodes the hypogene sphalerite is amber to dark brown to black and occurs as large crystallized masses, as veins and stringers, and in individual crystals and crystal groups in drusy parts of the lodes. Perfect tetrahedrons are present in places and dodecahedrons are common. Complex and distorted crystals, as well as euhedral crystal intergrowths, are locally abundant. In thin sections many of the crystals exhibit a colour zoning.

In nearly all occurrences the sphalerite is associated with siderite, galena, argentian tetrahedrite, pyrite, and quartz, and with dolomite and calcite in places. Frequently these minerals are highly intergrown or arranged in crude bands.

In some lodes sphalerite follows quartz and siderite in its depositional history, but in places the siderite has grown on sphalerite, and both siderite and quartz may fill fractures in masses of sphalerite, suggesting much overlapping in the depositional sequence.

In the brecciated parts of lodes the sphalerite is sheared and highly crushed and in places is recemented by veinlets of siderite, dolomite, calcite, and quartz.

In most lodes sphalerite varies in abundance with depth. In the oxidized parts it is present in small amounts as highly altered masses in a limonitic boxwork. Deeper down, as the oxidation lessens, more sphalerite is present, and in the hypogene zones it is an ubiquitous mineral. The details of the oxidation of sphalerite are described in the next section.

In polished sections the sphalerite is coarse to fine grained, the diameters of the grains and crystals ranging from 0.01 mm. to 3 cm. with an average of about 5 mm. The normal sphalerite possesses perfect cleavage, is isotropic, and exhibits little birefringence due to strain. Its most persistent associates are galena, argentian tetrahedrite, chalcopyrite, and pyrite; less frequently arsenopyrite, boulangerite, meneghinite, and pyrargyrite occur with sphalerite.

In most sections sphalerite appears to be later than pyrite and arsenopyrite, but in places a generation of fine-grained pyrite post-dates the sphalerite. In some fine-grained galena specimens, sphalerite occurs as blebs and patches, but more generally the sphalerite has mutual boundary relations with galena and with tetrahedrite suggesting nearly contemporaneous deposition of these minerals. In some sections, however, tetrahedrite rims the crystals of sphalerite, and both tetrahedrite and galena penetrate and cut sphalerite. In other sections galena is penetrated along cleavage planes by sphalerite. Most specimens of sphalerite contain oriented blebs of chalcopyrite, indicating exsolution of the latter. In a few lodes sphalerite veins chalcopyrite.

All the above relationships are somewhat difficult to interpret, but combined with field studies there appears to be at least three generations of hypogene sphalerite—a minor one associated with, but slightly later than, the quartz-pyrite-arsenopyrite phase of mineralization; the major period of deposition associated with the siderite-galena-tetrahedrite-pyrite phase; and a minor generation associated with late chalcopyrite. The last two are probably nearly contemporaneous.

The sphalerite in brecciated lodes is severely comminuted and mylonitized in places. It often shows the effects of strain and shearing and is intricately mixed with fragments and recrystallized patches of galena, siderite, chalcopyrite, and tetrahedrite. Quartz, siderite, dolomite, and calcite vein and cement the mylonitized sphalerite in places.

In the near surface parts of most lodes, sphalerite has been nearly completely removed leaving only limonitic and siliceous boxworks. In places highly altered residuals of sphalerite remain, and these are commonly coated with native sulphur, gypsum, and various other secondary minerals.

Small amounts of light amber coloured supergene sphalerite occur in the zones of reduction of a few lodes. In most occurrences this sphalerite is very fine grained and pulverulent. In others it forms minute crystals in fractures and porous parts. This sphalerite is generally associated with fine-grained supergene galena, siderite, hawleyite, marcasite, and acanthite.

