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MINOR ELEMENTS IN SOME SULFIDE MINERALS¹

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GL03755

*ECON GEOLOGY
50th Anniversary Volume*

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ABSTRACT

Data in the literature on the minor element content of galena, sphalerite and wurtzite, chalcopyrite, pyrite and marcasite, pyrrhotite, and arsenopyrite are summarized, with comments as to the significance of the results with respect to the temperatures and other conditions of formation.

INTRODUCTION

THE minor elements in sulfide ores have been investigated intensively during the past hundred years. The early work was aimed at finding new elements and new sources of the rarer elements; among the accomplishments of these studies were the discovery in sphalerite of the new elements indium by Reich and Richter in 1863, and gallium by Boisbaudran in 1874. The development of spectrographic methods of analysis has led to a great increase in the number of samples analyzed and has also resulted in a shift in the type of data reported from purely qualitative in the earlier work, to semiquantitative during the 1920's and 1930's, to a preponderance of quantitative analyses during the past 15 years.

The emphasis has also shifted; the aim of many of the recent investigations has been to obtain information about the processes of ore formation. A

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

Gavelin and Gabrielson (61, p. 3)² put it, "From a metallurgical point of view it is obviously of great importance to know the amount and distribution even of small concentrations of certain chemical elements that may be of importance for the refining processes and which may influence the character of the substances to be extracted from the ore. From a theoretical point of view a knowledge of the distribution of the minor constituents may in certain cases be expected to be valuable in elucidating the history of the formation of an ore deposit." Attention has been directed especially towards the correlation of the content of minor elements with the conditions of formation, particularly the temperature of formation.

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	A
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Yt	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Th	Pa	U												

La	Ce	Pr	Nd	Pm	Sm	Eu
Gd	Tb	Dy	Ho	Er	Tm	Yb
Lu						

FIG. 1. The chalcophilic elements. Shading to left—chalcophilic elements; dotted—siderophilic elements that are also markedly concentrated in sulfides; shading to right—lithophilic elements that are also markedly concentrated in sulfides.

The purpose of this paper is to summarize the widely scattered information available on the minor-element content of those sulfides for which the most data have been obtained, namely galena, sphalerite and wurtzite, chalcopyrite, pyrite and marcasite, pyrrhotite, and arsenopyrite. The smattering of data available on many other sulfides has had to be omitted for lack of space.

The data have been summarized in tables, two for each mineral. The first is a list of pertinent references with an indication of the type of analysis (qualitative, semiquantitative, or quantitative), and the elements detected or determined. The second table for each mineral summarizes the quantitative and semiquantitative determinations by arbitrarily selected concentration ranges. The figures given should be used with great caution. In the first place, in summary tables like these, one is forced, for example, to equate the

² Numbers in parentheses refer to references at end of paper.

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"Not Found" of the analyst whose sensitivity was 200 ppm (parts per million) with the "Not Found" of the analyst whose sensitivity was 5 ppm. In the second place, the samples analyzed ranged from very carefully selected and purified material to gross mixtures. I have tried to indicate in the discussion of each mineral what elements reported might be due to adventitious impurities.

The Chalcophilic Elements

From the data available on the relative concentrations of the elements in the metallic, sulfidic, and silicate parts of meteorites, and from data on the free energies of formation, the elements can be grouped according to their tendencies to occur as sulfides rather than as silicates or metals. Those that tend to be enriched in the sulfide phase are called chalcophilic. Figure 1 shows these and also those that are mainly concentrated in the metallic phase or in the silicate phase, but occur to an appreciable degree in sulfides. It should be emphasized that the classification is based on relative concentrations in the different phases and is not a measure of total amounts in them. This may be illustrated by gallium, a chalcophilic element, whose concentration is higher in sulfides than in silicates; nevertheless, because the total amount of sulfides in the Earth's crust is a very small fraction of the silicate portion, the latter contains nearly all of the gallium of the crust.

Mode of Occurrence of Minor Elements

Haberlandt (75), following Schneiderhöhn (169), has classified the ways in which minor elements occur in minerals. He distinguishes between occurrence as trace elements, including isomorphous substitution and adsorption, and occurrence as trace minerals. The last include the occurrence of distinct phases as oriented overgrowths, oriented intergrowths (for example those formed by exsolution), and various types of inclusions. The study of ore minerals by reflected light has shown that the occurrence of distinct phases of all these types is the rule, rather than the exception; a wealth of illustrations has been given by Bastin (10), Edwards (51), Ramdohr (153), and Schwartz (176) and need not be discussed here. The problem of isomorphous substitution in the sulfides does, however, require discussion.

Isomorphous Substitution in Sulfide Minerals

The naturally occurring oxides and silicates are predominantly ionic in character, that is, they are chiefly bonded by electrostatic attraction between oppositely charged ions. For this type of compound, the principal factor that determines the possibility of isomorphous substitution is one of volume, and a good first approximation to prediction of isomorphous substitution is given by Goldschmidt's rule that such substitution is possible if the ionic radii of the two elements being considered are within 15 percent of one another. An appreciable correction is necessary for the coordination number of the ion in the particular structure being considered, and recent work has shown

activity was 200 ppm (parts per million) whose sensitivity was 5 ppm. In the ... from very carefully selected and ... have tried to indicate in the discussion ... ed might be due to adventitious im-

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silicates are predominantly ionic in ... ed by electrostatic attraction between ... of compound, the principal factor that ... as substitution is one of volume, and ... of isomorphous substitution is given ... tion is possible if the ionic radii of ... within 15 percent of one another. ... for the coordination number of the ... sidered, and recent work has shown

the need for taking into account such factors as electronegativity, polariza- bility, and ionic potential [see, for example, Pauling (144), Ahrens (3, 4), Goldschmidt (62, p. 80-125), Shaw (181), Szadeczky-Kardoss (189), Ring- wood (158, 159), and Vendel (203)]. Nevertheless, the use of ionic radii

TABLE 1
APPARENT IONIC AND COVALENT RADII OF SOME ELEMENTS FROM
AHRENS (1952) AND PAULING (1940)

Element	Ionic radius (A)		Covalent radius (A)
	Valence	Radius	
Antimony	+3	0.76	1.41
Arsenic	+3	0.58	1.21
Arsenic	+5	0.46	—
Bismuth	+3	0.96	1.46
Cadmium	+2	0.97	1.48
Cobalt	+2	0.72	1.32
Copper	+1	0.96	1.35
Copper	+2	0.72	—
Gallium	+3	0.62	1.26
Germanium	+2	0.73	1.22
Germanium	+4	0.53	—
Indium	+3	0.81	1.44
Iridium	+4	0.68	1.32
Iron	+2	0.74	1.23
Iron	+3	0.64	—
Lead	+2	1.20	1.46
Manganese	+2	0.80	—
Mercury	+2	1.10	1.48
Molybdenum	+4	0.70	1.38
Molybdenum	+6	0.62	—
Nickel	+2	0.69	1.39
Osmium	+6	0.69	1.33
Palladium	+2	0.80	1.31
Palladium	+4	0.65	—
Platinum	+2	0.80	—
Platinum	+4	0.65	1.31
Rhenium	+4	0.72	—
Ruthenium	+4	0.67	1.33
Selenium	-2	1.98	1.17
Silver	+1	1.26	1.53
Sulfur	-2	1.84	1.04
Tellurium	-2	2.21	1.37
Tin	+2	0.93	1.42
Tin	+4	0.71	1.40
Thallium	+1	1.47	1.47
Thallium	+3	0.95	1.47
Tungsten	+6	0.62	1.44
Vanadium	+5	0.59	—
Zinc	+2	0.74	1.31

alone generally gives reasonably good predictions as to isomorphous substi- tutions.

The sulfides and sulfosalts, however, with the exception of galena (PbS) and alabandite (MnS), have mainly covalent bonding, in which the atoms are bonded by mutual sharing of electrons. Ionic radii do not apply to com-

pounds having this type of bonding. Table 1 lists ionic radii (after Ahrens, 3) and covalent or atomic radii (after Pauling, 144).

If one now attempts to predict isomorphism in the sulfides on the basis of either the ionic or the covalent radii and compares the predictions with the facts observed, as summarized in later sections of this paper, it is apparent that the agreement is very far from satisfactory. One reason for this is that the sulfides are not bonded entirely by covalent linkages; they behave as though they were bonded partly by ionic and partly by covalent linkages, and satisfactory representation of their bonding cannot be made except by considerations of quantum mechanics. Frueh (57) has shown that in some respects metallic bonding may need to be considered.

Ahrens (4, p. 22-23) has pointed out that "ionic radii may be used in a rather restricted way in sulfide minerals." If one examines the data for any mineral or pair of minerals, serious discrepancies appear. This can be illustrated by the pair galena-sphalerite. From the ionic radii (Pb 1.20 A, Zn 0.74 A), one would predict correctly that silver (1.26 A) and thallium (1.47 A) would be preferentially concentrated in galena, and that iron (0.74 A), manganese (0.80 A), gallium (0.62 A), and germanium (0.73 or 0.53 A) would be preferentially concentrated in sphalerite. One might predict correctly that indium (0.81 A) would appear in both minerals but with a preference for sphalerite and that tin (0.93 A) would appear in both minerals. One would certainly not predict, however, that bismuth (0.96 A) would appear almost exclusively in galena, whereas cadmium (0.97 A) appears almost exclusively in sphalerite, nor that antimony (0.76 A) is preferentially concentrated in galena, whereas mercury (1.10 A) is found more commonly in sphalerite than in galena. Nor does consideration of ionic potentials (4) improve the situation appreciably, except for mercury.

Similar difficulties of prediction are apparent with other minerals, and it is evident that at present predictions of isomorphous substitution in the sulfides cannot be safely made. The application of the methods of quantum mechanics, as by consideration of the energy levels required to form different types of directed covalent bonds, seems to offer the best hope of progress.

Effects of Conditions of Formation on Minor-Element Content

Many investigators have tried to use the minor-element content of sulfides as an indication of their temperature of formation, and some have drawn conclusions that are summarized below under the individual minerals. Haberlandt and Schroll (77) point out that the absolute amount of a given element or the relative proportions of two elements that can substitute isomorphously in a given mineral are affected (1) by conditions of temperature and pressure, (2) by regional factors, and (3) by factors relating to the type of wall rocks and the type of associated igneous rocks. Kullerud (110), in a very important paper, has studied equilibrium relations in the FeS-ZnS system and has shown that the iron content of sphalerite can be used as a geological thermometer, provided that the sphalerite was formed under equilibrium conditions in the presence of an excess of iron. (See further Ingerson, this

Table 1 lists ionic radii (after Ahrens, Pauling, 144).

isomorphism in the sulfides on the basis and compares the predictions with the sections of this paper, it is apparent satisfactory. One reason for this is that ionic radii are not strictly additive, but partly by covalent linkages, and the prediction cannot be made except by comparison (57) has shown that in some cases should be considered.

It is noted that "ionic radii may be used in a number of cases." If one examines the data for various elements, some discrepancies appear. This can be explained by the following factors:

From the ionic radii (Pb 1.20 Å, Ag 1.26 Å) and thallium (1.26 Å) substituted in galena, and that iron (0.74 Å), and germanium (0.73 or 0.53 Å) substituted in sphalerite. One might predict copper (0.73 Å) would appear in both minerals. However, that bismuth (0.96 Å) would appear in galena, and cadmium (0.97 Å) appears in sphalerite. Antimony (0.76 Å) is preferentially substituted in galena (0.76 Å) is found more commonly in sphalerite. The calculation of ionic potentials (4) for various elements, including mercury.

Comparison with other minerals, and it is noted that simultaneous substitution in the sulfides is possible. The methods of quantum mechanics, and the methods of quantum mechanics, are required to form different types of minerals. The best hope of progress.

Conclusions on Minor-Element Content

The minor-element content of sulfides is dependent on the conditions of formation, and some have drawn conclusions from the individual minerals. Haberlandt (73) has determined the absolute amount of a given element in a mineral, and has shown that elements that can substitute isomorphously in the sulfides under conditions of temperature and pressure, and the conditions of wall rocks.

Kullerud (110), in a very important paper, has shown that in the FeS-ZnS system and has shown that sphalerite can be used as a geological indicator of the conditions under which it was formed under equilibrium with iron. (See further Ingerson, this

Volume, p. 341-410). Kullerud showed that as the content in sphalerite of the minor elements other than iron was less than the amount required to saturate ZnS with any of these elements, they could not be used as geologic thermometers. The argument applies to the minor elements in any other mineral. The same viewpoint has been expressed more emphatically by Fryklund and Harner (59) for pyrrhotite and by Fryklund and Fletcher (58) for sphalerite; the latter state, "Available evidence indicates that equilibrium concentrations of the minor elements except for Mn (Fe is considered a major element) were never attained in the Coeur d'Alene district, and consequently formation temperatures could not affect minor-element concentration." Similar conclusions were expressed by Gavelin and Gabrielson (61) from their study of the Skellefte district, Sweden.

There is no doubt that this view is theoretically correct; it leads logically to the view that the concentrations of minor elements in sulfide minerals depend solely on the amounts of these elements present in the ore-forming solution. Nevertheless, I believe that the available data support many of the generalizations that have been made linking the concentrations of minor elements with temperature of formation or other factors. For example, the work done to date shows that there is a strong tendency for high gallium, high germanium, and low indium contents in sphalerites from deposits of the Mississippi Valley type, generally believed to have formed at low temperatures. We have no explanation of why this is so; perhaps it means simply that gallium and germanium tend to be present in greater amounts in this type of ore-forming solutions. Better methods of geologic thermometry are much needed, but in their absence one is justified in using the geologist's judgment, based largely on paragenesis, of the type of deposit he is dealing with. It seems justifiable, also, to infer that a sphalerite of high gallium and germanium content was probably formed at low temperature, provided that it is clearly understood that exceptions are to be expected, as, for example, if a regional trend has a greater effect than the generally observed trend due to temperature of formation. Additional arguments, with many examples, in justification of such inferences are given by Haberlandt (73, 74) and by Haberlandt and Schroll (77).

