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TEMPERATURE OF CRYSTALLIZATION OF PYRRHOTITE AND SPHALERITE FROM THE HIGHLAND-SURPRISE MINE, COEUR D'ALENE DISTRICT, IDAHO[1]

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ABSTRACT

The ore bodies of the Highland-Surprise Mine are replacements along shear zones in quartzose slate, quartzite, and phyllite of the Prichard formation of the Belt series (Precambrian). Pyrite, arsenopyrite, pyrrhotite, sphalerite, chalcopyrite, and galena are the chief metallic minerals and were probably deposited in that order.

Temperatures of formation were estimated for pyrrhotite-pyrite and sphalerite-pyrrhotite assemblages contained in the steeply dipping vein system. Measurements on sixty-two pyrrhotites indicate a range in temperature of crystallization between 370° and 492° C (no correction required for confining pressures $<2{,}000$ bars below 670° C), and measurements on fourteen sphalerites indicate crystallization temperatures between 375° and 460° C (uncorrected for confining pressure). No systematic temperature gradients were recognized.

Minor elements in twenty-three pyrrhotite, eight pyrite, thirteen sphalerite, and two galena samples were determined. Partition ratios of nickel and cobalt in pyrrhotite-pyrite and sphalerite-pyrrhotite pairs are erratic. This suggests (a) a dis-equilibrium distribution of these elements between the phases of each mineral pair and/or (b) crystallization of the mineral pairs under different physical conditions.

INTRODUCTION

IN the Highland-Surprise Mine of the Coeur d'Alene district, Idaho, several narrow, steeply dipping veins replace quartz-rich rocks of the Belt series of Precambrian age. Pyrrhotite, pyrite, and sphalerite coexist in many parts of the veins, thus offering an opportunity to apply the sphalerite-pyrrhotite and pyrrhotite-pyrite geothermometers (8, 1).

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[1] Publication authorized by the Director, U. S. Geological Survey.

Kullerud's method relates the iron content of sphalerite coexisting in equilibrium with pyrrhotite to the temperature and total pressure of crystallization. On the basis of calculation Kullerud indicates that a positive correction of 25° C/1,000 bars total pressure should be applied to the temperatures of crystallization. The method developed by Arnold relates the iron content of pyrrhotite coexisting in equilibrium with pyrite to the temperature and pressure of crystallization. Experiments indicate, however, that no correction of the crystallization temperatures need be made for pressures up to 2,000 bars at temperatures below 670° C.

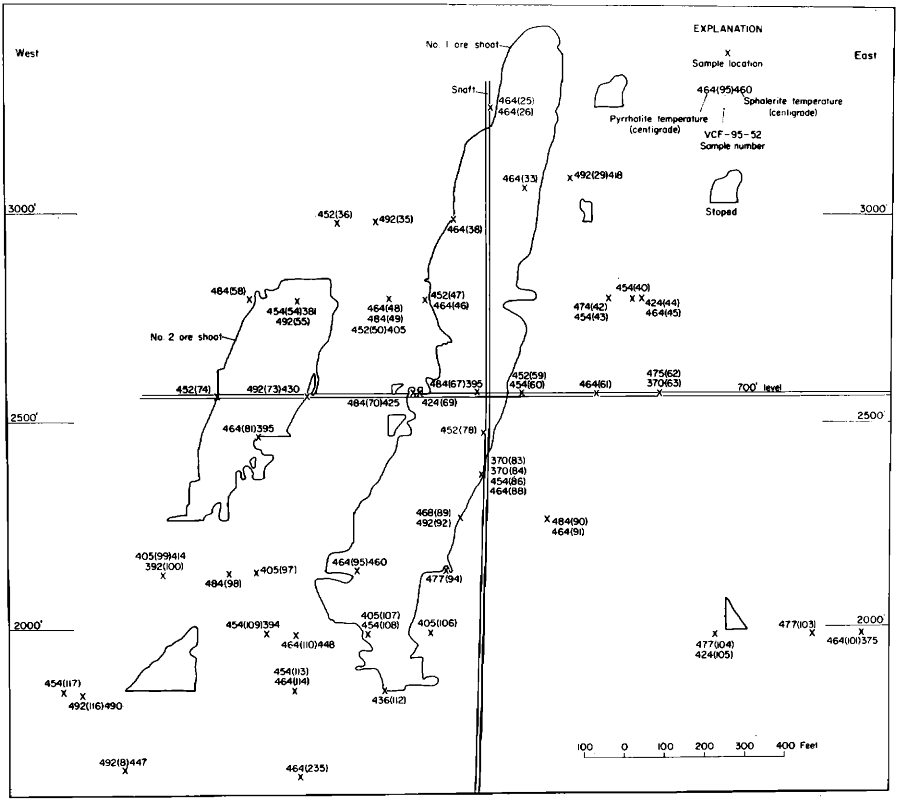


FIG. 1. Longitudinal N 70° W projection of the Highland-Surprise Mine showing temperatures of crystallization of sixty-two pyrrhotites and fourteen sphalerites. The veins are sufficiently narrow and coplanar that all samples may be presented on this projection.