GEOCHEMISTRY OF SPHALERITE

The results of complete chemical analyses of ten representative sphalerite samples are given in Table 2 and additional spectrographic analyses are shown in Table 3. The material for analysis was selected from composite samples of coarse-grained sphalerite taken over several sample widths of five feet or more across the stopes or veins at the places noted in the table. Care was taken to avoid sphalerite that exhibited colour zoning. Five grams of homogeneous sphalerite were split from the composite samples, crushed, ground, and hand picked for purity. The samples are clearly recognized as being composite samples, and the

TABLE 2. CHEMICAL ANALYSES OF SPHALERITE FROM KENO HILL—GALENA HILL LODES

	A-472	A-473	A-535	A-568	A-708	A-709	A-710	A-711	A-718	A-719
Zn	57.83	59.03	61.85	57.83	53.81	59.44	61.44	58.83	64.06	63.65
Fe	7.08	6.58	2.53	7.39	11.54	6.58	4.45	5.67	0.63	2.63
Cd	0.94	0.71	0.95	1.16	0.82	0.88	0.83	0.79	0.73	0.73
Mn	0.09	0.05	0.03	0.08	0.20	0.07	0.14	0.82	0.005	0.01
S	32.87	32.76	32.43	32.65	33.33	33.22	32.78	31.60	32.54	33.06
Sb	0.38	.007	0.19	0.02	0.001	0.007	0.001	0.003	0.004	0.04
As	0.001	0.000	0.000	0.000	0.000	0.000	0.000	N.F.	0.001	0.00
Ag	0.50	0.01	0.50	0.03	0.000	0.01	0.001	0.005	0.003	0.04
Cu	0.70	0.20	0.20	0.05	0.02	0.05	0.05	0.02	0.02	0.05
Pb	0.01	0.03	0.07	0.05	0.02	0.01	0.10	0.01	0.05	0.10
Sn	0.01	0.08	0.02	N.F.	N.F.	0.01	0.03	0.01	0.01	0.01
Total	100.41	99.46	98.77	99.26	99.74	100.28	99.82	97.75	98.05	100.32

Analyses of Zn, Fe, Cd, Mn, S by Mines Branch, Ottawa; Analyses of As, Sb, Cu, and Pb by M. A Jardine and G. Mihailov; Ag and Sn analyses by W. H. Champ.

N.F. = not found.

A-472, massive black sphalerite, Sadie Friendship mine, Keno Hill.
A-473, massive black sphalerite, Onek mine, Keno Hill.
A-535, Massive dark brown sphalerite, Lucky Queen mine, Keno Hill.
A-568, massive black sphalerite, Klondyke Keno mine, Keno Hill.
A-708, massive black sphalerite, Galkeno mine, Galena Hill.
A-709, massive black sphalerite, 775 foot level, Hector-Calumet mine, Galena Hill.
A-710, massive black sphalerite, 650 foot level, Hector-Calumet mine, Galena Hill.
A-711, massive dark brown sphalerite, 1,165 foot level, Hector-Calumet mine, Galena Hill.
A-718, late (supergene ?) reddish brown sphalerite crystals, Gambler vein, Keno Hill.
A-719, early massive, dark brown sphalerite, Gambler vein, Keno Hill.

TABLE 3. SPECTROGRAPHIC ANALYSES OF SPHALERITE FROM KENO HILL—GALENA HILL LODES
(Parts per million)

	A-472	A-473	A-535	A-568	A-708	A-709	A-710	A-711	A-718	A-719
Si	100–1000	100–1000	100–1000	10–100	10–100	10–100	10–100	10–100	> 1000	10–100
Al	10–100	10–100	100–1000	10–100	10–100	10–100	10–100	10–100	100–1000	10–100
Ti	N.F.	N.F.	100–1000	10–100	N.F.	N.F.	< 10	N.F.	100–100	N.F.
Ni	< 20	< 20	< 20	< 20	< 20	< 20	< 20	< 20	< 20	< 20
Co	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Ge	< 50	< 50	< 50	< 50	< 50	< 50	< 50	< 50	< 50	< 50
In	N.F.	10–100	10–100	N.F.	N.F.	N.F.	N.F.	N.F.	N.F.	N.F.
Se	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10

Qualitative spectrographic analyses by W. H. Champ.

N.F. = not found.

Sample descriptions are the same as those in Table 2.

chemical analyses consequently represent an average of the metal content present.