MINOR ELEMENTS IN SULFIDE MINERALS

Galena

Table 2 gives a list of papers on the minor elements in galena and indicates the type of data, the number of samples, and the elements found by each worker. Table 3 summarizes the quantitative and semi-quantitative data on the elements for which there are many determinations. Comments on these and data on the other elements are given below.

Antimony.—Antimony has been reported to be present in most samples of galena studied (Table 2). Wasserstein (210) found it in 80 percent of 60 samples studied, Pina de Rubies and Doetsch (145) in 88.3 percent of 562 samples, and Lopez de Azcona (119) in 84 percent of 720 samples; many

TABLE 2

SUMMARY OF REFERENCES ON GALENA

Under Type of Data, Q means quantitative analysis, S means semi-quantitative analysis, K means qualitative analysis. Under the elements listed, the symbol X means that the element was present, the symbol — means that the element was looked for, but not found.

Reference	Type of data	No. of samples	As	Sb	Bi	Cd	Cu	Ga	Ge	Fe	Mn	Ag	Sn	Tl	Zn	Others
Anderson (1953)	Q, K	19		X		X			X				X			In X
Bartlett (1889)	K	1	X	X		X		X						X		In X, Hg X, Se X
Bergenfelt (1953)	Q	7													X	Se X
Bernard (1953)	K	3	X	X	X	—	X	—		X	X	X	X			
Bernard (1954)	K	2					X			X		X				In X
Borovik and Prokopenko (1939)	K	?														In —
Borovik, Vlodavets and Prokopenko (1938)	Q	1														In —
Claussen (1934)	K	5	—	X	—		X			X	X	X	X		X	Cr, Ir, Mo, Pd, Sr, V, W, all X
Eberhard (1908, 1910)	K	2														Sc X, Y X
Edwards and Carlos (1954)	Q	10														Se X
Erametsa (1939)	Q	10														In —
Evrard (1945)	K	6		X		X	X	X		X	X	X		X	X	Ba X, Cr X, Sr X
Frondel et al. (1942)	K, S	?						X	—	X	X	X				Co —, In —
Fryklund and Fletcher (1955)	Q	1				—	X	—	—	X	X	X				
Goldschmidt and Peters (1933)	Q	1							—							
Goldschmidt and Strock (1935)	Q	2														Se X
de Gramont (1895)	K	?		X								X			X	Hg X
Grip (1948)	Q	1														

Reference	Type of data	No. of samples	As	Sb	Bi	Cd	Cu	Ga	Ge	Fe	Mn	Ag	Sn	Tl	Zn	Others
Claussen (1931)	K	5	-	X	-	-	X	-	-	X	X	X	X	-	-	In -
Eberhard (1908, 1910)	K	2	-	-	-	-	-	-	-	X	X	X	X	-	-	Cr, Ir, Mo, Pd, Sr, V, W,
Edwards and Carlos (1954)	Q	10	-	-	-	-	-	-	-	-	-	-	-	-	-	all X
Erametsa (1939)	Q	10	-	-	-	-	-	-	-	-	-	-	-	-	-	Sc X, Y X
Evrard (1945)	K	6	-	-	-	-	-	-	-	-	-	-	-	-	-	Se X
Frondel et al. (1942)	K, S	?	-	X	-	X	X	-	-	-	-	-	-	-	-	In -
Fryklund and Fletcher (1955)	Q	1	-	-	-	-	X	-	-	X	X	X	-	X	X	Ba X, Cr X, Sr X
Goldschmidt and Peters (1933)	Q	1	-	-	-	-	-	-	-	X	X	X	-	-	-	Co -, In -
Goldschmidt and Stroock (1935)	Q	2	-	-	-	-	-	-	-	-	-	-	-	-	-	-
de Gramont (1895)	K	?	-	X	-	-	-	-	-	-	-	-	-	-	-	Se X
Grip (1948)	Q	1	-	-	-	-	-	-	-	-	-	X	-	-	-	Hg X

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TABLE 2—Continued

Reference	Type of data	No. of samples	As	Sb	Bi	Cd	Cu	Ga	Ge	Fe	Mn	Ag	Sn	Tl	Zn	Others
Hartley and Ramage (1897)	K	8	-	-	-	-	X	-	-	X	X	X	-	-	-	Co ?, Ni X, Pd -, Pt -, Te ?
Hawley, Lewis and Wark (1951)	K	3	-	X	X	X	X	-	-	X	X	X	X	-	-	Mo -, Cr -, Ni -, V -
Hegemann (1949)	K	7	-	-	-	-	-	-	-	X	X	X	X	X	X	Co -, Au -, Te -
Hegemann and Leybold (1953)	Q	15	X	X	X	-	X	-	-	X	X	X	X	X	X	Ni X
Hegemann and Sybel (1955)	Q	22	X	X	X	-	X	-	-	X	X	X	X	X	X	Se X
Heier (1953)	Q	1	-	-	-	-	-	-	-	-	-	X	X	X	X	In X
Hiller and Smolczyk (1953)	Q, K	57	X	X	X	X	X	-	X	-	-	X	X	X	-	-
Hoehne (1934)	Q	111	X	X	X	-	-	-	-	-	-	X	X	-	-	-
Kinoshita and Muta (1950)	K	7	X	X	X	X	X	-	-	-	-	X	X	-	-	-
Kutina (1949)	K	1	-	-	-	-	X	-	-	-	-	X	X	X	X	In X
Leutwein and Herrmann (1954)	Q, K	50	X	X	X	-	X	-	-	-	-	X	X	X	X	-
Lopez de Azcona (1942)	K	720	X	X	X	X	X	X	X	X	X	X	X	X	X	Ba, Co, Au, In, Hg, Mo, Ni, Pt, Sn, V, W, all X
McLellan (1945)	K	?	-	-	-	-	-	-	-	-	-	X	-	-	-	In X
Moritz (1933)	S	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Newhouse (1934)	K	5	-	-	-	-	-	-	-	-	-	-	-	-	-	Cr X, Mo X, V X, W X
Noddack and Noddack (1931)	Q	1	X	X	X	-	X	-	-	-	-	X	X	-	-	Au X, Hg -, Mo X, Pt X, Re X, W -
Oftedal (1939)	Q	9	-	-	-	-	-	-	-	-	-	-	X	-	-	-

MINOR ELEMENTS IN SOME SULFIDE MINERALS

of the samples studied by the last two seem to have been impure. The figures in Table 3 are of somewhat doubtful value because galena so commonly occurs intergrown with sulfantimonites such as tetrahedrite; nevertheless, high contents of antimony have been reported in many samples stated to be homogeneous under the reflecting microscope. Tischendorf (195) found that the antimony content (present at least in part as tetrahedrite) decreased with decreasing temperature of formation.

Arsenic.—Arsenic has been found in only a small percentage of the galena samples analyzed spectrographically (Table 2). Many samples in which arsenic was found contained arsenopyrite, arsenides such as gersdorffite, or

TABLE 3

SUMMARY OF QUANTITATIVE DATA ON MINOR ELEMENTS IN GALENA

Element	Max. concn. ppm	No. of samples in each concentration range										Total No. of samples	Sensitivity ppm
		1% or more	5,000-9,999 ppm	1,000-4,999 ppm	500-999 ppm	200-499 ppm	100-199 ppm	50-99 ppm	10-49 ppm	<10 ppm	Not found		
As ^a	1%	1	2	11	9	16	9	1	1	—	179	229	10-100
Sb	3%	5	5	73	25	34	17	13	17	—	35	224	10-300
Bi	5%	23	1	28	18	26	19	8	43	36	125	327	1-100
Cd	1,000	—	—	1	1	2	3	—	1	—	51	59	10-100
Cu	3,000	—	—	5	4	2	16	3	14	5	2	51	1-10
Fe	5,000	—	1	5	5	3	3	5	13	3	51	89	1-10
Mn	2,000	—	—	1	1	1	—	—	19	15	53	90	1-10
Ni	100	—	—	—	—	—	1	2	10	2	25	40	1-5
Ag	3%	11	11	91	36	23	17	8	10	13	13	233	1
Tl	1,000	—	—	1	4	2	5	5	17	19	95	148	1-10
Sn ^b	1,300	—	—	2 ^c	6 ^c	9	9	5	28	24	255	338	3-100

^a Omitting samples reported to contain arsenopyrite or arsenides.

^b Omitting samples reported to contain cassiterite.

^c Some of these samples contained tetrahedrite.

sphalerite. Schroll (172) found the content of arsenic to vary inversely with the content of silver.

Bismuth.—Bismuth has been found in many samples of galena (Table 2); Pina de Rubies and Doetsch (145) found it in 19.5 percent of 562 samples, Lopez de Azcona (119) in 20 percent of 720 samples, and Wasserstein (210) in 50 percent of 60 samples. Bismuthinite, sulfosalts containing bismuth, or native bismuth may have been present in some of the samples, but high contents of bismuth have been reported in optically homogeneous samples. Oftedal (139) showed that galena of high bismuth content contained exsolved matildite (AgBiS₂) if sufficient silver were present, but that samples of high bismuth and low silver content showed only a pronounced octahedral parting; Wahlstrom (206) had found little difference in chemical composition between samples with cubic cleavage and octahedral parting. Leutwein and Herrmann (117) confirmed the presence of bismuth in solid solution as matildite, the unit cell size of the galena decreasing with increasing content of AgBiS₂.

In X	Ni X, V X	Te X	Sn X, V ?	Pt X
V -		V -	Mo -	
X	X			
		X		
	X	X	X	
		X		
X		X		
	X			
X		X		
	X	X	X	
X		X		
X X				
1	12	2	60	3
Q	Q	Q	Q	Q
		Q, K	Q, K	Q
Uvazub				
Skerl (1934)				
Taylor (1954)				
Tischendorf (1955)				
Tornquist (1930)				
Wahlstrom (1937)				
Wasserstein (1945)				
Wasserstein (1951)				
Yanischevsky and Razumnaya (1938)				
Zvyagintzev and Filippov (1935)				

Schroll (172) found that the bismuth content of East Alpine galena varied with the silver content, being highest near a granite gneiss massif and decreasing farther away from the massif. Tischendorf (195) reported that the content of bismuth varied with the content of silver and antimony, decreasing with decreasing temperatures of formation. Schroll (175) considers the presence of bismuth in galena to be a mark of high-temperature-magma-near deposits.

Cadmium.—Cadmium has been found in galena in many qualitative spectrographic studies (Table 2). Most of these samples are also reported to contain zinc and it seems likely that they contained sphalerite. However, Oftedal (138) reported 1,000 ppm cadmium in a high-bismuth galena that contained no zinc, and 10 ppm in another zinc-free galena, so that it is possible that cadmium may be present in solid solution in galena.

Chromium.—Chromium has been detected qualitatively by several investigators, but has been found in relatively few of the samples studied. Newhouse (133) reported X0 to X00 ppm chromium in each of 5 samples he studied.

Copper.—Copper has been detected qualitatively in galena by many workers (Table 2); the few quantitative determinations are summarized in Table 3. Bernard (13) and Oftedal (138) ascribed the copper they found to the presence of impurities. Chalcopyrite is commonly intergrown with galena, and tetrahedrite, bournonite, and other minerals have been reported as microscopic inclusions or intergrowths in galena (Ramdohr, 153).

Gallium.—Gallium has not been found in galena by most investigators; for example, Oftedal (138) did not find it in any of 51 samples. Its presence has been reported qualitatively (Table 2), but it seems likely that the samples contained sphalerite.

Germanium.—Germanium is not commonly present in galena, even in samples associated with germanium-bearing sphalerite (66; 138). Its presence has been reported qualitatively in a few samples (Table 2), and Orliac (141) reported 6 ppm germanium in a galena concentrate, which, however, contained 2.1 percent zinc.

Indium.—Indium, commonly present in sphalerite, has been reported present in relatively few samples of galena (Table 2). Quantitative data are few. Shaw (180) reported 0.91 ppm indium in one sample, and Anderson (5) found in 19 samples more than 100 ppm in one, 20 to 100 ppm in three, and 5 to 20 ppm in three.

Gold and the Platinum Metals.—Gold, platinum, palladium, ruthenium, rhodium, and iridium have been reported qualitatively in a few samples (Table 2). Noddack and Noddack (136) reported 30 ppm gold and 0.8 ppm platinum in one sample. Zvyagintzev and Filippov (215) reported 1, 2, and 5 ppm platinum in three samples.

Iron.—Iron has been reported in many qualitative analyses of galena (Table 2). Only a few quantitative spectrographic determinations of iron are available; these are summarized in Table 3. Oftedal (138), who analyzed 51 samples of galena, states that iron was not found in any pure sample.

bismuth content of East Alpine galena is the highest near a granite gneiss massif at Tischoendorf (195) reported the content of silver and antimony, and the content of silver and antimony, and the conditions of formation. Schroll (175) considers galena to be a mark of high-temperature.

found in galena in many qualitative spectra of these samples are also reported that they contained sphalerite. However, cadmium in a high-bismuth galena than in other zinc-free galena, so that it is possibly a solid solution in galena.

detected qualitatively by several investigators. A relatively few of the samples studied contained 10 ppm chromium in each of 5 samples.

detected qualitatively in galena by many workers. Determinations are summarized in Table 2. The copper they found to be associated is commonly intergrown with galena. Other minerals have been reported as microconstituents in galena (Ramdohr, 153).

found in galena by most investigators; it is present in any of 51 samples. Its presence is reported in 2, but it seems likely that the samples

commonly present in galena, even in the absence of sphalerite (66; 138). Its presence is reported in a few samples (Table 2), and Orlic has reported it in a galena concentrate, which, however,

is present in sphalerite, has been reported in galena (Table 2). Quantitative data are given for indium in one sample, and Anderson (195) reported 30 ppm gold and 0.8 ppm silver in one, 20 to 100 ppm in three.

gold, platinum, palladium, ruthenium, and rhodium were reported qualitatively in a few samples. Anderson (195) reported 30 ppm gold and 0.8 ppm silver in one, and Philippov (215) reported 1, 2, and

many qualitative analyses of galena. Spectrographic determinations of iron and lead are given in Table 3. Oftedal (138), who analyzed 10 samples, found iron as not found in any pure sample.

seems likely that some, if not all of the iron reported by others was due to admixed sphalerite or chalcopyrite.