In applying the experimental equilibrium relations to the natural assemblages it is assumed that equilibrium was initially attained and that no significant changes in the composition of the phases took place subsequent to deposition.

Umpleby and Jones (12) concluded that the Coeur d'Alene veins formed by deposition of the minerals in stages, and recent work by Fryklund (unpublished) agrees with this conclusion. Thus the minerals in each of the above pairs may not have crystallized simultaneously. If this is the case, it is assumed that equilibrium between minerals comprising each pair was attained in the solid state during or after deposition of the younger mineral.

The present study was initiated by Fryklund, who collected the specimens in 1952.

GEOLOGY AND MINERALOGY OF THE HIGHLAND-SURPRISE MINE

The mine is in the Pine Creek mineral belt of the Coeur d'Alene district, Shoshone County, Idaho. It ceased operation in 1955, and workings below the No. 4 adit level are inaccessible.

The country rocks of the mine consist of quartzose slate, quartzite, and phyllite of the Prichard formation of the Belt series of Precambrian age. The mineralogy of this formation remote from the veins is quartz, sericite, feldspar, and magnetite. Lithic fragments are abundant in this formation, which strikes approximately parallel to the veins and dips steeply to the north.

The mine had three producing veins formed by replacement along shear zones within the Prichard formation. Only one of these, the Surprise vein, located at the west end of the mine (Fig. 1), is of interest here. It strikes approximately N 65°W and ranges in dip from nearly vertical in the upper levels to approximately 60° S below the 1,650-foot level. As exposed in the main workings of the mine, the strongly mineralized part of the vein has a strike length of 1,400 feet. Below the 1,450-foot level the vein splits into several branches. The strongly mineralized portion of the vein consists essentially of a rectangular-shaped body of pyrrhotite containing two sphalerite-galena ore shoots.

The most important primary ore minerals in their probable order of crystallization are massive pyrite, arsenopyrite, pyrrhotite, sphalerite, chalcopyrite, and galena. There is a small amount of siderite and a somewhat larger amount of ankerite; tetrahedrite is rare. There are a few minute veinlets of late pyrite, late quartz, calcite, and chlorite. In the sixty-two specimens studied pyrrhotite is generally the most abundant sulfide. Pyrite occurs in all but thirteen of the specimens.

Pyrrhotite in some cases is slightly to moderately altered to marcasite and pyrite. Secondary pyrite occurs as clusters of minute euhedral grains lying along the borders of pyrrhotite grains. The alteration of pyrrhotite is probably hypogene, as primary sphalerite and galena cut marcasite in other mines in the district. Rhoden (9) has described a similar situation in the Silvermines district, Eire.

Early pyrite occurs in masses and scattered euhedral and anhedral grains. Massive pyrite is fractured and cut by veinlets of younger sulfides, including pyrrhotite. The age relations of scattered euhedral and anhedral pyrite are difficult to determine, but the fact that they are penetrated by pyrrhotite veinlets suggests that they are also older than pyrrhotite.

Sphalerite generally occurs in irregularly shaped grains and masses. It appears to replace pyrrhotite and to be replaced by galena. In a number of instances sphalerite veinlets cut pyrrhotite, demonstrating that sphalerite is younger than pyrrhotite. No exsolution textures of pyrrhotite in sphalerite