The mole per cent sulphide has been calculated for the four essential constituents and is shown in Table 4. It will be noted that there is little difference in the percentages regardless of whether they are calculated on the basis of the original analyses or on the assumption that the analytical sum of the contained major constituents as sulphide should equal 100 per cent providing that the samples were free of other contaminants. With the exception of one adjustment, the analyses are apparently very reliable. The adjustment is in the high manganese content of sample A-711, originally reported to contain 0.82 per cent Mn. This value does not appear to be reasonable and may be in error, especially when compared with those of the other samples.

TABLE 4. CALCULATED MOLE PER CENT SULPHIDES

	ZnS		FeS		CdS		MnS	
Sample No.	a	b	a	b	a	b	a	b
A–472	86.64	86.61	12.42	12.42	0.82	0.81	0.15	0.16
A–473	87.83	87.84	11.47	11.46	0.61	0.61	0.09	0.09
A–535	94.56	94.57	4.54	4.53	0.85	0.84	0.06	0.06
A–568	85.99	85.99	12.86	12.86	1.00	1.00	0.15	0.15
A–708	79.10	79.08	19.86	19.86	0.70	0.70	0.36	0.36
A–709	87.75	87.75	11.37	11.37	0.75	0.75	0.13	0.13
A–710	91.29	91.30	7.75	7.75	0.72	0.72	0.24	0.24
A–711*	89.06	89.04	10.06	10.06	0.69	0.70	0.19	0.20
A–718	98.21	98.21	1.13	1.13	0.65	0.65	0.01	0.01
A–719	94.76	94.76	4.59	4.59	0.63	0.63	0.02	0.02

(*a*) Mole per cent calculated on basis ZnS + FeS + CdS + MnS = 100%.
(*b*) Mole per cent calculated from original analysis.
*Weight per cent Mn revised from original analysis (Table 2) and taken as 0.11 on basis of Mn content of A–709 and A–710.

The manganese content of the Keno Hill samples increases with the iron content, a correlation also noted by Krause (1961), Sims & Barton (1961), and others. When this relationship is expressed graphically for the Keno Hill sphalerites there is some scatter of the individual points but the magnitude of the deviations is reasonable except for the extremely anomalous value of A-711. The cell edge, when corrected for the analytically reported manganese content, also gives an anomalous value. It is on these two counts that the writers feel justified in making the correction to the manganese content of A-711 shown in Table 4 thus bringing this sphalerite in line with the other nine samples.

Zinc sulphide can exist in three polymorphys—sphalerite (βZnS) with a cubic face-centered lattice, wurtzite (αZnS) with a hexagonal close-packed structure, and a γZnS modification with a threefold rhombohedral structure. It has been shown by Buck & Strock (1955) that as the temperature increases, the inter-atomic forces become more directional and the symmetry of the ZnS structure reduces from the fourfold cubic structure of sphalerite to the threefold rhombohedral structure of γZnS, and finally to the threefold hexagonal structure of wurtzite. These authors also found that γZnS is stable at temperatures ranging from 600°–1020° C.

Ideally sphalerite has a face-centered cubic-stacking arrangement of ZnS layers. In these each Zn atom is co-ordinated with four sulphur atoms and each sulphur in turn with four zinc atoms. The bonding is largely of a covalent nature with some ionic character. The metallic character of the crystals is weak. Sphalerite-type ZnS is isostructural with βCdS (hawleyite), βMnS, InAs, InSb, SnSb, and numerous other cadmium, zinc, and mercury selenides and tellurides. Voltzite, Zn(S,As) yields a similar *x*-ray powder pattern to that of sphalerite (Strunz, 1957) and may have an analogous structure.

In addition to the mixed bonding mentioned above, natural sphalerites contain ZnS layers with both cubic and hexagonal packing (Smith, 1955), a feature that introduces an additional complexity in the interpretation of lattice substitutions. In view of the possible presence of hexagonal packing in sphalerite it seems desirable to point out that the hexagonal modification of ZnS, wurtzite, is isomorphous with γMnS, αCdS (greenockite) and several other manganese, cadmium, and indium compounds.