Manganese.—Manganese has been reported in many qualitative analyses of galena (Table 2); the few quantitative analyses are summarized in Table 2. It seems probable that some, if not all of the manganese reported was due to admixed sphalerite.

Nickel.—Nickel has not been reported in most analyses of galena, but its presence has been detected in a few samples (Table 2); the few quantitative determinations are summarized in Table 3.

Mercury.—Mercury has been reported qualitatively in a few of the samples studied (Table 2). The only quantitative determination is by Grip (71), who found 70 ppm mercury in one sample.

Molybdenum.—Molybdenum has been reported qualitatively in a few samples of galena by several workers (Table 2). The only quantitative determination, by Noddack and Noddack (136), gave 20 ppm molybdenum.

Selenium and Tellurium.—Galena is known to form solid solutions with clausthalite (PbSe) (48) and very probably also forms solid solutions with altaite (PbTe), so that one might expect that selenium and tellurium would be present in galena. Few data are available; the spectrographic sensitivity is poor for these elements. Qualitative data are given by Saito (162) and Hoehne (96); the latter found selenium in 6 of 111 samples. Schmidt (165) reported 3 ppm Se in one sample; Goldschmidt and Stroock (68) found 0.8, 0.8, and 2.3 ppm selenium in 3 samples. Heier (93) stated that the unit cell size of a galena sample indicated the presence of approximately 10 mol percent PbSe, but this neglects the possible effect of other substituents on the cell size. Bergenfelt (12) found in galena samples from northern Sweden less than 10 ppm selenium in 2 samples, but in other samples 50, 200, 1200, 10,000 (= 1%), and 15,000 (= 1.5%) ppm selenium. The two highest samples were from the Boliden Mine where sulfosalts rich in selenium (cosalite, kobellite) are known to occur. Bergenfelt also found that the Se:S ratios for galena concentrates were consistently higher than those for chalcopyrite, sphalerite, or pyrite concentrates. There is apparently, however, a marked regional concentration, as Edwards and Carlos (52) not only found much less selenium (1 to 3 ppm in 8 samples, 13 and 14 ppm in two others) in ten Australian samples, but also found lower Se:S ratios in galena than in pyrite, chalcopyrite, pyrrotite, and some sphalerite.

Tellurium has been reported qualitatively by Oftedal (138) in 3 of 51 samples, by Hawley, Lewis, and Wark (81), and by Schroll (175). The only quantitative determinations are by Schroll (172, 175), who reports 100 and 300 ppm tellurium.

Silver.—Silver is reported to be present in nearly all spectrographic analyses of galena, doubtless in part because of its great sensitivity, usually given as 1 ppm (Table 2). The quantitative data are summarized in Table 3. Many of these samples were studied optically and silver minerals were identified in only a few. The presence of matildite, Ag₂BiS₂, both in true solid solution and as an exsolved phase, has been proved, (see under Bismuth, above).

Schroll (172) found that the content of silver varied directly with those of antimony and bismuth and inversely with the content of arsenic. Tischendorf (195) reported that the content of silver, bismuth, and antimony all decreased with decreasing temperature of formation.

Thallium.—Thallium has been reported qualitatively in galena by many investigators (Table 2). The quantitative data are summarized in Table 3. According to Oftedal (138), thallium is found exclusively in the galena and not in the sphalerite of galena-sphalerite occurrences. Analyses of sphalerite by others do not agree with this conclusion, but thallium does seem to be preferentially concentrated in galena.

Tin.—Tin has been reported qualitatively by many workers (Table 2), who found it in about 40 percent of the samples studied. The quantitative data are summarized in Table 3. The tin content is low in most samples, relatively few having more than 100 ppm, and some of these contained tetrahedrite.

Vanadium.—Vanadium has been reported qualitatively in a few samples (Table 2). Newhouse (133) found X0 to X00 ppm vanadium in each of 5 samples he examined. Taylor (194) reported 17 ppm vanadium in an impure sample from Broken Hill, Rhodesia.

Zinc.—Zinc has been reported in many chemical and spectrographic analyses of galena (Table 2). But Oftedal (138) states that it is never found in pure galena and that inclusions of sphalerite are always present in samples that contain zinc. Hegemann and Leybold (90) and Hegemann and Sybel (92) report quantitative determinations of zinc in 20 of 38 samples studied. They found up to 3 percent zinc, but nothing is said of the purity of the samples.

Other Elements.—Silicon, aluminum, magnesium, and titanium have been reported qualitatively in many samples; sodium, lithium, beryllium, and zirconium in a few, yttrium and scandium in a single sample. The presumption is that these should be ascribed to impurities in the samples. Calcium, barium, and strontium have been reported in many samples by Claussen (43) (Ca, Sr), Frondel et al. (56), Lopez de Azcona (119), Pina de Rubies and Doetsch (145), Rösler (160) (Sr), Saito (162) (Sr), and Wasserstein (209) (Sr). The presence of calcium has generally been ascribed to impurities, and, as barite is commonly associated with galena, barium and strontium might also be due to impurities. However, barium and strontium have been reported in carefully selected galena samples, and their ionic radii are so close to that of lead that they might well be present in solid solution.

Cobalt has been reported in a few samples, but may be present in associated pyrite or other minerals. Tungsten has been detected in a few samples (Table 2). It was found in concentrations X0 to X00 ppm by Newhouse (133) in all 5 samples studied; verification of this is needed. Strock (187) reported 15 ppm lithium in a galena concentrate. Noddack and Noddack (136) found 0.01 ppm of rhenium in a sample of galena. Rankama (154, 155) found no tantalum and 0.1, 0.6 ppm niobium in 2 samples. No other determinations of these elements in galena have been reported.

Sphalerite, Wurtzite, and "Schalenblende"

The minor elements in sphalerite have been studied more than those of any other ore mineral; approximately 100 papers give qualitative or quantitative data. Indium and gallium were discovered in sphalerite; zinc ores are still the principal sources of these elements and also of cadmium and germanium. Wurtzite, the hexagonal dimorph of sphalerite, has been studied much less. The two minerals are considered together here, because many samples of zinc sulfide that have been studied were of the "schalenblende" type, that is, they were fine-grained concentrically banded samples whose mineralogical identity was not established; such samples may be sphalerite or wurtzite or mixtures of the two. In Table 5, the data for "schalenblende" are given separately. Most authors have not specifically designated such samples, however, so that many are undoubtedly included under sphalerite.

The possible effect of the minor-element content on the stability relations of polymorphs is a subject of great interest (55). Unfortunately, so few analyses of wurtzite have been made that significant conclusions are hard to draw. More research on these and other polymorphs is much needed.

Table 4 is a summary of the papers dealing with sphalerite and shows the type of analysis and the elements for which data are given. Table 5 summarizes the quantitative and semiquantitative determinations of the elements for which there is much data. Discussion of these and of the other elements is given below.

Antimony.—Antimony has been reported qualitatively in nearly half the samples of sphalerite studied (Table 4). The quantitative data are summarized in Table 5. It remains uncertain whether antimony occurs in pure sphalerite. Oftedal (138, p. 84) stated that it does not; he found it in only 14 of 111 samples studied and 9 of these contained appreciable amounts of lead. Hoehne (96) found up to 5,500 ppm antimony in 7 of the 14 samples studied, but impurities such as tetrahedrite, arsenopyrite, or stannite were present in each. Schroll's data (173, 174) indicate that antimony is present in the zinc sulfides, with higher concentrations in wurtzite and "schalenblende." The data of Table 5 show very clearly that many of the samples of high antimony content are also high in lead; in view of the established high content of antimony in galena, it seems probable that admixed galena accounts for much of the antimony reported in the zinc sulfides.

Arsenic.—The presence of arsenic has been reported qualitatively in about one-sixth of the samples studied, see Table 4. The available quantitative data are summarized in Table 5. Many of the samples that had high contents of arsenic may have contained impurities and this is especially true of the "schalenblende" type. Many, for example, contained 1 percent or more lead, yet galena does not generally contain much arsenic. It is impossible to judge what minerals might be present in these fine-grained aggregates. It does seem probable that pure sphalerite may contain at least moderate amounts of arsenic.

Bismuth.—Bismuth has been reported qualitatively in about one-sixth of the samples of sphalerite studied; no qualitative data on wurtzite are available.

the content of silver varied directly with the content of arsenic. Tischevsky (194) reported qualitatively in galena by many authors. The quantitative data are summarized in Table 5. Thallium is found exclusively in the galena and sphalerite occurrences. Analyses of sphalerite lead to the conclusion, but thallium does seem to be present in galena. The tin content is low in most samples studied. The tin content is low in most samples studied, but some of these contained tetra-lead. Vanadium has been reported qualitatively in a few samples of sphalerite. Oftedal (138) reported 17 ppm vanadium in an analysis of a sample from Rhodesia. The presence of vanadium in many chemical and spectrographic analyses of sphalerite is always present in samples studied by Leybold (90) and Hegemann and Sybel (91). The zinc content in 20 of 38 samples studied, but nothing is said of the purity of the samples. Vanadium, magnesium, and titanium have been reported in many samples; sodium, lithium, beryllium, and scandium in a single sample. The presence of these elements as impurities in the samples has been reported in many samples by Oftedal (138), Lopez de Azcona (119), Pina de Abajo (160) (Sr), Saito (162) (Sr), and others. The presence of calcium has generally been associated with galena, barium and strontium with sphalerite. However, barium and strontium have been reported in selected galena samples, and their ionic nature at they might well be present in solid solution. Vanadium, but may be present in associated with galena. The presence of vanadium has been detected in a few samples of sphalerite. The quantitative data on this is needed. Stroock (187) reported 17 ppm vanadium in a sample of galena. Rankama (154), and others have reported vanadium in 2 samples. No other elements have been reported.

TABLE 4

SUMMARY OF REFERENCES ON SPHALERITE AND WURTZITE

Under Type of Data, Q means quantitative analysis, S means semi-quantitative analysis, K means qualitative analysis. Under N Samples, S means sphalerite plus "schalenblende," W means wurtzite. Under the elements listed the symbol X means that the element was the symbol — means that the element was looked for, but not found.

Reference	Type of data	No. of samples	Sb	As	Cd	Co	Cu	Ga	Ge	In	Pb	Mn	Ni	Ag	Tl	Sn	Others
Abramov and Rusanov (1938)	S	237S			X			X	X	X							
Ahlfeld and Moritz (1933)	S	2S 1W			X			X	—		X	X			X	X	
Anderson (1953)	S, K	24S	X		X				X	X						X	
Bartlett (1889)	K	1S	X	X	X			X		X					X		Hg X, Se X
Beck (1937)	Q, K	3S						X	X	X							Se X
Bergenfelt (1953)	Q	14S															
Bernard (1953)	K	11S	X	X	X		X	X		X	X	X		X		X	
Bernard (1954)	K	1S	X	X	X		X							X			
Biewendt (1902)	Q	?S			X												
Bjørlykke and Jarp (1950)	Q	2S				X											
Boisbaudran (1875, 1876)	K	?S						X									
Borovik, Lizunov, and Shcherbina (1941)	S	49S						X									
Borovik and Prokopenko (1939, 1941)	K	?S								X							
Borovik and Prokopenko (1938)	K	58S							X	X							
Borovik and Sosedko (1937)	K	?S						X									
Borovik, Vlodavetz and Prokopenko (1938)	Q	42S								X							
Bose and Dutta (1950)	K, Q	1S			X			X	X		X			X		X	Fe X
Brewer and Baker (1936)	K	1W 2S								X							
Brewer, Cox and Morris (1955)	Q	12S							X								
Buchanan (1917)	K	6S							X								

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TABLE 4—Continued

Reference	Type of data	No. of samples	Sb	As	Cd	Co	Cu	Ga	Ge	In	Pb	Mn	Ni	Ag	Tl	Sn	Others
Hassler and Roys (1934)	K	1S		—	X	—		X	X	—	X	—		—		X	Cr X, V X, Bi, Au, Pd, Pt, all — Mo —, V — Bi, Hg, Mo, Ti, V, all X
Hawley, Lewis, and Wark (1951)	K	1S	—	—		X	X			X	X	X	X			—	
Hegemann (1949)	K, Q	10S		X	X		X				X	X					Bi, Hg, Mo, Ti, V, all X
Hegemann and Kostyra (1954)	Q	10S	X	X	X	X	X	X	X	X	X	X	X	X	X	X	
Hillebrand and Scherrer (1916)	K	4S						X	X								
Hoehne (1934)	Q	14S	X	X												X	Bi X
Juretzka (1915)	Q	?S			X												Re —
Kimura and Koyama (1936)	K, Q	16S						—	X	X					—		
Kimura, Nagashima, et al. (1952)	S	10S							X								
Kinoshita and Muta (1950)	K	9S	X	X	X		X		X	—	X			X		X	Au X
Kirkland (1892)	K	3W															
Kleinert (1949)	Q	1S						X	X								
Kruglyakova and Yasinskaya (1952)	Q	20S			X							X					Fe X
Kullerud (1953)	Q	54S			X	X	X	X	X		X	X	X	X		X	Fe X
Kutina (1949)	K	1S	X		X		X	X	X	X	X	X	X	X		X	
Kutina (1953a)	K, Q	3S		X	X	X	X	X		X	X	X	X	X		X	
Kutina (1953b)	K	8S		X	X		X		X		X	X	X		X		Hg X
Kutina (1953c)	K	1S			X		X	X	X	X	X	X		X		X	Bi X
de Launay and Urbain (1910)	K	?S	X				X	X	X	X				X		X	Bi X, Hg X
Lebedev (1954)	Q, K	1S		X	X		X		X		X				X		
Llord y Gamboa (1909)	K	?S			X						X		X				
Marks and Hall (1946)	Q	3S							X								
Marks and Jones (1948)	Q	2S								X							
McLellan (1945)	K	?S								X							
Meigen and Scharschmidt (1924)	Q, K	4S			X		X	—		—	X	X		X			