TABLE 1

ESTIMATED TEMPERATURES OF FORMATION OF PYRRHOTITE AND SPHALERITE

Sample No.[*]	Pyrrhotite[†]		Sphalerite[‡]		Sulfide minerals given in decreasing order of abundance[§]	
	Atomic percent metals	Estimated temp., °C	Weight percent FeS	Estimated temp., °C		
VCF-25-52)	46.72	464	-	-	(1) py (2) po (3) sph	po altered[¶]
VCF-26-52)	46.72	464	-	-	(1) po	
VCF-29-52	46.58	492	11.62	418	(1) po (2) py (3) sph (4) g (5) asp	po altered[¶]
VCF-33-52	46.72	464	-	-	(1) po (2) asp (3) py (4) g (5) sph	
VCF-38-52	46.72	464	-	-	(1) py (2) po (3) asp (4) ccp (5) sph	po altered[¶]
VCF-35-52	46.58	492	-	-	(1) po (2) asp (3) sph (4) g (5) ccp	
VCF-36-52	46.78	452	-	-	(1) po (2) sph (3) g (4) ccp (5) py	
VCF-44-52)	46.92	424	-	-	(1) py (2) po (3) asp (4) ccp	
VCF-45-52)	46.72	464	-	-	(1) po (2) asp (3) py (4) ccp	po altered[¶]
VCF-40-52	46.77	454	-	-	(1) po (2) asp (3) py (4) sph	
VCF-42-52)	46.67	474	-	-	(1) po (2) asp (3) py	
VCF-43-52)	46.77	454	-	-	(1) po (2) py (3) asp (4) g	
VCF-46-52)	46.72	464	-	-	(1) po (2) py (3) g (4) sph (5) ccp	
VCF-47-52)	46.78	452	-	-	(1) po (2) asp (3) py (4) ccp	
VCF-48-52)	46.72	464	-	-	(1) po (2) g (3) asp (4) py (5) ccp (6) sph	
VCF-49-52)	46.62	484	-	-	(1) po (2) py (3) sph (4) g	
VCF-50-52)	46.78	452	11.12	405	(1) po (2) g (3) sph (4) ccp (5) asp (6) py	
VCF-54-52)	46.77	454	10.27	381	(1) sph (2) g (3) po (4) py	po altered[¶]
VCF-55-52)	46.58	492	-	-	(1) po (2) py (3) sph (4) g (5) ccp	po altered[¶]
VCF-58-52	46.62	484	-	-	(1) po (2) py (3) asp	
VCF-62-52)	46.66	475	-	-	(1) po (2) py (3) asp (4) ccp	
VCF-63-52)	47.14	370	-	-	(1) po (2) asp (3) py (4) ccp (5) g	
VCF-61-52	46.72	464	-	-	(1) po (2) asp (3) py (4) sph (5) ccp (6) g	po altered[¶]
VCF-59-52)	46.78	452	-	-	(1) po (2) asp (3) py (4) ccp (5) g	po altered[¶]
VCF-60-52)	46.77	454	-	-	(1) po (2) asp (3) py	
VCF-67-52	46.62	484	10.76	395	(1) sph (2) po (3) g (4) asp (5) ccp	
VCF-69-52	46.92	424	-	-	(1) po (2) ccp (3) asp (4) g (5) py	
VCF-70-52	46.62	484	11.80	425	(1) po (2) py (3) sph	
VCF-73-52	46.58	492	11.99	430	(1) g (2) sph (3) po	
VCF-74-52	46.78	452	-	-	(1) po (2) asp (3) py (4) ccp	
VCF-78-52	46.78	452	-	-	(1) po (2) asp (3) sph (4) ccp (5) g (6) py	po altered[¶]
VCF-81-52	46.72	464	10.71	393	(1) po (2) sph (3) g (4) ccp (5) asp (6) py	
VCF-83-52)	47.14	370	-	-	(1) po (2) asp	
VCF-84-52)	47.14	370	-	-	(1) po (2) asp (3) ccp	
VCF-86-52)	46.77	454	-	-	(1) po (2) asp	
VCF-88-52)	46.72	464	-	-	(1) po (2) py (3) asp (4) ccp	po altered[¶]

(continued)

TABLE 1 - PAGE 2

ESTIMATED TEMPERATURES OF FORMATION OF PYRRHOTITE AND SPHALERITE

Sample No.*	Pyrrhotite†		Sphalerite‡		Sulfide minerals given in decreasing order of abundance§	
	Atomic percent metals	Estimated temp., °C	Weight percent FeS	Estimated temp., °C		
VCF-90-52)	46.62	484	-	-	(1) po (2) py (3) ccp (4) asp	
VCF-91-52)	46.72	464	-	-	(1) po (2) py (3) asp	
VCF-89-52)	46.69	468	-	-	(1) po (2) asp (3) py (4) sph (5) g	
VCF-92-52)	46.58	492	-	-	(1) po (2) py (3) g (4) sph	po altered¶
VCF-94-52	46.65	477	-	-	(1) po (2) py (3) sph	
VCF-95-52	46.72	464	13.07	460	(1) po (2) sph (3) g (4) ccp (5) asp	
VCF-97-52	47.01	405	-	-	(1) po (2) py (3) asp (4) sph	po altered¶
VCF-98-52	46.62	484	-	-	(1) po (2) asp (3) g	
VCF-99-52)	47.01	405	11.50	414	(1) po (2) asp (3) ccp (4) sph (5) g	
VCF-100-52)	47.06	392	-	-	(1) po (2) asp (3) ccp (4) py	
VCF-101-52	46.72	464	10.00	375	(1) po (2) sph (3) ccp (4) g	
VCF-103-52	46.65	477	-	-	(1) po (2) py (3) asp (4) ccp	po altered¶
VCF-104-52)	46.65	477	-	-	(1) po (2) g (3) asp (4) py	
VCF-105-52)	46.92	424	-	-	(1) po (2) py (3) asp (4) g (5) ccp	po altered¶
VCF-106-52	47.01	405	-	-	(1) po (2) asp (3) py (4) ccp (5) g	
VCF-107-52)	47.01	405	-	-	(1) po (2) asp (3) ccp (4) g	
VCF-108-52)	46.77	454	-	-	(1) po (2) asp (3) py (4) ccp	
VCF-109-52	46.77	454	10.75	394	(1) po (2) py (3) asp (4) g (5) sph (6) ccp	
VCF-110-52	46.72	464	12.64	448	(1) po (2) g (3) sph (4) asp (5) py (6) ccp	
VCF-112-52	46.86	436	-	-	(1) po (2) g (3) sph (4) ccp (5) py	
VCF-113-52)	46.77	454	-	-	(1) py (2) po (3) sph (4) asp (5) ccp	
VCF-114-52)	46.72	464	-	-	(1) py (2) po (3) ccp (4) sph (5) g	
VCF-116-52	46.58	492	13.92	490	(1) sph (2) g (3) po	
VCF-117-52	46.77	454	-	-	(1) po (2) sph (3) py (4) ccp	
VCF-235-52	46.72	464	-	-	(1) po (2) asp (3) py (4) ccp (5) sph	
VCF-8-54	46.58	492	12.60	447	(1) sph (2) g (3) po (4) py (5) asp	po altered¶

*Sample numbers within brackets collected within several feet of each other.