The sphalerite lattice is remarkably tolerant to substitution of iron, cadmium, and manganese and nearly all natural sphalerites are diadochic compounds of ZnS with FeS (up to 42 per cent), CdS (up to 2 per cent), and MnS (up to 9 per cent). These substitutions can be explained on energetic grounds since all of these sulphides, with the exception of FeS, are isostructural in one or other of their modifications with ZnS, and the various radii of the substituting metals are similar. Thus the covalent radii of Cd (1.48 Å), Fe (1.24 Å) and Mn (1.26 Å) are similar to Zn (1.31 Å) and fall within the generally accepted 15 per cent range of substitution. The ionic radii are likewise similar—Zn^{2+} (.71 Å), Cd^{2+} (.97 Å), Fe^{2+} (.74 Å), Mn^{2+} (.80 Å)—for all except cadmium. The normalized radii of Zn, Cd, Fe, and Mn in *AX* type sulphides are close—Zn (1.19Å), Cd (1.35 Å), Fe (1.10 Å), Mn (1.13 Å)—and the lattice energy coefficients of the four metals fall within relatively narrow limits—Zn(610), Fe (580), Mn (560), Cd (550).

All of the Keno Hill sphalerites contain iron, cadmium, and manganese (Table 2), elements that were undoubtedly incorporated in the lattice sites of the sphalerite during crystallization as a result of the energetic considerations discussed above. The iron content ranges between 0.63 and 11.54 per cent, with the lowest content in the late, probably low temperature sample. The manganese content of the sphalerites is relatively low despite the fact that associated siderites are rich in manganese (up to 17 per cent MnO). This probably means that the carbonate lattice has a greater affinity for Mn than the sphalerite lattice in a crystallizing milieu where manganese is abundant. The cadmium content of the sphalerites varies over a narrow range (0.71–1.16 per cent). There is no linear or logarithmic correlation between the cadmium content and that of either zinc or iron, nor is there any particular relationship between early (high temperature?) and late (low temperature?) sphalerites. This suggests that neither the presence of major elements nor temperature has affected the incorporation of cadmium. It follows, therefore, that the availability of the element in the solutions or the diffusion currents is the main consideration in the uptake of Cd during crystallization of the Keno Hill sphalerites.

All of the sphalerite samples contain some silver, copper, lead, arsenic, and antimony. Probably the bulk of these elements is present in microcrystalline particles and blebs of chalcopyrite, tetrahedrite, and galena, minerals that can often be seen in polished sections of the sphalerite. This is also confirmed in a general way by the apparent sympathetic variations of the Ag, Cu, As, and Sb contents of some samples. Consideration should be given, however, to the possibility that small amounts of these elements may occupy lattice sites in the sphalerite. The covalent radius of copper (1.35 Å) and the ionic radius, Cu^{2+} (.72 Å), are close to those of zinc (1.31 Å), Zn^{2+} (.71 Å), and some substitution should be possible. The large size of the lead atom and ion (1.69 Å), Pb^{2+} (1.24 Å), however, precludes much substitution of this element. Substitution of silver in any quantity also seems unlikely because of the difference in its charge. It seems possible that arsenic would occupy some of the sulphur sites as would also perhaps antimony. The data on voltzite, Zn(S,As), suggests that such substitutions take place.

Most of the sphalerite samples contain tin in amounts up to 800 ppm. These contents exceed by a wide margin those that one would expect in the small particles of admixed galena and other sulphides, and since no stannite or cassiterite were observed in polished sections of the sphalerite, it is concluded that the tin is most probably present in lattice sites. The covalent radius of tin (1.40 Å) and the ionic radius, Sn^{4+} (.71 Å) are close to those of zinc (1.31 Å), Zn^{2+} (.71 Å) but the charge is double. A limited multiple substitution of 1Sn for 2Zn may, however, be possible, thus equalizing the charge distribution. In addition a certain degree of substitution of Sn^{2+} (0.93 Å) may take place in the zinc sites despite the large size of the stannous ion. Alternatively it is to be noted that the compound SnSb is isostructural with sphalerite (Strunz, 1957),[1] and it seems possible that as Sn is substituted for Zn, Sb may simultaneously substitute in some of the S sites.