Yasinskaya (1952)	Q	20S				X														Fe X
Kullerud (1953)	K	54S				X														Fe X
Kutina (1949)	K, Q	1S	X			X														Fe X
Kutina (1953a)	K	3S				X														Hg X
Kutina (1953b)	K	8S				X														Bi X
Kutina (1953c)	K	1S				X														Bi X, Hg X
de Launay and Urbain (1910)	K	?S	X			X														
Lebedev (1954)	Q, K	1S				X														
Llord y Gamboa (1909)	K	?S				X														
Marks and Hall (1946)	Q	3S				X														
Marks and Jones (1948)	Q	2S				X														
McLellan (1945)	K	?S				X														
Meigen and Scharschmidt (1924)	Q, K	4S				X														

TABLE 4—Continued

Reference	Type of data	No. of samples	Sb	As	Cd	Co	Cu	Ga	Ge	In	Pb	Mn	Ni	Ag	Tl	Sn	Others
Morinaga (1952)	K	44S						X	X	X							
Morris and Brewer (1954, 1955)	Q	3S 2W						X									Mo X, V X
Moritz (1933)	S	2S			X		X	X			X	X		X	X		
Murakami (1950)	Q	3S							X								
Nair and Rajan (1954)	Q	1S															Cr X, Mo X, V X, W X
Newhouse (1934)	S	6S															Bi, Cr, Au, Hg, Mo, Pt, Re, Sc, Te, V, W, all X
Noddack (1936)	Q, S	1S	X	X	X	X	X	X	X	X	X	X	X	X	X	X	Bi, Au, Hg, Mo, V, Pt, Re, W, all X
Noddack and Noddack (1931)	Q	1S	X	X	X		X		X		X			X		X	Bi, Fe, Hg, Mo, all X
Oftedal (1939)	Q	8S															Bi, Fe, Hg, Mo, all X
Oftedal (1940)	Q	111S	X	X	X	X	X	X	X	X	X	X	X	X	X	X	Bi X
Orliac (1949)	Q	11S	X			X			X				X				
Papish (1928)	K	1S							X								
Papish and Stilson (1930)	K	80S						X	X		X	X	X	X		X	Hg X
Pina de Rubies and Lopez de Azcona (1936)	Q	1S				X	X	X	X							X	Hg X, Mo X
Pina de Rubies and Lopez de Azcona (1937)	K	5S			X	X	X	X	X	X				X			Hg X, Bi -
Pouba (1951)	K	4S	X	-	X		X		X			X		X	X		
Prokopenko (1941a, 1941b, 1941c)	K	?S								X							Nb X, Ta X
Rankama (1944, 1948)	Q	4S															
Rimatori (1904)	K, Q	8S							X	X							Bi X
Rimatori (1905)	K	15S					X	X		X							
Rost (1939)	Q, K	4S				X	X	X	X			X	X	X			Rh X, Se X
Saito (1953)	K	3S	X	X			X		X		X	X		X			
Saksela (1951)	Q	7S															Se X
Schmidt (1925)	Q	3S															

MINOR ELEMENTS IN SOME SULFIDE MINERALS

TABLE 4—Continued

Reference	Type of data	No. of samples	Sb	As	Cd	Co	Cu	Ga	Ge	In	Pb	Mn	Ni	Ag	Tl	Sn	Others
Schneiderhöhn (1930)	K	1S		X													Fe X
Schroll (1950)	S	41S		X	X	X		X	X			X		X	X		Fe X, Hg —, Te —
Schroll (1953a)	Q	31S	X	X	X	X	X	X	X	—		X	X	X	X	X	Bi X, Fe X, Hg X
Scholl (1953b, 1955)	Q	60S	X	X	X	X		X	X	X	X	X	X	X	X	X	
		16W							X								
Scutt (1926)	K	1S															
Shaw (1952a, 1952b)	Q	1S								X					X		V —
Skerl (1934)	K	7S															Hg X
Soltsien (1886)	Q	3S															
Stadnichenko et al. (1953)	Q	2S							X								
Stoiber (1940)	S, K	75S		X	X	X		X	X	X		X	X		X	X	Bi X, Hg X
Strickland (1955)	Q	1S							X								Li X
Strock (1936)	Q	5S														X	
Strock (1945)	Q	7S	X			X		X	X	X			X				V X
Taylor (1954)	Q	1S			X								X				
Tischendorf (1955)	K	2S	X	X	X		X	X	X	X	X		X	X	X		
Tornquist (1930)	K	7S		X													
Urbain (1909)	K	64S	X	X	X	X	X	X	X	X	X	X		X	X		Bi X, Mo X
Urbain, Blondel, and Obiedoff (1910)	K	1S							X								
Urbain and Campo (1909)	K	7S			X			X	X	X	X						
Vogel (1894)	K	2S								X							
Waring (1917)	Q	7S			X										X		
Warren and Thompson (1945)	S, K	164S	X	X	X		X	X	X	X	X	X		X		X	Bi, Fe, Au, Te, Ti, V, all X
Yanishevsky and Razumnaya (1938)	K	7S															Mo —
Zak (1951)	Q	1S			X					X		X					Fe X, Hg X
Zvyagintzev and Phillipov (1935)	Q	2S															Pt X

TABLE 5
QUANTITATIVE DATA ON MINOR ELEMENTS IN SPHALERITE (S), WURTZITE (W), AND "SCHALENBLLENDE" (SC)

TABLE 5—Continued

Element	Type of sample	Max. concn. ppm	Number of samples reported in each concentration range										Total No. samples	Sensitivity ppm
			1% or more	5,000-9,999 ppm	1,000-4,999 ppm	500-999 ppm	200-499 ppm	100-199 ppm	50-99 ppm	10-49 ppm	<10 ppm	Not found		
Ga	S	3,000	—	—	15 ^j	7	57 ^k	160	115 ^l	212 ^m	70	326	962	1-100
Ga	W	5,000	—	1	4	1	—	3	—	3	—	7	19	10
Ga	SC	500	—	—	—	1	1	2	4	4	—	16	28	10
Ge	S	1,000	—	—	49 ⁿ	11	66 ^o	84	104 ^p	91	46	508	959	1-100, mostly 1-10
Ge	W	5,000	—	1	6	1	2	1	—	2	3	3	19	1-100, mostly 1-10
Ge	SC	3,000	—	—	9	5	5	4	2	4	1	1	31	1-100, mostly 1-10
In	S	1%	2	5	43 ^q	18	52 ^r	87	58	168 ^s	58	447	938	1-30
In	W	5,000	—	1	—	—	1	—	—	3	3	9	17	5
In	SC	10	—	—	—	—	—	—	—	1	—	27	28	5
Pb	S	10%	43	15	58	20	22	19	8	29	16	47	277	5-20
Pb	W	3%	1	1	2	5	2	1	1	.1	—	3	17	5-20
Pb	SC	5%	6	3	14	2	1	2	—	—	—	—	28	5-20

^j Including 3 samples stated to contain 1,000-10,000 ppm.

^k Including 45 samples stated to contain 100-1,000 ppm and 2 samples stated to contain 100-500 ppm.

^l Including 16 samples stated to contain 10-100 ppm.

^m Including 57 samples stated to contain 1-100 ppm.

ⁿ Including 6 samples stated to contain 1,000-10,000 ppm.

^o Including 39 samples stated to contain 100-1,000 ppm.

^p Including 82 samples stated to contain 10-100 ppm.

^q Including 10 samples stated to contain 1,000-10,000 ppm.

^r Including 29 samples stated to contain 100-1,000 ppm and 2 samples stated to contain more than 100 ppm.

^s Including 65 samples stated to contain 10-100 ppm and 4 samples stated to contain less than 30 ppm.

TABLE 5—Continued

Element	Type of sample	Max. concn. ppm	Number of samples reported in each concentration range							Total No. samples	Sensitivity ppm			
			1% or more	5,000-9,999 ppm	1,000-4,999 ppm	500-999 ppm	200-499 ppm	100-199 ppm	50-99 ppm			10-49 ppm	<10 ppm	Not found

Pb	S	10%	43	15	58	20	22	19	8	1	27	28	5
Pb	W	3%	1	1	2	5	2	1	1	29	47	277	5-20
Pb	SC	5%	6	3	14	2	1	2	1	1	16	17	5-20
												28	5-20

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- ^j Including 3 samples stated to contain 1,000-10,000 ppm.
- ^k Including 45 samples stated to contain 100-1,000 ppm and 2 samples stated to contain 100-500 ppm.
- ^l Including 16 samples stated to contain 10-100 ppm.
- ^m Including 57 samples stated to contain 1-100 ppm.
- ⁿ Including 6 samples stated to contain 1,000-10,000 ppm.
- ^o Including 39 samples stated to contain 100-1,000 ppm.
- ^p Including 82 samples stated to contain 10-100 ppm.
- ^q Including 10 samples stated to contain 1,000-10,000 ppm.
- ^r Including 29 samples stated to contain 100-1,000 ppm and 2 samples stated to contain more than 100 ppm.
- ^s Including 65 samples stated to contain 10-100 ppm and 4 samples stated to contain less than 30 ppm.

TABLE 5—Continued

Element	Type of sample	Max. concn. ppm	Number of samples reported in each concentration range										Total No. samples	Sensitivity ppm
			1% or more	5,000-9,999 ppm	1,000-4,999 ppm	500-999 ppm	200-499 ppm	100-99 ppm	50-99 ppm	10-49 ppm	<10 ppm	Not found		
Mn	S	5.4%	27	58	163 ^t	34	104 ^u	24	116 ^v	38 ^w	1	87	652	1-100
Mn	W	5,000	—	2	4	3	1	2	2	—	—	3	17	10-30
Mn	SC	3,000	—	—	2	6	1	3	1	10	—	4	27	10-30
Hg	S	1%	1	—	4	5	10	15	19	28	1	142	225	10-30
Hg	W	3,000	—	—	1	1	1	1	2	1	—	10	17	10-30
Hg	SC	1,000	—	—	1	1	—	—	1	3	—	23	29	10-30
Ni	S	300	—	—	—	—	7	8	5	42	7	142	211	1-50
Ni	W	100	—	—	—	—	—	2	1	—	—	13	16	50
Ni	SC	300	—	—	—	—	4	2	5	—	—	16	27	50
Se	S	900	—	—	—	1	3	—	1	9	27	—	41	1-5
Ag	S	1%	3	11 ^x	36	2	66 ^y	15	107 ^z	57	90	71	448	1-5
Ag	W	3,000	—	—	5	1	1	1	1	2	3	2	16	1-5
Ag	SC	3,000	—	—	1	1	—	1	—	9	8	9	29	1-5
Tl	S	5,000	—	1	6 ^{aa}	2	13 ^{bb}	4	10	25 ^{cc}	18	231	310	1-100
Tl	W	500	—	—	—	1	1	1	3	3	2	6	17	3
Tl	SC	1%	1	2	7	2	2	5	3	4	1	1	28	3
Sn	S	1%	1	1	42 ^{dd}	17	28 ^{ee}	66	15	38	25	352	585	3-100
Sn	W	1%	1	1	1	—	1	—	4	4	—	4	16	3
Sn	SC	50	—	—	—	—	—	—	3	4	8	12	27	3

- ^t Including 14 samples stated to contain 1,000-10,000 ppm.
- ^u Including 65 samples stated to contain 100-1,000 ppm.
- ^v Including 83 samples stated to contain less than 100 ppm.
- ^w Including 13 samples stated to contain 10-100 ppm.
- ^x Including 7 samples stated to contain more than 1,000 ppm.
- ^y Including 57 samples stated to contain 100-1,000 ppm.
- ^z Including 85 samples stated to contain less than 100 ppm.
- ^{aa} Including 3 samples stated to contain 1,000-10,000 ppm.
- ^{bb} Including 11 samples stated to contain 100-1,000 ppm.
- ^{cc} Including 10 samples stated to contain 10-100 ppm.
- ^{dd} Including 4 samples stated to contain 1,000-10,000 ppm.
- ^{ee} Including 12 samples stated to contain 100-1,000 ppm.

MINOR ELEMENTS IN SOME SULFIDE MINERALS

The quantitative data, summarized in Table 5, show that most of the samples that contain much bismuth have high lead content. It seems likely that much of the bismuth reported in sphalerite is from admixed galena or other impurities.

Cadmium.—Cadmium is reported in practically all chemical and spectrographic analyses of the zinc sulfides (Table 4). The quantitative spectrographic analyses are summarized in Table 5. They show for sphalerite a very high concentration in the range from 1,000 to 5,000 ppm; similar results are given in a compilation of 130 chemical analyses of sphalerite in Doelter and Leitmeier (46), in data on Silesian zinc ores by Juretzka (101), and on Tri-State zinc ores by Waring (207). The few results for wurtzite apparently indicate a higher average content of cadmium; this is in accord with the 14 chemical analyses cited in Doelter and Leitmeier (46), of which 8 showed more than 1 percent cadmium. More data are needed.

The cadmium content of sphalerite seems to be independent of the conditions of formation; there is no clear indication of systematic differences in sphalerites from low-temperature and high-temperature deposits (60; 138; 185). In banded zinc sulfides, the tendency is towards higher cadmium content in the light-colored bands, and less cadmium in the dark, iron-rich bands (113).