†Atomic percent metals determined by X-ray method of Arnold (1); temperatures estimated from Figure 2.

‡Weight percent FeS determined by chemical analyses, and temperatures (uncorrected for pressure) estimated from Figure 4. Analysts: S. M. Berthold, U. S. Geological Survey, and Hugh Warren, Palo Alto High School, Palo Alto, Calif. U. S. G. S. laboratory Nos. 154113 through 154149 correspond respectively to sample Nos. VCF-50, 70, 81, 101, 109, 110, 116-52. No laboratory numbers for remaining analyses.

§po, pyrrhotite; py, pyrite; asp, arsenopyrite; sph, sphalerite; g, galena; ccp, chalcopyrite. Abundances established from polished section study.

¶Marcasite and pyrite are present within the pyrrhotite and represent hypogene alteration as described in the text.

were recognized. In thin section sphalerite did not show color zoning, which if present would imply a lack of equilibrium during crystallization.

ANALYTICAL TECHNIQUES

The composition of pyrrhotite from sixty-two samples summarized in Table 1 was determined by an X-ray spacing method (1), which related d_{102}

TABLE 2

SPECTROGRAPHIC ANALYSES OF TWENTY-THREE PYRRHOTITES, EIGHT PYRITES, THIRTEEN SPHALERITES, AND TWO GALENAS FROM THE HIGHLAND-SURPRISE MINE

Laboratory No.	Sample No.	Mineral	Ni	Co	Mn	Cu	Cd	Zn	Ag
153427	VCF-25-52	pyrrhotite	0.062	<0.0004	0.0026	0.0040	<0.02	0.18	-
153428	VCF-26-52	pyrrhotite	0.054	0.0020	0.0046	0.044	<0.02	0.20	-
153408		pyrite	0.055	0.0022	<0.0002	0.075	n.d.*	<0.06	-
153429	VCF-29-52	pyrrhotite	0.0013	0.0051	0.0056	0.020	<0.02	1.4	-
153409		pyrite	0.045	0.16	<0.0002	0.047	n.d.	<0.06	-
153419		sphalerite	0.0009	0.0030	0.016	0.22	0.36	-	-
153430	VCF-33-52	pyrrhotite	0.062	<0.0004	0.028	0.0050	<0.02	0.09	-
153410		pyrite	0.040	0.040	<0.0002	0.64	n.d.	<0.06	-
153432	VCF-36-52	pyrrhotite	0.043	<0.0004	0.0015	0.075	<0.02	0.24	-
153433	VCF-38-52	pyrrhotite	0.0052	0.0013	0.0078	0.26	<0.02	<0.04	-
153460		pyrite	0.016	0.024	0.0011	0.036	n.d.	<0.06	-
153434	VCF-40-52	pyrrhotite	0.022	0.0015	0.0012	0.018	<0.02	0.10	-
154114	VCF-42-52	pyrrhotite	0.042	0.0077	0.0013	0.070	-	0.14	-
153435	VCF-46-52	pyrrhotite	0.011	0.017	0.0026	0.0044	<0.02	0.12	-
153436	VCF-47-52	pyrrhotite	0.0095	0.0044	0.0011	0.021	<0.02	0.11	-
153437	VCF-48-52	pyrrhotite	0.066	0.013	0.0044	0.020	<0.02	0.51	-
153438	VCF-50-52	pyrrhotite	0.058	0.017	0.054	0.070	<0.02	0.34	-
153447		galena	0.0092	0.020	0.019	0.070	n.d.	-	0.085
154143		sphalerite	0.0009	0.0037	0.020	0.041	0.26	-	-
153463	VCF-54-52	pyrrhotite	0.033	0.010	0.080	0.018	<0.02	1.8	-
153420		sphalerite	0.0008	0.0058	0.016	0.10	0.44	-	-
153439	VCF-55-52	pyrrhotite	0.0044	0.0040	0.026	0.0058	<0.02	0.08	-
153412		pyrite	0.020	0.025	0.0030	0.080	n.d.	<0.06	-
153440	VCF-67-52	pyrrhotite	0.011	0.0048	0.026	0.010	<0.02	0.60	-
153421		sphalerite	0.010	0.0050	0.031	0.14	0.26	-	-
154144	VCF-70-52	sphalerite	0.0010	0.0050	0.020	0.018	0.22	-	-
153441	VCF-73-52	pyrrhotite	0.019	0.017	0.0020	0.0020	<0.02	6.5	-
153422		sphalerite	0.001	0.0096	0.016	0.016	0.36	-	-
153448		galena	<0.0004	0.0006	0.0006	0.0020	n.d.	-	0.0028
154145	VCF-81-52	sphalerite	0.0005	0.0049	0.020	0.18	0.23	-	-
153442	VCF-88-52	pyrrhotite	0.0010	0.0015	0.0036	0.0088	<0.02	0.08	-
153413		pyrite	0.019	0.085	<0.0002	0.045	n.d.	<0.06	-
153443	VCF-89-52	pyrrhotite	0.0064	0.012	0.0022	0.060	<0.02	0.90	-
153415		pyrite	0.018	0.050	0.0011	0.055	n.d.	<0.06	-
153444	VCF-95-52	pyrrhotite	0.018	0.0090	0.0007	0.016	<0.02	0.35	-
154115	VCF-98-52	pyrrhotite	0.010	0.010	0.0008	0.018	-	0.13	-
153445	VCF-99-52	pyrrhotite	0.038	0.012	0.0006	0.050	<0.02	<0.04	-
153416		pyrite	0.063	0.20	0.0006	0.39	n.d.	<0.06	-
153424		sphalerite	0.0011	0.0070	0.014	0.22	0.32	-	-
154146	VCF-101-52	sphalerite	0.0010	0.0012	0.017	0.074	0.28	-	-
154116	VCF-106-52	pyrrhotite	0.030	0.016	0.0008	0.070	-	0.15	-
154147	VCF-109-52	sphalerite	0.0006	0.0048	0.014	0.26	0.26	-	-
154148	VCF-110-52	sphalerite	0.0018	0.0064	0.035	0.058	0.21	-	-
154149	VCF-116-52	sphalerite	0.0014	0.0060	0.068	0.018	0.21	-	-
153426	VCF-8-54	pyrrhotite	0.022	0.0082	0.012	0.0050	0.16	25.0	-
153418		sphalerite	0.0017	0.0050	0.033	0.0096	0.40	-	-