[1] Goldschmidt (1954) states, however, that SnSb is isomorphous with galena.

Indium is commonly found in sphalerites, but those at Keno Hill appear to be relatively low in the element. It is generally stated, following the work by Erämetsä (1938), that indium is captured in the sphalerite structure as In^{3+} (0.81 Å). This ion is similar to Zn^{2+} (0.71 Å) in radius but not in charge, and hence for crystal stability some other univalent element, probably Cu^{+} (.96 Å) must be taken into the sphalerite structure. Alternatively since InSb is isostructural with sphalerite, some substitution of In for Zn and Sb for S also seems acceptable.

The germanium content of the samples was not determined precisely but is below 50 ppm. This is in general agreement with the findings of Stoiber (1940), Goldschmidt (1954, p. 387), and others for deposits of the Keno Hill type which according to these authors supposedly formed at intermediate to high temperatures.

As noted above, sphalerite is greatly reduced in amount in the oxidized zones as a result of oxidation. Its major constituents go into solution according to the following simplified reactions.

$$\begin{aligned}&ZnS \text{ (zinc component)} + 2O_2 = ZnSO_4\\&CdS \text{ (cadmium component)} + 2O_2 = CdSO_4\\&FeS \text{ (iron component)} + 2O_2 = FeSO_4\\&MnS \text{ (manganese component)} + 2O_2 = MnSO_4\end{aligned}$$

Both zinc and cadmium sulphate are highly mobile because of their marked solubility, and both are leached from the oxidized zones. In the lower parts of some oxidized zones the zinc sulphate may react with carbonate or carbonate-bearing solutions yielding smithsonite and gypsum, both of which occur in some deposits.

$$ZnSO_4 + CaCO_3 + 2H_2O = ZnCO_3 + CaSO_4.2H_2O$$

Under certain conditions in the zones of reduction cadmium sulphate in solution is reduced to hawleyite by H_2S derived from the action of free sulphuric acid on sphalerite and other sulphides.

$$CdSO_4 + H_2S = CdS + H_2SO_4$$

The iron and manganese sulphates are relatively immobile in the oxidized zones because the ferrous and manganous ions are oxidized to the Fe^{3+} and Mn^{4+} states, undergo hydrolysis, and are precipitated as limonite and wad.

UNIT CELL MEASUREMENT OF SPHALERITE

In the ZnS-FeS system at equilibrium, there is an increase in the replacement of zinc by iron with increasing temperature of formation of sphalerite and this is attended by an increase in the cell edge (Kullerud, 1953). The correlation of the iron content and cell dimensions has been checked for the Keno Hill sphalerites employing the revisions and corrections suggested by Skinner *et al.* (1959), and Skinner (1961). In the latter paper, Skinner concluded that the unit cell of a particular sphalerite can be expressed in terms of its composition by the function.

$$a = 5.4093 + 0.000456x + 0.00424y + 0.00202z$$

where x, y, and z, are the respective contents of FeS, CdS, and MnS in mole per cent and a is in Å.

X-ray powder patterns of the Keno Hill sphalerite samples were taken with a standard Norelco 11.46 cm. diameter camera using filtered copper radiation. A room temperature of 24° C was maintained by air-conditioning and no correction was applied. The asymmetric Straumanis method was used in compensating for film shrinkage. X-ray spindles consisted of a thin glass fibre which was dipped in vaseline and coated with powdered sphalerite. Under a 50× binocular microscope the mounts were shaped into symmetrical spindles with an outer diameter of less than 0.15 mm.

Two spindles which gave x-ray patterns with sharp resolution of the $K\alpha_1$, and $K\alpha_2$ lines in the back reflection region were prepared from each sphalerite sample. The films were given several weeks to attain normalcy. Films were measured by a vernier with a 0.05 mm. graduation, but estimations were made to the nearest 0.01 mm. and successfully reproduced to 0.02 mm. Fluorescent lighting in the measuring device gave little heat, but each pattern was placed on the viewing glass with the light on at least an hour before being measured. At least two films were measured for each sample. Each film was measured three times and reversed after each reading.