Cobalt.—Cobalt has been reported to be present in about one-third of the sphalerites studied qualitatively (Table 4). The quantitative data, summarized in Table 5, show cobalt in about half the samples. Some of the cobalt reported may be in chalcopyrite, nearly always present in sphalerite, or, less likely, may be present in admixed pyrite or arsenopyrite, but probably some of the cobalt is actually present in the sphalerite itself.

According to Oftedal (138) and Gabrielson (60), sphalerites from high-temperature contact-metamorphic and carbonate-skarn deposits generally contain more cobalt than those from other types of deposits. There does not, however, seem to be a correlation between the contents of cobalt and iron (138); this agrees with the data of Kullerud (110), which show very little correlation of cobalt content with temperature of formation.

Copper.—The presence of copper has been reported in nearly all sphalerites analyzed (Table 4). No data on copper in wurtzite have been published.

The quantitative results summarized in Table 5, probably represent nothing more than a measure of the contamination of the sample by copper minerals and especially by chalcopyrite. Oftedal (138, p. 71) stated that every sample that contained as much as 1,000 ppm copper was found to contain inclusions of chalcopyrite. These showed textures commonly attributed to exsolution. Such textures have been reported by many workers (153, p. 348–350). The true solubility of chalcopyrite in sphalerite, appreciable at high temperatures, is apparently very low at room temperature.

Gallium.—Gallium has been reported to be present in about three-fourths of the sphalerite samples studied (Table 4). The quantitative results are summarized in Table 5. There is general agreement by most workers (including, among others, Abramov and Rusanov, 1; de Launay and Urbain, 115; Gabrielson, 60; Oftedal, 138; Stoiber, 185; Schroll, 173) that the

5, show that most of the samples are lead-free. It seems likely that much of the lead is in admixed galena or other minerals.

Quantitatively all chemical and spectroscopic analyses are in agreement (Table 4). The quantitative spectroscopic data for sphalerite are generally in the range 100 to 5,000 ppm; similar results were obtained in analyses of sphalerite in Doelter ores by Juretzka (101), and on a few results for wurtzite and sphalerite by Juretzka and Juretzka; this is in accord with the results of Leitmeier (46), of which 8 analyses are needed.

The data appear to be independent of the conditions of formation of systematic differences in temperature deposits (60; 138; 139) and towards higher cadmium content in the dark, iron-rich bands.

Lead is present in about one-third of the samples. The quantitative data, summarized in Table 5, show that lead is always present in sphalerite, or in arsenopyrite, but probably not in wurtzite itself.

In (60), sphalerites from high-temperature deposits generally contain more lead than those of low-temperature deposits. There does not seem to be any correlation between the contents of cobalt and iron and lead in sphalerite (110), which show very little lead.

Lead is reported in nearly all sphalerites and wurtzites. Quantitative data have been published.

Lead is probably represented by nothing in the sample by copper minerals (110). Juretzka (71) stated that every sample of sphalerite found to contain inclusions of lead is probably attributed to exsolution. Juretzka and Juretzka (153, p. 348-350). The results of Juretzka and Juretzka are appreciable at high temperatures.

Lead is present in about three-fourths of the samples. The quantitative results are in general in agreement by most workers (in particular, de Launay and Urbain, 115; Stoiber, 185; Schroll, 74; 75; Schroll, 173) that the

gallium content is most likely to be high in sphalerites from low-temperature deposits such as those of the Mississippi Valley type and in those from low-temperature quartz veins. The data of Kullerud (110), the only worker who determined temperatures of formation by a direct method, do not show a close correlation of gallium content with temperature of formation.

Germanium.—Germanium has been reported present in about half the samples studied (Table 4). The quantitative data are summarized in Table 5.

Wurtzite and "schalenblende," on the basis of the few samples analyzed, generally contain more germanium than sphalerite. The dark bands of "schalenblende" ore contain more germanium than the light bands (Kutina, 113). Nearly all of the investigators agree that sphalerite from low-temperature deposits such as those of the Mississippi Valley type tend to be higher in germanium content than those from mesothermal or high-temperature deposits (de Launay and Urbain, 115; Graton and Harcourt, 69; Stoiber, 185; Oftedal, 138; Gabrielson, 60; Warren and Thompson, 208), but many exceptions have been noted. The data of Kullerud (110) show practically no correlation between germanium content and temperature of formation.

Gold.—Gold has been reported qualitatively in 21 of 180 samples studied (Table 4). Quantitative data have been published for 3 samples that contained 0.5, 1-10, and 3 ppm gold, respectively (Goldschmidt and Peters, 65; Noddack, 135; Noddack and Noddack, 136).

Indium.—Indium has been found in about half the samples studied (Table 4). The quantitative data are summarized in Table 5. The few results available seem to indicate that indium occurs in higher concentrations in sphalerite than in wurtzite, and that the "schalenblendes" have extremely low contents of indium. Nearly all workers agree that indium is most likely to be present in appreciable amounts in sphalerites from deposits classed as mesothermal or high-temperature types, whereas it is likely to be absent or present in low concentrations in sphalerites from deposits of low-temperature type (de Launay and Urbain, 115; Abramov and Rusanov, 1; Prokopenko, 151; Stoiber, 185). As a direct corollary, indium is more likely to be high in dark sphalerites than in light-colored ones, and the indium content generally varies inversely with the contents of gallium and germanium. Numerous exceptions to these generalizations have been noted.

Lead.—Lead is reported in nearly all analyses of sphalerite (Table 4). The quantitative results, summarized in Table 5, presumably should be taken as a measure of the degree of contamination of the samples. Pure sphalerite is stated by Oftedal (138) to be lead-free, and other investigators' work also indicates that galena or other lead minerals were present in nearly all samples reported to contain appreciable amounts of lead.

Manganese.—Manganese is reported in most analyzed sphalerites. The quantitative data are summarized in Table 5. There is general agreement that the manganese content varies with the iron content and that it is highest in samples from high temperature deposits (de Launay and Urbain, 115; Stoiber, 185; Warren and Thompson, 208; Gabrielson, 60; Schroll, 74; Fryklund and Fletcher, 58). The results of Kullerud (110) agree with this, in general, but with many exceptions.

Mercury.—Mercury has been reported to be present in about one-fourth of the sphalerites analyzed. The quantitative data are summarized in Table 5. Mercury is found in the highest concentrations in sphalerite of low temperature deposits, according to de Launay and Urbain (115) and Oftedal (138). Kutina (113) found more mercury in the dark bands of "schalenblende" ores from Moresnet, Belgium, than in the light bands.

Molybdenum.—Molybdenum has not been looked for by most investigators and has been reported to be present in about 5 percent of the samples in which it was looked for. Semiquantitative analyses are available for only five samples, all reported to contain 10–100 ppm molybdenum.

Nickel.—Nickel has not been looked for by most investigators. The references are listed in Table 4 and the quantitative data are summarized in Table 5. Some of the nickel reported may have been present in other minerals, especially pyrite, but probably sphalerite does contain small amounts.

Selenium.—The few data on selenium in sphalerite are summarized in Tables 4 and 5. In the samples studied by Bergenfelt (12) from northern Sweden, an area characterized by high selenium, sphalerite was very much lower in selenium content than associated galena, chalcopyrite, or pyrite. The data of Edwards and Carlos (52) also show low concentrations of selenium in sphalerite, but they found even less in galena.

Silver.—Silver has been reported to be present in about 80 percent of the samples analyzed (Tables 4, 5). The content of silver reported may be merely a measure of the amount of impurities in the samples. According to Oftedal (138), nearly all the samples in which he found more than 50 ppm silver contained galena, silver sulfosalts such as tetrahedrite, or native silver. It remains uncertain whether pure sphalerite contains any silver; if it does, the concentration is probably small.

Thallium.—Thallium has not been looked for by most workers, but has been found in about one-fourth of the samples analyzed. The quantitative data, summarized in Table 5, show a remarkable concentration in the "schalenblende" type. Kutina (113) and Schroll (174) have found that thallium is higher in the dark, lead-rich bands of such ores. This may be in part due to the presence of galena, but some of these "schalenblende" samples contain more thallium than the associated galena. It may be that minerals such as hutchinsonite, $(\text{Tl,Pb})\text{Ag}_2\text{As}_{10}\text{S}_{17}$, known to occur in this association (178), are present.

Tin.—The presence of tin has been reported in about half the samples studied. The available quantitative data are summarized in Table 5. The tin reported may have been present in part in some of the samples in galena or chalcopyrite, but there is little doubt that some tin is present in sphalerite. The maximum tin content of pure sphalerite is probably less than 1,000 ppm; nearly all samples containing much tin have been found to have inclusions of stannite or cassiterite, or both (60, 96, 208).

In general, the tin content is more likely to be high in sphalerite from deposits formed at high to intermediate temperatures (115; 185; 208). Kullerud (110) determined temperatures of formation and minor-element content of 54 sphalerites. Of these 33 did not contain tin; most of these were

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been looked for by most investigators. The quantitative data are summarized in Table 5. Inclusions in sphalerite of low temperature at Urbain (115) and Oftedal (138). Dark bands of "schalenblende" ores.

present in about 80 percent of the samples. According to the results of the analyses, which he found more than 50 ppm of silver as tetrahedrite, or native silver. It contains any silver; if it does, it is probably present in about 80 percent of the samples.

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from low-temperature deposits. Only one of the remaining 21 contained much tin and had a low temperature of formation (150°, 95 ppm tin), so that the results agree in general with the conclusions of other workers.

Vanadium.—Few data are available on the occurrence of vanadium in sphalerite (Table 4). All of the 36 samples for which quantitative or semi-quantitative determinations other than zero have been published contained 10 to 100 ppm vanadium. Warren and Thompson (208), who reported 29 of these, thought that vanadium occurred most commonly in sphalerite from low-temperature deposits.

Other Elements.—Among the other elements that have been reported qualitatively in sphalerite, silicon, aluminum, calcium, titanium, and magnesium may with some confidence be ascribed to the presence of silicate gangue minerals, and the same may be true for beryllium, barium, chromium, scandium, and yttrium. Tungsten has been reported qualitatively and two determinations gave 2 and 1–10 ppm. Of the platinum metals, palladium and rhodium are each reported qualitatively by one investigator; quantitatively Zvyagintzev and Filippov (215) found 0.4 and 1.5 ppm platinum in 2 samples, the Noddacks (136) reported 0.2 ppm palladium in 1 sample, and Noddack (135) 7 ppm total platinum metals. Rhenium was reported qualitatively by Evrard (54); Noddack (135) found 0.1 ppm in 1 sample. The same investigator also reported 1–10 ppm of scandium, thorium, uranium, and bromine; 0.4 ppm total rare earths; and 10–100 ppm tellurium. Rankama (154, 155) analyzed four samples and reported up to 0.2 ppm each of Nb₂O₅ and Ta₂O₅. Strock (187) found 0, 0, 0, 30, and 40 ppm lithium in 5 samples.

Chalcopyrite

A summary of the type of data available and the elements studied is given in Table 6. The quantitative data for cobalt, indium, manganese, nickel, selenium, silver, and tin are summarized in Table 7.

Arsenic.—Hoehne (96) found 255, 1,720, and 3,820 ppm arsenic in 3 samples; the latter two, however, contained arsenopyrite. Noddack and Noddack (136) reported 250 ppm in 1 sample. Oftedal (138) mentions that arsenic was doubtfully present in 2 samples, one of which may have contained about 1,000 ppm.

Bismuth.—Bismuth was found in 4 of 32 samples studied by Gavelin and Gabrielson (61) and as a trace in 1 of 3 samples by Oftedal (138). Noddack and Noddack (136) reported 5 ppm bismuth in a sample.

Cobalt.—The quantitative data are summarized in Table 7. Auger (7), whose results are given in terms of relative intensities, found that the cobalt content of chalcopyrite increased with depth in both ore bodies at Noranda, Quebec.

Indium.—Indium has been reported qualitatively by several investigators (Table 6). The quantitative data are summarized in Table 7.

Lead.—Lead has been reported qualitatively (Table 6). Noddack and Noddack (136) reported 100 ppm lead in one sample. Auger (7) gives

TABLE 6

SUMMARY OF REFERENCES ON CHALCOPYRITE

Under Type of Data, Q means quantitative analysis, S means semi-quantitative analysis, K means qualitative analysis. Under the elements listed, the symbol X means that the element was present, the symbol — means that the element was looked for, but not found.

Reference	Type of data	No. of samples	As	Sb	Bi	Cd	Co	Ge	In	Pb	Ni	Pt metals	Ag	Sn	Zn	Others
Anderson (1953)	Q, S	7							X							
Auger (1941)	S, K	1								X	X		X		X	Ti X, V X
Bergenfelt (1953)	Q	22														Se X
Bernard (1954)	K	1			X					X						
Björlykke and Jarp (1950)	Q	2					X									Ga X
Borovik, Lizunov and Shcherbina (1941)	Q	6														
Borovik and Prokopenko (1939, 1941)	K	?							X							
Borovik and Prokopenko (1938)	K	3						—	X							
Borovik, Vlodayets and Prokopenko (1938)	Q	3							X							
Brewer and Baker (1936)	S	4							X							
Carstens (1941a)	Q	5														Se X
Carstens (1945)	K	1	—	—		—	X				X		X	—	—	Cr X, Mo —, Ti X, V —
Eberhard (1908, 1910)	K	7														Sc X, Y —
Edwards and Carlos (1954)	Q	21														Se X
Erametsa (1939)	Q	25							X							
Gavelin and Gabrielson (1947)	Q, K	32			X		X				X			X		Mn X
Goldschmidt and Peters (1932)	Q	1										—	X			Au X
Goldschmidt and Peters (1933)	Q	2						X								
Haberlandt and Schiener (1951)	Q	2					—				X			X		
Hartley and Ramage (1897)	K	1							X	X	X		X			Ti X

results in terms of relative intensities for the variation of the lead content with depth at Noranda, Quebec; he found little change.