These results have an over-all accuracy of ±15 percent of the reported value, except near the limit of detection where only one significant figure is reported.

Analysts: Janet D. Fletcher and Nola B. Sheffey, U. S. Geological Survey.

*n.d., not detected.

to the composition of synthetic pyrrhotite solid solutions. Arnold and Reichen (2) demonstrated that the metal content of natural pyrrhotites may be determined by this X-ray method to about ±0.23 atomic percent if less than a total of 0.6 weight percent Ni, Co, and Cu occur in solid solution.

The maximum concentration of combined nickel, cobalt, and copper in twenty-one pyrrhotites is only 0.27 weight percent (Table 2). Assuming that the combined concentration of these elements in the remaining forty-one pyrrhotites is similarly low, the amount of substitution is insufficient to affect d_{102} and hence the measured compositions.

The d_{102} values were determined as described elsewhere (2) using a wide-angle focusing X-ray diffractometer and a Philips powder camera (Straumanis film mounting, 114.59 mm diameter). Lake Toxaway quartz was used as internal standard. Measurements obtained from samples employing both types of X-ray equipment were identical within the limit of error of the measurements (±0.02° 2θ). All $(102)\alpha$ reflections were single and moderately sharp showing that no inversion to monoclinic symmetry had taken place.

TABLE 3

SUMMARY OF MINOR ELEMENT CONCENTRATIONS IN PYRRHOTITE, PYRITE, AND SPHALERITE

Element	Pyrrhotite 23 determinations		Pyrite 8 determinations		Sphalerite 13 determinations	
	Range (weight percent)	Mean	Range (weight percent)	Mean	Range (weight percent)	Mean
Ni	0.066–0.001	0.027	0.063–0.016	0.035	0.01 –0.0005	0.0018
Co	0.017–<0.0004	0.0075	0.2 –0.0022	0.0732	0.0096–0.0012	0.0052
Mn	0.08 –0.0006	0.012	0.003–<0.0002	0.0015	0.068 –0.014	0.025
Cu	0.075–0.002	0.0281	0.080–0.036	0.056	0.26 –0.0096	0.10
Cd	<0.02	—	—	—	0.44 –0.21	0.29
Zn	—	—	<0.06	—	—	—

Mineral separations for chemical and spectrographic analyses were made on the basis of density or magnetic susceptibility. Inclusions of chalcopyrite and sphalerite within the mineral concentrates could not be completely removed; therefore, the values reported for copper and zinc reflect impurities to a large extent.

TRACE ELEMENTS

The concentrations of nickel, cobalt, manganese, copper, cadmium, and zinc were determined spectrographically for twenty-three pyrrhotites (Table 2). Eight pyrites were analyzed for nickel, cobalt, manganese, copper, and zinc; and thirteen sphalerites were analyzed for nickel, cobalt, manganese, copper, and cadmium. Two galenas were analyzed for silver. The concentration range of each minor element from Table 2 is given in Table 3. Erratically high values, which are interpreted as being due to admixed impurities, have not been included in the table. To permit a comparison between the concentration of minor elements in the various minerals the mean concentration for each minor element is also given in Table 3.