The d-spacings were calculated from the Bragg equation and the cell edges were determined using $K\alpha_1$ lines of the (511), (440), (531), (620), and (553) reflections ($\lambda = 1.54050$ Å). For each film the three measured 2θ values obtained from a reflection were averaged and the results extrapolated to $\theta = 90°$ using the function

$$\tfrac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right)$$

For comparison, the cell edge of a spinel standard from the United States Bureau of Mines was measured in this manner and the agreement found to be within 0.0001 Å. As an independent check, a sphalerite film was randomly selected and a cell edge determination was made by J. F. Rowland of the Mines Branch. The difference between Rowland's value and our cell edge value was less than 0.0002 Å. As the reproducibility of the measurements lies within this range, the limit of error in the measurements of the parameters is arbitrarily taken as double this value, that is, ±0.0004 Å.

In Table 5 the unit cells of the Keno Hill samples of sphalerite, as determined by the method described above, are compared with those calculated by Skinner's function referred to at the beginning of this section. The mole per cent values used in the calculation are those of Table 4, column (a).

TABLE 5. MEASURED AND CALCULATED CELL EDGES OF SPHALERITE, KENO HILL-GALENA HILL AREA, YUKON

Sample No.	Measured cell edge	Calculated cell edge	Difference
A-472	5.4189	5.4185	−0.0004
A-473	5.4178	5.4173	−0.0005
A-535	5.4142	5.4151	+0.0009
A-568	5.4203	5.4197	−0.0006
A-708*	5.4219	5.4220	+0.0001
A-709	5.4183	5.4180	−0.0003
A-710	5.4169	5.4164	−0.0005
A-711	5.4171	5.4169	−0.0002
A-718	5.4122	5.4126	+0.0004
A-719	5.4144	5.4141	−0.0003

*Professor F. G. Smith kindly examined a fraction of A-708 by diffractometer and reports that from the spread of (333) the variation in unit cell dimensions extends at least ±0.0024 Å from his mean of 5.423 Å.

It will be seen that the agreement between the measured and calculated values is good. This is more apparent when the cell edges of the Keno Hill sphalerites are plotted (Fig. 2) against the iron-bearing sphalerites

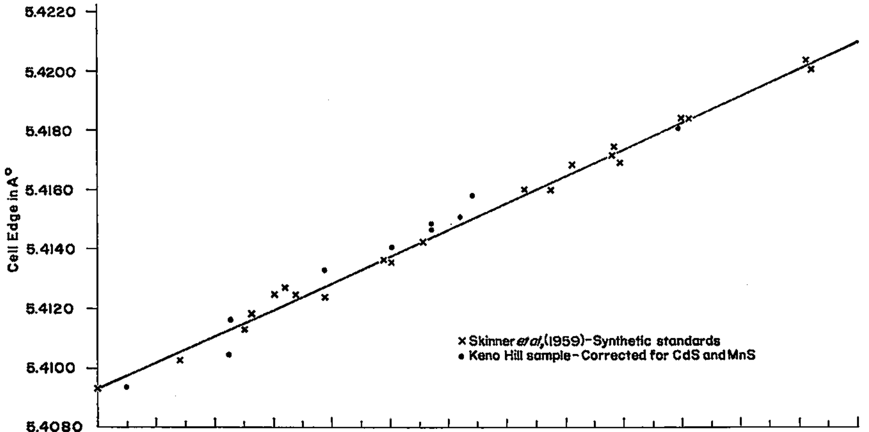

FIG. 2. Relationship of cell edge and FeS content of synthetic and Keno Hill sphalerites.

used by Skinner *et al.* (1959) to derive the function for iron content versus cell edge.

The agreement with Skinner's (1961) work is interesting considering the number of papers that have appeared recently stating that the iron content of sphalerite does not vary linearly with the cell edge. Skinner (1961) has commented on several of these papers, but two additional ones have appeared more recently (Van Aswegen & Verleger, 1960) (Krause, 1961).