Manganese and Nickel.—Manganese and nickel have been reported qualitatively (Table 6). The quantitative data are summarized in Table 7. Auger (7) gives data on nickel in terms of relative intensities; he found little variation in nickel content with depth.

Platinum Metals and Gold.—Goldschmidt and Peters (62) found 0.2 ppm gold and no platinum or palladium in one sample. Zvyagintzev and Fillipov (215) found 1.0 ppm platinum in 1 sample, none in 2 others. Analyses of 30 samples from various environments are given by Hawley, Lewis, and Wark (81), Hawley and Rimsaite (82), and Hawley, Rimsaite, and Lord (83). The palladium content ranged from traces to 34.3 ppm, with most samples in

TABLE 7
SUMMARY OF QUANTITATIVE DATA ON MINOR ELEMENTS IN CHALCOPYRITE

Element	Max. concn. ppm	No. of samples in each concentration range										Total No. samples	Sensitivity ppm
		1% or more	5,000-9,999 ppm	1,000-4,999 ppm	500-999 ppm	200-499 ppm	100-199 ppm	50-99 ppm	10-49 ppm	<10 ppm	Not found		
Co	1,000-2,000	—	—	2	1	6 ^a	1	5	13 ^b	—	60	88	10
In	1,000	—	—	4	3	—	—	5	2	6	13	33	1-10
Mn	1-2%	2	—	1	1	5	2	1	16	5	3	36	10
Ni	1,000-2,000	—	—	2	—	11 ^c	4	3	22 ^d	4	39	85	10-15
Se	2,100	—	—	2	2	7	5	4	22	1	—	43	1-10
Ag	2,300	—	—	1	2	1 ^e	1	1	2	—	—	8	?
Sn	770	—	—	—	1	1	3	2	2	—	1	10	10

^a Including 4 samples stated to contain 100-1,000 ppm. One sample contained arsenopyrite.

^b Including 6 samples stated to contain 10-100 ppm.

^c Including 10 samples stated to contain 100-1,000 ppm.

^d Including 17 samples stated to contain 10-100 ppm.

^e Including 1 sample stated to contain 100-1,000 ppm.

the range of 0.02 to 2.0 ppm; only two samples, with 34.3 and 14.8 ppm had more than 2 ppm. Platinum was absent or present in traces in about half the samples and the highest content found was 3.8 ppm. Rhodium was present in still smaller amounts, the highest content being 0.27 ppm. Ruthenium was found in 3 samples, one containing 0.09 ppm, the others in amounts reported as traces. Noddack and Noddack (136) found 20 ppm gold, 0.1 ppm platinum, and none of the other platinum group metals in one sample.

Selenium.—Sludge from the electrolytic refining of copper is now the main source of selenium. The quantitative data on selenium in chalcopyrite are summarized in Table 7. The highest selenium contents are those reported by Bergenfelt (12) from mines in northern Sweden; most of the recent analyses by Edwards and Carlos (52) from Australian localities show much lower selenium contents, which may indicate that regional effects are more important than the conditions of formation.

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or the variation of the lead content and little change. Lead and nickel have been reported qualitatively and data are summarized in Table 7. The relative intensities; he found little

Widt and Peters (62) found 0.2 ppm in one sample. Zvyagintzev and Phillipov found none in 2 others. Analyses of 30 given by Hawley, Lewis, and Warkentin, Hawley, Rimsaite, and Lord (83). 34.3 ppm, with most samples in

MINOR ELEMENTS IN CHALCOPYRITE

Concentration range	Concentration range					Total No. samples	Sensitivity ppm
	10-100 ppm	50-99 ppm	10-49 ppm	<10 ppm	Not found		
1	5	13 ^b	—	60	88	10	
1	5	2	6	13	33	1-10	
1	16	5	3	36	10	10	
1	8	22 ^d	4	39	85	10-15	
1	4	22	1	—	43	1-10	
1	1	2	—	—	8	?	
1	2	2	—	1	10	10	

ppm. One sample contained arseno-
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ppm. with 34.3 and 14.8 ppm had present in traces in about half was 3.8 ppm. Rhodium was content being 0.27 ppm. Ruthenium 0.09 ppm, the others in amounts (136) found 20 ppm gold, 0.1 ppm group metals in one sample. The finding of copper is now the main element in chalcopyrite are contents are those reported by others; most of the recent analyses in localities show much lower contents. These effects are more important

Silver.—Silver has been reported qualitatively by many workers (Table 6). Auger (7) gives data on the variation with depth at Noranda, Quebec. The few quantitative data are summarized in Table 7.

Tin.—Tin has been reported qualitatively by many workers (Table 6). Gavelin and Gabrielson (61) found it in 52 percent of the samples examined. The tin content may be present as exsolved stannite (153). The quantitative data are summarized in Table 7.

Other Elements.—The following additional elements have been reported in chalcopyrite, (see Table 6): Sb, Cd, Cr, Ga, Ge, Mo, Re, Sc, Tl, Ti, V, W, and Y. The following quantitative determinations have been published:

- Antimony* 20 ppm in 1 (136).
- Cadmium* 180 ppm in 1 (136).
- Gallium* 100, 50, 10, 0, 0, and 0 ppm in 6 samples (21).
- Germanium* 10 and 50 ppm Ge in 2 (66).
- Molybdenum* 70, 70, 900 ppm in 3 (136; 212).
- Rhenium* 0.08 ppm in 1 (136).
- Thallium* 0.03 ppm in 1 (179).
- Titanium* Approx. 700 ppm in 1 (7).
- Tungsten* 2 ppm in 1 (136).
- Vanadium* 250 and 100-1000 ppm in 2 (136; 7).
- Zinc* Approx. 1 percent in 1 (7), 3,500 ppm in 1, none in 2 others (161).
Auger (7) found an increase in the zinc content of chalcopyrite with depth at Noranda, Quebec.

Pyrite and Marcasite

Much has been published on the minor elements in pyrite, very little on those in marcasite. Table 8 summarizes the references, and Table 9 gives a summary of the data on some of the elements.

Arsenic.—The presence of arsenic has been reported by many workers. Despite the uncertainty caused by the presence of admixed arsenopyrite and other arsenic-bearing minerals, arsenic probably does occur in pure pyrite. Neuhaus (132) and Hoehne (97) reported that optically homogenous pyrite contained about 5 percent and 2.70 percent, respectively; Neuhaus found that such pyrite had a unit cell with a 5.442 A compared to that of pure pyrite, a 5.411 A, and concluded that the arsenic was present in true solid solution.

Carstens (35, 36, 37) found little difference in the arsenic content of sedimentary pyrite (mostly 600-900 ppm) and of hydrothermal pyrite (mostly 400-700 ppm). The data of Talluri (191) show more than 0.1 percent arsenic in 23 of 33 samples of pyrite of eruptive origin, whereas only 3 of 16 sedimentary pyrite samples contained that much arsenic. Hawley (80) found more arsenic in low-temperature than in high-temperature pyrite in four veins in the Porcupine district, Ontario.

Hawley (80) also gives data on the variation of arsenic content with depth in two mines. Considerable variation was shown, but no definite trend with depth was established. One set of samples showed higher arsenic content in

TABLE 8

SUMMARY OF REFERENCES ON PYRITE (P) AND MARCASITE (M)

Under Type of Data, Q means quantitative analysis, S means semi-quantitative analysis, K means qualitative analysis. Under the elements listed, the symbol X means that the element was present, the symbol — means that the element was looked for, but not found.

Reference	Type of data	No. of samples	As	Sb	Bi	Co	Cu	In	Pb	Mn	Ni	Ag	Sn	V	Zn	Others
Ahlfeld and Moritz (1933)	S	3P					X			X		X			X	Cd —, Ge —
Anderson (1953)	K	8P 2M		—				—								
Antipov (1896)	Q	2M	X													Tl X
Auger (1941)	S, K	124P				X		X	X	X	X	X	X	X	X	Cd, Cr, Mo, Nb, Ti, Y, all X
Bergenfelt (1953)	Q	24P														Se X
Bernard (1953)	K	5P	X	X	X		X		X	X		X	X		X	
Bernard (1954)	K	1P	X				X									Ba X
Bernard and Padera (1954)	K	2P														
Bjørlykke (1945)	Q	27P				X										
Bjørlykke and Jarp (1950)	Q	35P				X										Ga X
Borovik, Lizunov, and Shcherbina (1941)	Q	11P														Ge —
Borovik and Prokopenko (1938, 1939)	K	7P						X								
Borovik, Vlodavets, and Prokopenko (1938)	Q	5P						X								
Brewer and Baker (1936)	K	3P						—						X	X	Ba, Cr, Mo, Sr, all X
Cambel and Kupčo (1953)	K	17P				X	X			X	X					Se X
Carstens (1941a, b, c)	Q	12P				X	X				X	X	X	X	X	Cd, Mo, Se, Ti, all X; Ga,
Carstens (1942a)	K, Q	10P	—	—	—	X	X	—	X	X	X	X	X	X	X	Ge, Tl, all —
Carstens (1942c)	Q	7P				X					X					
Carstens (1943)	S	2P												X		
Claussen (1934)	K	5P	—	—	X	X	X		X	—	X	—	X	X	—	Au, Mo, Pd, Tl, W, Zr, all X; Cr, Ir, Sr, all —
Eberhard (1910)	K	7P														Y X, Sc —
Edwards and Carlos (1954)	Q	60P 5M														Se X
Erametsa (1939)	Q	10P						—								
Evrard (1945)	K	1M 4M					X		X	X		X	X		X	Ge X, Tl X

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Brookopenko (1938)	K	3P																
Brewer and Baker (1936)	K	17P																
Cambel and Kupco (1953)	Q	12P					X	X										
Carstens (1941a, b, c)	K, Q	10P	-	-	-		X	X				X	X	X		X	X	Ba, Cr, Mo, Sr, all X Se X
Carstens (1942c)	Q	7P					X	X				X	X	X		X	X	Ca, Mo, Se, Ti, all X; Ga, Ge, Ti, all -
Carstens (1943)	S	2P											X					
Claussen (1934)	K	5P	-	-	X		X	X					X			X	X	
Eberhard (1910)	K	7P													X			
Edwards and Carlos (1954)	Q	60P														X		Au, Mo, Pd, Ti, W, Zr, all X; Cr, Ir, Sr, all -
Erametsa (1939)	Q	5M																Y X, Se - Se X
Evrard (1945)	K	1M 4M																
							X			X	X		X	X		X		Ge X, Ti X

TABLE 8—Continued

Reference	Type of data	No. of samples	As	Sb	Bi	Co	Cu	In	Pb	Mn	Ni	Ag	Sn	V	Zn	Others
Gavelin and Gabrielson (1947)	Q, K	134P			X	X				X	X		X		X	Se X
Goldschmidt and Hefter (1933)	Q	1P														Ga X
Goldschmidt and Peters (1931)	Q	3M														Ge X
Goldschmidt and Peters (1933)	Q	7P														
Goldschmidt and Peters (1934)	S, K	2P	X													Se X
Goldschmidt and Strock (1935)	Q	8P 1M														
Haberlandt and Schiener (1951)	Q	18P				X					X					
Hartley and Ramage (1897)	K	9P 1M					X	X	X	X	X	X				Ga X, Ti X
Hawley (1952)	Q, S	±200P	X		X	X			X	X	X	X	X	X	X	Ba, Cr, Au, Mo, Sr, Te, Ti, all X
Hawley, Lewis, and Wark (1951)	Q, K	10P 2M	X	X	-	X	X		X	X	X	X	X	X	X	Cr, Au, Pd, Pt, Ti, all X
Hawley and Rimsaite (1953)	Q	3P														Pd, Pt, Rh, all X
Hawley, Rimsaite, and Lord (1953)	Q	1P														Pd X
Hayase and Otsuka (1953)	K	4P				X	X						X			Ti X
Hegemann (1939, 1941)	Q	16P								X						
Hegemann (1943)	Q	644P				X	X			X	X				X	
Hegemann (1949)	Q	9P 2M	X			X	X		X	X	X			X		Mo X, Ti X
Hegemann and Leybold (1954)	Q	14P	X	X	X	X	X		X	X	X	X	X	X	X	Au X, Ti X, Ti X
Hoehne (1934)	Q	3P 1M	X	-									X			
Hoehne (1952)	Q	14P 3M	X													
Horalek (1951)	Q	7P				X										
Huttenhain (1939)	K, Q	?P	X	X		X	X		X		X	X				Au X
Kimura, Nagashima, et al. (1952)	S	3P														Ge -

TABLE 8—Continued

Reference	Type of data	No. of samples	As	Sb	Bi	Co	Cu	In	Pb	Mn	Ni	Ag	Sn	V	Zn	Others
Kinoshita and Muta (1950)	K	26P 2M	X	X	X		X	X	X	X		X	X	X	X	Ge, Au, Hg, Te, W, all X
Kutina (1949)	K	1P	X	X			X		X							Au X
Minguzzi (1947)	Q	16P	X	X	X	X	X		X	X	X	X	X			Ba, B, Cr, Au, W, all X
Minguzzi and Talluri (1951)	Q, K	46P	X	X	X	X	X		X	X	X	X	X	X		
Moritz (1933)	S	1P					X							X		Tl X
Murakami (1950)	Q, K	2P 10M	X		X				X	X						
Nakabe (1951)	Q	1P				X										
Neuhaus (1942)	S	2P	X											X		Mo X, W X
Newhouse (1934)	S, K	5P									X					
Nickel (1954)	Q	16P	X	X	X	X	X		X	X	X	X	X	X		Cd, Ge, Au, Hg, Mo, Pt metals, Re, W, all X
Noddack and Noddack (1941)	Q	3P 1M	X	X	X		X		X			X	X			
Oftedal (1940)	S	2P				X										
Onishi and Sandell (1955)	Q	2P	X													
Prokopenko (1941c, 1941d)	K	?P						X								Nb X, Ta X
Rankama (1944, 1948)	Q	6P													X	
Rost (1939)	Q, K	78P				X	X		X	X	X	X			X	Rh, Ru, Se, Ti, all X
Saito (1953)	K	6P	X				X		X	X	X			X		Pt metals X
Schneiderhöhn (1929a, b)	S, K	1P				X										
Schneiderhöhn (1930)	K	?P	X													
Schroll (1953b)	Q, K	M 11P	X						X		X				X	Tl X
Shaw (1952a, 1952b)	Q	11M 1P						-								Tl X
Talluri (1951)	Q	1M 53P	X													Se X
Tsuge and Terada (1950)	Q	?P														
Vahatalo (1953)	Q	M 1P				X	X			X	X			X		Se X, Te X
Vakhrushev (1940)	Q	4P									X					Tl X
Vogel (1894)	K	2P														
Vogt (1893)	Q	4P				X					X					Se X
Williams and Byers (1934)	Q	21P														
Zvyagintzev and Fillipov (1948)	Q	2M 4P														Pt X

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TABLE 9

SUMMARY OF QUANTITATIVE DATA ON MINOR ELEMENTS IN PYRITE (P) AND MARCASITE (M)

... in each concentration range

M...