The average nickel contents of pyrite and pyrrhotite are nearly identical, with a slightly higher value for pyrite. This suggests that at these low concentrations (and under the prevailing pressures and temperatures) nickel enters pyrite and pyrrhotite with about equal ease. Sphalerite contains considerably less nickel than either pyrite or pyrrhotite; however, nickel is slightly more concentrated in the more iron-rich sphalerites.

Pyrite contains the highest average amount of cobalt, followed by pyrrhotite, and then sphalerite. Cobalt is slightly enriched in the more iron-rich sphalerites. The average relationship for nickel and cobalt in the three sulfides can be summarized as follows:

pyrrhotite, $[Ni] > [Co]$; pyrite, $[Co] > [Ni]$; sphalerite, $[Co] > [Ni]$.

Cadmium is essentially restricted to sphalerite. This has been noted in the literature for other areas (5). Manganese is present in all sphalerites and generally shows an increase in concentration as iron in sphalerite increases. In general, manganese shows the greatest concentration in sphalerite, the least concentration in pyrite, and an intermediate value in pyrrhotite.

Partition ratios for nickel and cobalt in eight pairs of coexisting pyrrhotite and pyrite and seven pairs of coexisting pyrrhotite and sphalerite were obtained from the trace-element data given in Table 2. The ratios obtained for each mineral pair are erratic; whereas, ideally, equilibrium trace-element ratios should lie on a smooth curve if the temperature and pressure of crystallization were constant. Kretz (6, 7) has discussed this in connection with the partition of elements between coexisting silicates. The explanation for these erratic results is not known. However, a variation of temperature and/or pressure during crystallization, lack of attainment of an equilibrium distribution of trace elements, and errors in trace-element analyses owing to sample contamination may be responsible.

ESTIMATED TEMPERATURES OF CRYSTALLIZATION

Pyrrhotite Geothermometer.—Table 1 summarizes the estimated temperatures of crystallization of pyrrhotite at a total pressure of less than 2,000 bars. The estimates were obtained from the pyrrhotite solvus (1), which is reproduced in Figure 2. The uncertainty of these estimates is approximately ±50° C because of the uncertainty in the composition determinations. Minor element concentrations in these pyrrhotites are believed to be too low to significantly affect the temperature estimates.

Tests of uniformity of composition on masses and individual grains of pyrrhotite were made by sampling within grains and at contacts with pyrite. No difference in composition was detected in any grain or mass.

The temperature estimates are summarized in a histogram (Fig. 3). The estimates range between 370° and 492° C. The average of these temperatures is 456° C. The histogram shows a maximum between 460° and 470° C, suggesting one major episode of crystallization. Assuming that the error in each temperature estimate is ±50° C, the total range in temperatures is somewhat greater than can be accounted for by the error in measurement; pyrrhotite, therefore, probably crystallized over a range of temperatures.

The agreement between temperature estimates obtained from samples located very close together (bracketed samples of Table 1) is generally good. In twelve out of fourteen cases the agreement of the estimates is well within the limit of error of measurement. The maximum differences between the estimates in the two remaining cases are 105° C (VCF-62, 63–52) and 94° C (VCF-83, 84, 86, 88–52). The reason for such large differences is not clear. However, local alteration of pyrrhotite to pyrite or marcasite may be responsible.