Krause analyzed 23 sphalerites and measured their cell edges with an accuracy of ±0.001 Å. However, he apparently made no corrections to the cell edge for the manganese and cadmium content. When Krause's cell measurements are appropriately corrected and plotted, his sphalerites, particularly those with a high iron content, show a considerable scatter (Fig. 3). It is our opinion that more precise data than that given by Krause is necessary before his claim can be substantiated that the iron content does not vary linearly with the cell edge. Especially important would be the verification of Krause's data for the low iron sphalerites, because his curve for this data has a significantly steeper slope (Fig. 3) compared to that given by Skinner *et al.* (Fig. 2).

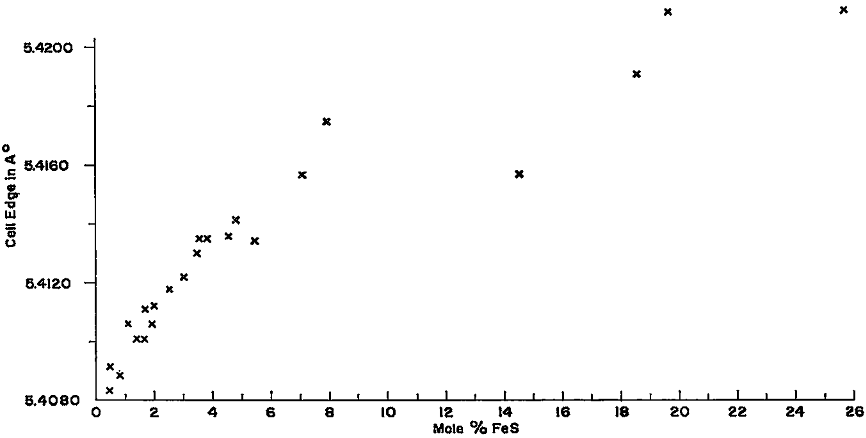

FIG. 3. Relationship of cell edge and FeS content corrected for CdS and MnS from the data of Krause (1961).

Van Aswegen & Verleger studied six synthetic sphalerites and concluded that substitution of Fe for Zn in sphalerite does not obey Vegard's law when the FeS content is very high. Samples with a low iron content (<20 mol per cent FeS) plot as a straight line which parallels that obtained by Skinner *et al.* (1959) but is 0.0016 Å higher. Van Aswegen & Verleger used a flat film technique in which their six synthetic samples were exposed on a single film in order to show the relative changes in cell dimensions. In terms of absolute cell sizes, the data of Skinner *et al.* (1959) must be regarded as being more accurate.

The agreement with Skinner's (1961) work is of further interest in view of the fact that we used bulk sampling methods that may have resulted in the incorporation of sphalerites with some compositional inhomogeneities. Such inhomogeneities would be expected to appear in the powder patterns as diffuse or doubled lines in the back-reflection region, yet such characteristics were not observed. This does not mean, however, that such inhomogeneities may not be present. Skinner also apparently used relatively large samples for his work on natural sphalerites and found excellent agreement between the measured and calculated cell edges.

GEOTHERMOMETRY

There is no pyrrhotite in the mineral assemblage of the Keno Hill deposits and hence the method employed by Kullerud (1953), Benson (1960), Arnold (1962), and others cannot be employed. Pyrite is present, however, in all veins and appears to have crystallized both earlier and later than sphalerite. It would seem, therefore, that equilibrium between sphalerite and FeS_2 may have been attained and hence the temperatures obtained from the mole per cent FeS could be the minimum crystallization temperatures.

Sims & Barton (1961) have discussed the various factors that influence the iron content of sphalerite in equilibrium with pyrite. They state that although the temperature has a strong effect on the iron content of sphalerite in pyrite-sphalerite assemblages, the activity of sulphur can be even more significant. The equilibrium data of Barton & Kullerud (1958) modified by Sims & Barton (1961) is shown in Fig. 4, and the minimum and maximum temperatures of formation of Keno Hill sphalerites obtained from their data are given in Table 6.