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Schneiderhöhn (1930)	K	1P	X	X	X	X	X	X	X	Rh, Ru, Se, Ti, all X Pt metals X
Schroll (1953b)	Q, K	?P	X							
Shaw (1952a, 1952b)	Q	11P 11M 1P 1M		X					X	Tl X
Talluri (1951)	Q	53P	X							Tl X
Tsuge and Terada (1950)	Q	?P								
Vahatalo (1953)	Q	M								Se X
Vakhrushev (1940)	Q	1P		X	X		X	X		
Vogel (1894)	Q	4P								
Vogt (1893)	K	2P								
Williams and Byers (1934)	Q	4P		X						Se X, Te X Tl X
	Q	21P						X		
Zvyagintzev and Fillipov (1915)	Q	2M 4P								Se X Pt X

TABLE 9
SUMMARY OF QUANTITATIVE DATA ON MINOR ELEMENTS IN PYRITE (P) AND MARCASITE (M)

Element	Max. concn. ppm	Type of sample	No. of samples in each concentration range										Total No. samples	Sensitivity ppm	
			1% or more	5,000-10,000 ppm	1,000-4,999 ppm	500-999 ppm	200-499 ppm	100-199 ppm	50-99 ppm	10-49 ppm	<10 ppm	Not found			
As	±5%	P	9	2	13	22	7	4	4	5	—	33	99	10-50?	
As	7,800	M	—	1	—	1	1	2	—	1	—	—	6	10-50?	
Sb	700	P	—	—	—	1	1	3	1	1	1	27	35	50?	
Sb	—	M	—	—	—	—	—	—	—	—	—	2	2	?	
Bi	100	P	—	—	—	—	—	1	—	4	1	11	17	10-100?	
Bi	—	M	—	—	—	—	—	—	—	—	—	1	1	?	
Co	>2.5%	P	26	45	188	134	197	120	62	160	16	149	1,097	2-500, mostly 10-30	
Cu	~6%	P	78	52	97	94	64	39	75	74	109	103	785	1-10	
Pb	5,000	P	—	2	3	4	7	—	1	2	—	5	24	10	
Pb	200	M	—	—	—	—	1	—	—	—	—	—	1	?	
Mn	1%	P	1	16	68	59	80	87	34	130	25	427	927	5-100	
Ni	~2.5%	P	5	9	60	71	163	117	96	340	39	155	1,055	2-20	
Ni	—	M	—	—	—	—	—	—	—	—	—	2	2	?	
Se	300	P	—	—	—	—	—	3	10	16	43	40	3	115	1-10
Se	11	M	—	—	—	—	—	—	—	—	1	7	1	9	1-10
Ag	200	P	—	—	—	—	1	1	6	7	19	39	73	5-30	
Tl	100	P	—	—	—	—	—	1	3	1	1	11	17	10	
Tl	5,300	M	—	1	5	3	—	—	—	—	—	3	12	10	
Sn	400	P	—	—	—	—	2	1	1	3	—	11	18	10	
Sn	4	M	—	—	—	—	—	—	—	—	1	—	1	?	
Ti	600	P	—	—	—	1	8	2	1	2	—	7	21	10	
Ti	80	M	—	—	—	—	—	—	1	—	—	—	1	10	
V	~1,000	P	—	—	1	—	—	5	1	8	—	3	18	?	
V	200	M	—	—	—	—	1	—	—	—	—	2	3	?	
Zn	~4.5%	P	64	58	72	29	16	22	—	—	—	460	722	100	

MINOR ELEMENTS IN SOME SULFIDE MINERALS 1003

detectable by probe to 1000 ppm sensitivity

fine-grained material than in coarse crystals of pyrite, but the reverse was true in a second set of samples. In two sets of samples, Hoehne (97) found much more arsenic in pyrite than in marcasite from the same deposit.

Antimony.—The data on antimony in Table 9 are too few to permit any conclusions to be drawn; the antimony reported might well be due to impurities.

Bismuth.—In addition to the few data in Table 9, Hawley (80) records intensity ratios for 28 samples, 19 from the Powell-Rouyn mine, Quebec. These show a slight decrease in the average bismuth content with depth. Coarse material was higher in bismuth than fine-grained material.

Cobalt.—The cobalt content of pyrite has been the subject of much investigation, as is apparent from Tables 8 and 9. Artificial CoS_2 and the mineral cattierite (103), which contains nearly 90 percent CoS_2 , are isostructural with pyrite, so that a complete series appears to be possible. Intermediate members seem, however, to be very rare; Johansson (100) gives an analysis with 13.90 percent cobalt. Hegemann (87) stated that nearly all samples containing more than 1 percent cobalt showed zoning phenomena and that many contained cobaltite.

The data indicate that generalizations as to the cobalt content and the Co:Ni ratio must be made with considerable caution. Pyrite from sulfide ore deposits generally contains appreciable amounts of cobalt and has $\text{Co} > \text{Ni}$, but many exceptions have been noted; although considerable variation has been reported in pyrite from a single deposit, both the Co content and the Co:Ni ratio appear to be characteristics of the individual deposit (61, 80).

According to Carstens (35, 37, 38, 40), pyrite of sedimentary origin is characterized by containing less than 100 ppm cobalt and $\text{Co} < \text{Ni}$, whereas pyrite of hydrothermal origin has 400–2400 (average about 500) ppm cobalt and $\text{Co} > \text{Ni}$. His generalizations as to pyrite of sedimentary origin have been confirmed; Hegemann (87) reported $\text{Co} < \text{Ni}$ in 68 of 74 such samples, only two of which contained more than 100 ppm Co, and Talluri (191) found $\text{Co} < \text{Ni}$ in 10 of 13 samples of sedimentary origin. Far more variation is shown by the analyses of pyrite of hydrothermal origin; the content of Co reported ranges from traces to more than 1 percent, and although most samples have $\text{Co} > \text{Ni}$, the reverse relation is not uncommon.

Pyrite from high-temperature deposits (17, 87) is generally high in cobalt. Hawley (80) gave analyses of four pairs of samples for which temperatures of formation had been measured. The cobalt content was higher in the high-temperature sample in all four pairs, and the Co:Ni ratio was higher in the high-temperature sample in three of the four. Gavelin and Gabrielson (61) also found that the cobalt content and the Co:Ni ratio were higher in high-temperature deposits, but noted exceptions and considered that the effect of temperature was slight. Hegemann (87) found that in metamorphosed sulfide deposits the cobalt content increased with increasing degree of metamorphism. Gavelin and Gabrielson (61) considered that the effect of type of wall rock was slight; Hawley (80) found some indication of higher cobalt content in samples from slate or sericite than in samples from quartz.

of pyrite, but the reverse was found in some samples, Hoehne (97) found the same deposit.

Table 9 are too few to permit any conclusion, but might well be due to im-

Table 9, Hawley (80) records the bismuth content with depth in the Powell-Rouyn mine, Quebec, fine-grained material.

has been the subject of much investigation. Artificial CoS_2 and the mineral NiS_2 are isostructural with FeS_2 , where possible. Intermediate members (100) gives an analysis with $\text{Co} > \text{Ni}$ and that nearly all samples containing phenomena and that many

to the cobalt content and the effect of temperature. Pyrite from sulfide deposits of cobalt and has $\text{Co} > \text{Ni}$, but shows considerable variation in $\text{Co}:\text{Ni}$ ratio, both the Co content and the $\text{Co}:\text{Ni}$ ratio of the individual deposit (61, 80). Pyrite of sedimentary origin is generally $\text{Co} < \text{Ni}$, whereas pyrite of igneous origin (average about 500) ppm cobalt content of sedimentary origin have $\text{Co} < \text{Ni}$ in 68 of 74 such samples, and Talluri (191) found $\text{Co} < \text{Ni}$ in pyrite of igneous origin. Far more variation is found in pyrite of igneous origin; the content of Co is generally $\text{Co} < \text{Ni}$, and although most samples are common.

(87) is generally high in cobalt. In some samples for which temperatures of formation were higher in the high-temperature series, the $\text{Co}:\text{Ni}$ ratio was higher in the high-temperature series. Gavelin and Gabrielson (61) found that the $\text{Co}:\text{Ni}$ ratio were higher in high-temperature series. It is considered that the effect of temperature on the $\text{Co}:\text{Ni}$ ratio in metamorphosed sulfide deposits is a function of the degree of metamorphism. The effect of type of wall rock on the $\text{Co}:\text{Ni}$ ratio of higher cobalt content in pyrite is also a function of quartz.

The variation of cobalt content with depth in several Canadian mines has been studied by Auger (7) and Hawley (80). The data show increases, decreases, and no change in the cobalt content with depth for different mines.

Copper.—Copper has been reported to be present in most samples of pyrite analyzed (Table 8), but it seems probable that most, if not all, of it is present as admixed chalcopyrite or other copper minerals. Pyrite of hydrothermal deposits generally contains more copper than pyrite of sedimentary deposits, according to Carstens (35, 37, 38).

Gold.—Gold has been determined quantitatively (Table 8) in 36 samples of pyrite and 1 marcasite, the content reported being less than 10 ppm except for 5 samples (12, 20, 20, 70, and 200 ppm Au) reported by Minguzzi (123) and by Hegemann and Leybold (91). Detailed studies of the distribution of gold in pyrite of individual mines have been made by Hawley (80), the data being given in terms of relative intensities. Because much, if not all, of the gold reported is present as free gold (7; 80), its gold content varies greatly from sample to sample. No marked trends of gold content with temperature of formation, type of wall rock, or depth in a deposit were established; structural controls, such as proximity to a contact, appeared to have a greater effect.

Lead.—Few data are available on the lead content of pyrite. It is probable that the lead reported represents admixed galena or other sulfides. In addition to the results summarized in Table 9, Auger (7) and Hawley (80) give results in terms of relative intensities on the variation of lead content of pyrite with depth in various Canadian gold mines. The lead content showed slight increases with depth in some of the mines, but it is uncertain whether these are significant. The effects of temperature of formation, grain size, and variation in host rock (80) on the lead content of pyrite seem to be small.

Manganese.—Hauerite, MnS_2 , is isostructural with pyrite, but the type of bonding is apparently different (86), so that there is only very limited replacement of iron by manganese in pyrite. The data are summarized in Table 9; no determinations were found of manganese in marcasite. In addition, data in terms of relative intensities are given by Auger (7) and Hawley (80). Auger found a decrease in manganese content with depth at one mine; Hawley found slight increases at two mines, slight decreases at two others, and no trend at another. His data on the effects of grain size, wall-rock variation, and temperature of formation do not seem to indicate any significant trends. Gavelin and Gabrielson (61) found no appreciable differences in the manganese content of pyrite from higher or lower temperature deposits. They found a slight tendency, of doubtful significance, for pyrite from zinc-rich ores to contain more manganese than pyrite from copper-rich ores.

Nickel.—Artificial NiS_2 and the minerals vaesite (nearly pure NiS_2) and bravoite, $(\text{Ni,Fe})\text{S}_2$, are isostructural with pyrite. In the series FeS_2 - NiS_2 , natural material has not yet been reported in the range NiS_2 60 to 90 percent, but the systematic variation of unit cell size and specific gravity indicates that the complete series can exist (8; 103; 15). Samples of high nickel content are commonly zoned and some contain admixed millerite or other nickel

sulfides (86, 87). On these grounds Hegemann and also Kalb (102) believe that there is not a continuous series between pyrite and bravoite.

The quantitative data are summarized in Table 9, which shows clearly that nickel is generally present in lower amounts than is cobalt. Generalizations as to the nickel content of pyrite from various types of deposits are even less certain than those for cobalt. Pyrite of high-temperature and hydrothermal sulfide deposits has only a slightly higher average nickel content than pyrite of sedimentary origin and the ranges of concentration overlap. Variations of the Co:Ni ratio have been discussed above under Cobalt. Hawley found that the nickel content was a little higher in high-temperature samples; Gavelin and Gabrielson found little or no effect of temperature of formation.

The variation of the nickel content of pyrite with depth has been studied by Auger (7) and Hawley (80) for seven deposits. No systematic trend could be determined, both increases and decreases being noted. Hawley found considerable variation of the nickel content with different wall rocks. Gavelin and Gabrielson (61) reported that pyrite of zinc-rich ores had a slightly higher nickel content than pyrite of copper-rich ores.

Platinum Metals.—Analyses of 9 samples of pyrite and one marcasite have been published, as indicated in Table 8. Schneiderhöhn (166, 167) found 10–100 ppm of Pt and Pd, and 0.1–1 ppm Ru, Rh, and Ir. The other analyses show much less, up to 0.38 ppm Pt and 0.5 ppm Pd.