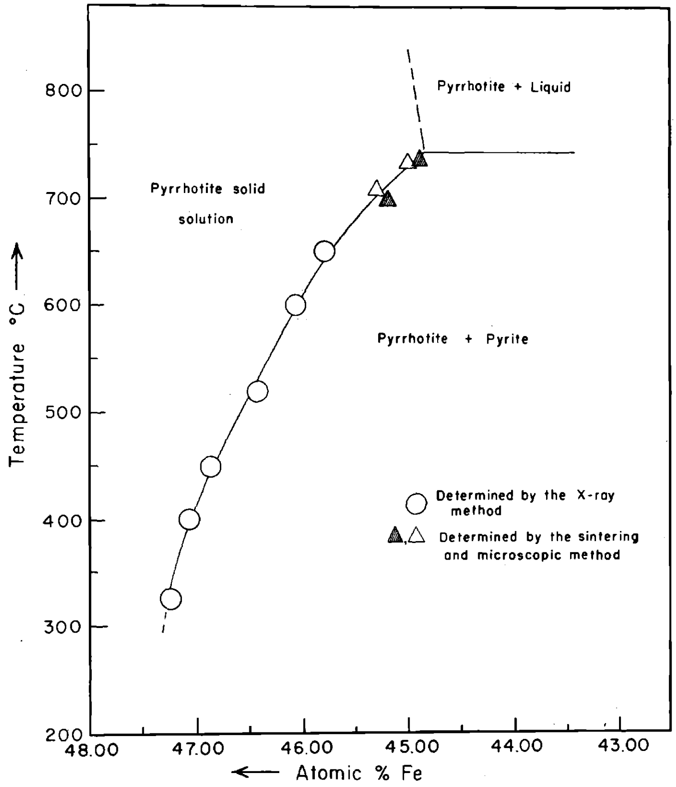
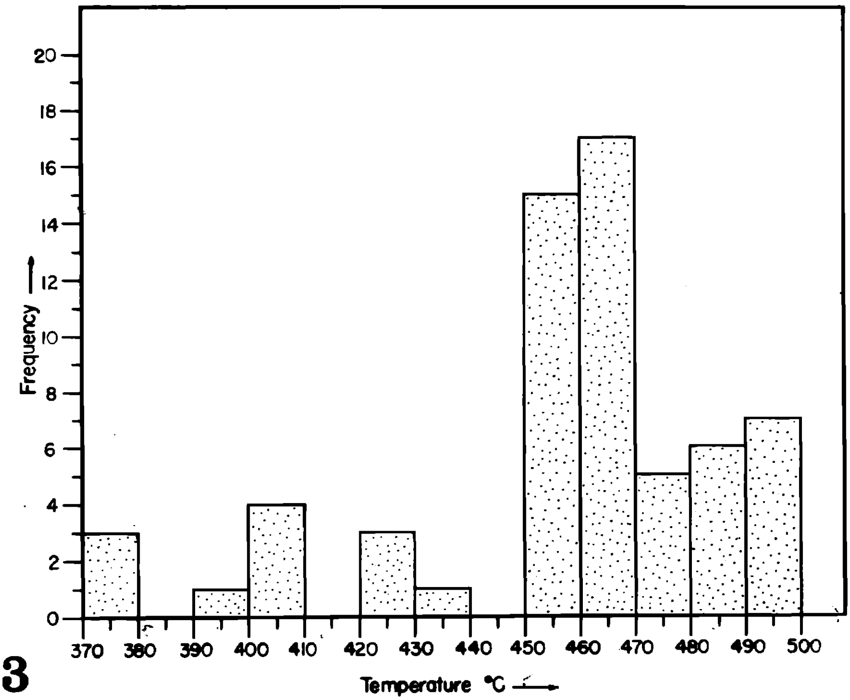
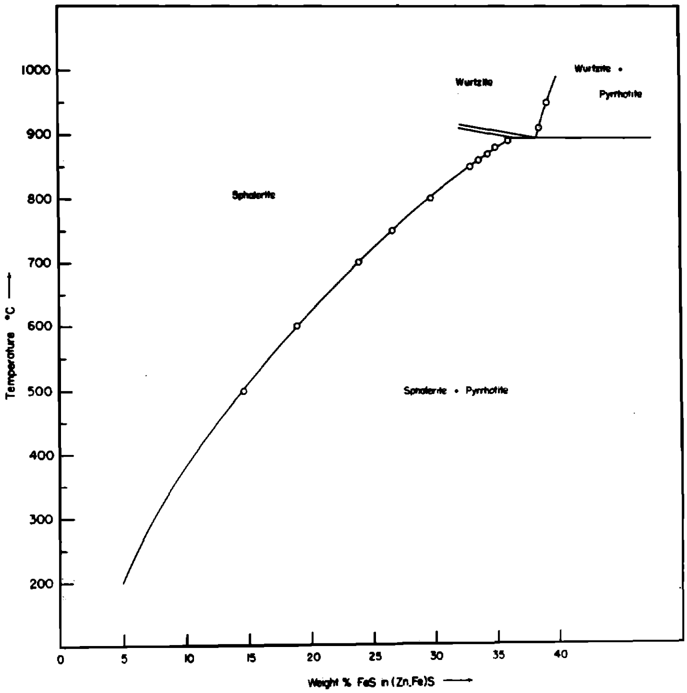


FIG. 2. Part of the FeS-FeS_2 equilibrium diagram modified from Arnold (1) showing the pyrrhotite solvus at a total pressure of <15 atmospheres.

Pyrite was not observed in thirteen of the sixty-two polished sections examined. Comparison of the range of crystallization temperatures of pyrrhotite from these thirteen samples with that of the remaining samples reveals no appreciable difference. The temperature estimates in both instances range from 370° to 492° C.


20
18
16
14
12
10
8
6
4
2
0
Frequency
370
380
390
400
410
420
430
440
450
460
470
480
490
500
Temperature °C

3


1000
900
800
700
600
500
400
300
200
Temperature °C
Wurtzite
Wurtzite +
Pyrrhotite
Sphalerite
Sphalerite + Pyrrhotite
0
5
10
15
20
25
30
35
40
Weight % FeS in (Zn,Fe)S

4

Sphalerite Geothermometer.—The iron content of sphalerite coexisting with pyrrhotite in fourteen different samples was determined by wet chemical methods (Table 1). The uncertainty in these values is about ±0.15 weight percent iron or ±0.23 weight percent FeS.

The estimated temperatures of crystallization of these sphalerites, uncorrected for confining pressure, are also summarized in Table 1. They range between 375° and 490° C. The average of these temperatures of crystallization is 420° C. These temperature estimates were obtained from the sphalerite solvus (Fig. 4) determined by Kullerud (8). The error in iron determination gives an uncertainty of ±8° C in these temperatures.