Within the Sp + Py + V area, a sphalerite containing 11.4 mole per cent FeS, such as samples A-470 and A-709, that crystallized in equilibrium with pyrite, could have formed at any temperature from 420° to 710° C. in the absence of pyrrhotite. Without knowing the sulphur vapour pressure there is no way of determining the precise temperature within this maximum-minimum range. One sample (A-708), however, with 19.86 mole per cent FeS falls within a relatively restricted maximum–minimum range of 600°–615° C.

The minimum temperature of this sample (600° C.) seems inordinately high for the crystallization temperature of sphalerite in the Galkeno

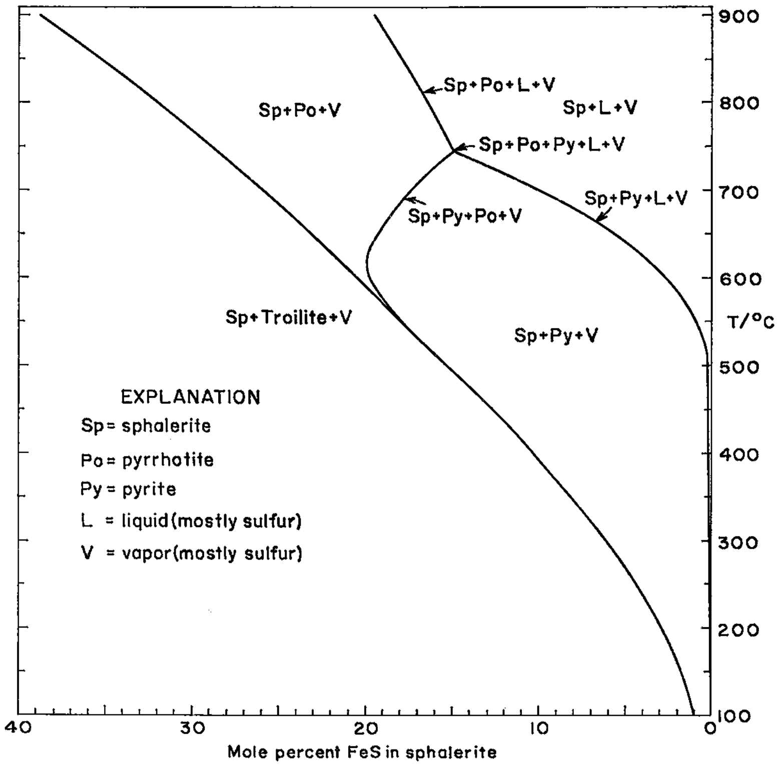

FIG. 4. Composition of sphalerite in equilibrium with various phases in the Fe-Zn-S system (from Sims & Barton Jr., 1961).

TABLE 6. TEMPERATURE OF FORMATION OF SPHALERITE, KENO HILL AREA

Sample No.	Mine	Moles % FeS	Estimated temperature of formation[1]	
			Minimum	Maximum
A–472	Sadie Friendship	12.42	450	725
A–473	Onek	11.47	425	715
A–535	Lucky Queen	4.54	255	635
A–568	Klondyke Keno	12.86	455	730
A–708	Galkeno	19.86	600..	615
A–709	Hector-Calumet	11.37	420	710
A–710	Hector-Calumet	7.75	340	670
A–711	Hector-Calumet	10.06	380	700
A–718	Gambler	1.13	110	560
A–719	Gambler	4.59	260	635

[1] Estimated temperature of formation from Figure 4.

veins on two counts. First, this vein is younger than those carrying a pyrite and arsenopyrite assemblage which according to Clark (1960) cannot coexist above 491° ±12° C. We must assume, therefore, that the mineralization temperatures increased after the first wave of mineralization, an assumption which seems unlikely since the Galkeno vein has a typical mesothermal mineral association. Secondly it is difficult to understand why the wall rocks of the Galkeno vein did not adjust to such a high temperature. One would expect high temperature skarn or hornfels minerals whereas what is present is low grade sericite, chlorite, and carbonaceous phyllites, schists, and quartzites.

For the other sphalerite samples it is evident that no unique temperature of crystallization can be assigned. One can only give a range and this is so great as to be of limited usefulness. It would seem, therefore, that the sphalerite geothermometer is not applicable to the Keno Hill deposits at the present state of our knowledge.

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