The analyses in Table 2 show a maximum individual concentration of 0.44 weight percent cadmium and 0.068 weight percent manganese in sphalerite, and a maximum combined concentration of 0.456 weight percent of these elements. Studies by Kullerud (8) and Skinner (10) on the effect of manganese, by Kullerud (8) on the effect of cadmium, and by Toulmin (11) on the effect of copper on the sphalerite-pyrrhotite equilibrium relations show that no corrections need be applied to the temperature estimates owing to the low concentration of these elements.

Arsenopyrite-Pyrite-Pyrrhotite Relation.—Arsenopyrite, pyrite, and pyrrhotite coexist in many parts of the Highland-Surprise Mine. Clark (3) has shown that the maximum temperature at which these phases can coexist in equilibrium is 491° C. This value is almost identical with the maximum temperature estimated by the pyrrhotite and sphalerite geothermometers.

COMPARISON OF PYRRHOTITE AND SPHALERITE TEMPERATURES

The estimated crystallization temperatures of pyrrhotite and sphalerite are shown in Figure 1, plotted at the respective sample locations. No systematic temperature gradient is evident on the basis of either group of temperatures. It can be noted, however, that an average of the sphalerite temperatures above the 700-foot level is 406° C, whereas that below this level is 427° C.

A comparison of the range of pyrrhotite temperatures (370° to 492° C) with the range of sphalerite temperatures (375° to 490° C) shows that they correspond very closely. Reference to Table 1 reveals, however, that one sphalerite temperature is 9° C higher, whereas the remaining thirteen sphalerite temperatures are as much as 89° C lower than the corresponding pyrrhotite temperatures. A similar relationship between pyrrhotite and sphalerite temperatures was found by Ferris (4) in a study of the Coronation Mine, in the Flin Flon area, Saskatchewan.

In general, the agreement between the pyrrhotite and sphalerite temperatures is improved by applying a positive correction for pressure to the sphalerite temperatures amounting to 25° C/1,000 bars (8). For example, by assuming a pressure of 2,000 bars the maximum difference of 89° C between

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FIG. 3. Histogram showing the distribution of sixty-two temperatures of crystallization of pyrrhotite in 10° C intervals.

FIG 4. Portion of the ZnS-FeS phase diagram after Kullerud (8) showing the sphalerite solvus at a total pressure of <1 atmosphere.

the pyrrhotite and sphalerite temperatures reduces to only 39° C, which is within the uncertainty in the methods.

CONCLUSIONS

This study indicates that crystallization of pyrrhotite and sphalerite took place at temperatures ranging between 370° and 490° C. The accuracy of these temperatures cannot be properly evaluated; however, the fact that the temperatures obtained from the two methods agree within reasonable limits justifies confidence in the estimates.

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REFERENCES

1. Arnold, R. G., 1962, Equilibrium relations between pyrrhotite and pyrite from 325° to 743° C: ECON. GEOL., v. 57, p. 72–90.
2. Arnold, R. G., and Reichen, L. E., 1962, Measurement of the metal content of naturally occurring, metal-deficient, hexagonal pyrrhotite by an X-ray spacing method: Am. Mineralogist, v. 47, p. 105–111.
3. Clark, L. A., 1960, The Fe-As-S system: Phase relations and applications. Part 2: ECON. GEOL., v. 55, p. 1631–1652.
4. Ferris, C. S., Jr., 1961, Temperature of formation of the Coronation ore body, Flin Flon area, Saskatchewan: M.S. thesis (unpublished), University of Saskatchewan.
5. Fleischer, M., 1955, Minor elements in some sulfide minerals: ECON. GEOL., 50th Anniv. Vol., p. 970–1024.
6. Kretz, R. A., 1959, Chemical study of garnet, biotite, and hornblende from gneisses of southwestern Quebec, with emphasis on distribution of elements in coexisting minerals: Jour. Geology, v. 67, p. 371–402.
7. Kretz, R. A., 1960, The distribution of certain elements among coexisting calcic pyroxenes, calcic amphiboles, and biotites in skarns: Geochim. et Cosmochim. Acta, v. 20, p. 161–191.
8. Kullerud, G., 1953, The FeS-ZnS system; a geological thermometer: Norsk geologisk Tidsskr., v. 32, p. 61–147.
9. Rhoden, H. N., 1959, Mineralogy of the Silvermines district, County Tipperary, Eire: Mineralog. Mag., v. 32, p. 128–139.
10. Skinner, B. J., 1959, Effect of manganese on the sphalerite geothermometer (Abstr.): Geol. Soc. America Bull., v. 70, p. 1676.
11. Toulmin, P., 3rd, 1960, Effect of Cu on sphalerite phase equilibria—a preliminary report (Abstr.): Geol. Soc. America Bull., v. 71, p. 1993.
12. Umpleby, J. B., and Jones, E. L., Jr., 1923, Geology and ore deposits of Shoshone County, Idaho: U. S. Geol. Survey Bull. 732, 156 p.