Selenium.—The available analyses are summarized in Table 9, except those of Tsuge and Terada (197), who found 0.2 to 39, average 12.6 ppm selenium. Carstens (35, 37) found no selenium in pyrite of sedimentary origin and more than 10 ppm Se in pyrite of hydrothermal origin. Edwards and Carlos (52) found that pyrite and marcasite of sedimentary supergene origin had low contents of Se and very high S:Se ratios, mostly above 100,000; in contrast, most pyrite of hydrothermal origin had S:Se ratios below 20,000. A few pyrites of hydrothermal origin, however, had S:Se ratios above 100,000, so that some caution is necessary in using this criterion of origin.

Silver.—The quantitative data are summarized in Table 9. Additional data in terms of intensity ratios are given by Auger (7) and Hawley (80). The variation of the silver content with depth was determined by them for 7 deposits; both increases and decreases with depth were noted. Hawley found that the silver content was higher in the low-temperature pyrite than in the high-temperature pyrite of three of four pairs studied; as, however, part at least of the silver was present in native gold that may have been introduced after the pyrite formed, the results may not be significant. Hawley also found that in 6 of 7 samples, the silver content decreased with increasing distance from a porphyry contact. He also studied the variation in silver content of pyrite with changes in the type of host rock.

Thallium.—The few quantitative data on thallium are summarized in Table 9. The notable enrichment of thallium in marcasite as compared to pyrite is evident; no explanation has been offered. It will be recalled that the "schalenblende" type of ZnS shows a similar enrichment in thallium.

Tin.—In addition to the scanty data summarized in Table 9, Hawley (80)

mann and also Kalb (102) believe pyrite and bravoite. Table 9, which shows clearly units than is cobalt. Generalizations of various types of deposits are even of high-temperature and hydrothermal higher average nickel content ranges of concentration overlap. discussed above under Cobalt. little higher in high-temperature or no effect of temperature of

pyrite with depth has been studied in deposits. No systematic trend of decreases being noted. Hawley's pyrite with different wall rocks. pyrite of zinc-rich ores had a higher copper-rich ores.

of pyrite and one marcasite S. Schneiderhöhn (166, 167) ppm Ru, Rh, and Ir. The other and 0.5 ppm Pd.

summarized in Table 9, except and 0.2 to 39, average 12.6 ppm titanium in pyrite of sedimentary hydrothermal origin. Edwards' pyrite of sedimentary supergene origin, mostly above 100,000; had S:Se ratios below 20,000. However, had S:Se ratios above this criterion of origin.

summarized in Table 9. Additional data of Auger (7) and Hawley (80). was determined by them for 7 pyrites were noted. Hawley found higher in high-temperature pyrite than in the low-temperature pyrite studied; as, however, part at least that may have been introduced is significant. Hawley also found that silver content increased with increasing distance from the vein. Variation in silver content of

thallium are summarized in Table 9. It will be recalled that the enrichment in thallium. summarized in Table 9, Hawley (80)

as recorded analyses in terms of relative intensity ratios. His data indicate considerable irregular variation of the tin content with depth in individual pyrites, with temperature of formation, grain size, and wall rock, but no certain trends can be identified.

Titanium.—In addition to the data summarized in Table 9, Auger (7) and Hawley (80) reported spectrographic analyses in terms of relative intensities. No consistent trend in titanium content with depth was found. Hawley's data show considerable variation in titanium content with variation in host rock, but this may have been in part due to inclusions. The results indicate higher titanium contents in fine-grained pyrite than in coarse pyrite from the same mine.

Vanadium.—The few quantitative determinations are summarized in Table 9. Auger (7) found a notable increase (from about 300 to about 1000 ppm) with depth in both ore bodies at Noranda, but the data of Hawley (80), given in terms of intensity, show no variation or very slight decreases with depth in four other Canadian mines. Hawley's data also indicate no significant variations of vanadium content with grain size or with variation in wall rock. Carstens (41), on the basis of a few analyses, reported vanadium to be absent in pyrite of hydrothermal sulfide deposits and present in pyrite of sedimentary deposits.

Zinc.—The zinc reported in analyses of pyrite is probably to be regarded as a measure of the amount of admixed sphalerite present; probably very little is present in isomorphous substitution (86). Data in terms of intensity ratios are given by Auger (7) and Hawley (80), who studied the variation of zinc content with depth in five mines. They found no marked trends, both increases and decreases being noted, with the latter more common. Variations with degree of fineness and with variation of wall rock were also studied by Hawley; the data do not seem to indicate any notable trends.

Other Elements.—Qualitative tests for various elements are reported in Table 8; following are additional data:

Cadmium.—Noddack and Noddack (136) found 10 ppm in 1 of 3 pyrites, none in 1 marcasite.

Chromium.—No quantitative determinations are available, but Auger (7) and Hawley (80) give data in the form of relative intensities. Auger reported a sharp decrease in the chromium content with depth at the Hollinger mine, but Hawley found both increases and decreases, none marked, with depth in four Canadian mines. Auger found that pyrite from massive sulfide deposits contained little or no chromium, whereas, that from vein type deposits contained large amounts of chromium.

Gallium.—Goldschmidt and Peters (1931) found 5 ppm Ga in 1 of 3 marcasites analyzed; Borovik, Lizunov, and Shcherbina (21) found 50–100 ppm Ga in 6 pyrites, none in 5.

Germanium.—Goldschmidt and Peters (66) reported 50, 30, 5, 5, 5, 0, 0 ppm Ge in 7 samples of sedimentary pyrite; Noddack and Noddack (136) reported 20, 10, and 8 ppm Ge in 3 samples of pyrite, 90 ppm Ge in a marcasite.

Indium—The presence of indium has been reported in pyrite by several workers (Table 8). Borovik, Vlodayets, and Prokopenko (26) found 10, < 10, < 10, 0, and 0 ppm In in 5 samples of pyrite.

Mercury—Noddack and Noddack (136) reported 0.4 ppm Hg in a pyrite sample; two others and a marcasite contained no mercury.

Molybdenum—Noddack and Noddack (136) reported 5, 10, and 20 ppm Mo in 3 pyrites and 30 ppm in a marcasite; Hegemann (88) found 10 ppm in 3 pyrites, none in 6 pyrites and 2 marcasites. Auger (7) stated that molybdenum was absent in pyrite from massive sulfide deposits, but commonly present in pyrite of vein-type deposits. Hawley (80) gave data in the form of relative intensities for pyrite from four Canadian deposits. No significant variations of the molybdenum content with depth, wall rock, or fineness of grain were noted.

Rhenium—Noddack and Noddack (136) found 0.01 ppm Re in 2 samples of pyrite, none in a third, and 0.03 ppm Re in a marcasite.

Strontium and Barium—No quantitative data are available. Auger (7) and Hawley (80) gave results in terms of intensity ratios on the variation with depth in individual mines. Hawley found marked variation of the barium and strontium contents of pyrite from different host rocks.

Tantalum and Niobium—Rankama (154, 155) found 0.08 ppm Ta in one of six pyrites analyzed, and 0.07, 0.7 ppm Nb in two of the same samples.

Tellurium—Vakhrushev (202) reported 20, 20, 290, and 340 ppm tellurium in four samples. Hawley (80) studied the variation of tellurium content, in terms of intensity ratios, with depth in individual mines. The tellurium content varied, in general, with the gold content; tellurium was probably present as gold tellurides. Little variation was observed in the tellurium content of pyrite from different wall rocks.

Pyrrhotite and Troilite

Table 10 summarizes the references on pyrrhotite and troilite; Table 11 summarizes the quantitative data for the elements on which most work has been done.

Antimony—Noddack and Noddack (136) reported 10 ppm in one of three pyrrhotite samples and 4 ppm in one of three troilites from meteorites.

Arsenic—Noddack and Noddack (136) reported 20, 50, and 150 ppm As in three pyrrhotites, 100, 200, and 600 ppm As in three troilites from meteorites. Onishi and Sandell (140) found much lower contents, 8 and 11 ppm as in two composites of troilites from meteorites.

Bismuth—Noddack and Noddack (136) reported 3 ppm Bi in 1 of 3 pyrrhotites, 0.2 ppm Bi in 1 of 3 troilites from meteorites.

Chromium—Rost (161) reported 30, 50, and 60 ppm Cr in 3 samples.

Cobalt—The quantitative data on cobalt are summarized in Table 11. Part at least of the cobalt reported is probably present as intergrown or exsolved pentlandite (153, p. 409-411); the limit of isomorphous replacement of iron by cobalt in pyrrhotite is not known, but is apparently below 1 percent (161, 86).

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been reported in pyrite by several authors. Prokopenko (26) found 10 ppm of pyrite.

Auger (7) reported 0.4 ppm Hg in a pyrite sample. He found no mercury.

Auger (136) reported 5, 10, and 20 ppm of mercury in pyrite.

Hegemann (88) found 10 ppm of mercury in pyrite.

Auger (7) stated that mercury is common in massive sulfide deposits, but common in pyrite.

Lawley (80) gave data in the form of a table.

Canadian deposits. No significant variation was observed with depth, wall rock, or fineness of grind.

Auger (136) found 0.01 ppm Re in 2 samples of pyrite.

Auger (7) found 0.01 ppm Re in a marcasite.

Auger (7) found 0.01 ppm Re in a pyrite.

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Auger (7) found 0.01 ppm Re in a pyrite.

Gavelin and Gabrielson (61) found no general trend in the cobalt content or the Co:Ni ratio in the pyrrhotites they studied; they seemed to be specific characteristics of individual ore deposits rather than to indicate systematic variation with temperature of formation or type of deposit. Gavelin and Gabrielson noted that, in general, pyrrhotite from the copper-rich ore tended to be higher in cobalt content than pyrrhotite from zinc-rich ore, but there were many overlaps. Auger (7) gave data on the variation of cobalt content with depth at the Noranda Mine, Quebec. He found an increase with depth. Fryklund and Harner (59) found erratic variation of the cobalt content along 1,500 feet of a single ore shoot in the Coeur d'Alene district.

Copper.—Much, if not all, of the copper reported in pyrrhotite, as summarized in Table 11, is probably present as admixed or exsolved chalcopyrite or cubanite.

Germanium.—Noddack and Noddack reported 60, 20, and 0 ppm Ge in 3 pyrrhotites, very large amounts of Ge in 2 and 600 ppm Ge in 1 of 3 troilites from meteorites.

Gold.—Goldschmidt and Peters (65) reported 0.5 ppm Au in one sample. Noddack and Noddack (136) found 2 ppm Au in one of three pyrrhotites and 0.5, 0.2, and none in three troilites analyzed. Schneiderhöhn (166, 167) found 1–10 ppm Au in 1 sample; Schneiderhöhn and Moritz (170) 1–5 ppm Au in 1 sample.

Lead.—Noddack and Noddack (136) reported 30, 90, and 100 ppm Pb in 3 pyrrhotites, 60, 500, and 900 ppm Pb in 3 troilites from meteorites. Auger (7) found little variation in the lead content at different depths in the Noranda Mine, Quebec.

Manganese.—The quantitative data are summarized in Table 11. The apparent lack of isomorphous substitution of iron by manganese in pyrrhotite is ascribed by Hegemann (86) to the different types of bonding in FeS and MnS; alabandite has nearly ionic bonding. Gavelin and Gabrielson (61) found no systematic variation of manganese content with temperature of formation, composition of ore, or geological milieu.

Molybdenum.—Noddack and Noddack (136) reported 20, 30, and 40 ppm Mo in 3 pyrrhotites, 10, 15, and 40 ppm Mo in 3 troilites from meteorites. Sandell and Kuroda (164) found 6 ppm Mo in a troilite from a meteorite.

Nickel.—The quantitative data are summarized in Table 11; some uncertainty is caused by the common occurrence of intergrowths of pentlandite (153, p. 409–411). Hegemann (86, 87) believed that the upper limit of nickel content in isomorphous substitution may be about 1 percent nickel. Hegemann (87) stated that samples from high-temperature deposits tended to have higher nickel contents, but Gavelin and Gabrielson (61) found little effect of temperature of formation. They found a tendency for higher nickel content in pyrrhotite from zinc-rich ores compared with that from copper-rich ores. Auger (7) reported little change in nickel content with increasing depth at the Noranda Mine, Quebec, and Fryklund and Harner (59) reported erratic variations of nickel content along 1,500 feet of a single shoot in the Coeur d'Alene district, Idaho.

Platinum Metals.—Many determinations of the platinum metals in pyr-

Troilite

on pyrrhotite and troilite; Table 11 summarizes elements on which most work has been done.

Auger (136) reported 10 ppm in one of three troilites from meteorites.

Auger (136) reported 20, 50, and 150 ppm As in three troilites from meteorites.

Auger (136) found much lower contents, 8 and 10 ppm As in two troilites from meteorites.

Auger (136) reported 3 ppm Bi in 1 of 3 troilites from meteorites.

Auger (136) reported 50, and 60 ppm Cr in 3 samples.

Cobalt are summarized in Table 11.

Probably present as intergrown or as a separate phase.

The limit of isomorphous replacement is known, but is apparently below 1 percent nickel.

TABLE 10

SUMMARY OF REFERENCES ON PYRRHOTITE AND TROILITE

Under Type of Data, Q means quantitative analysis, S means semi-quantitative analysis, K means qualitative analysis. Under the elements listed, the symbol X means that the element was present, the symbol — means that the element was looked for, but not found.

Reference	Type of data	No. of samples	As	Co	Cu	Au	Pb	Mn	Ni	Pt metals	Ag	Sn	Ti	V	Zn	Others
Anderson (1953)	K	8														Cd, Ge, In, Sb, all —
Auger (1941)	S	14		X			X		X		X			X	X	Sb X
Bernard (1953)	K	4	X		X		X	X			X	X				
Bjørlykke and Jarp (1950)	Q	8		X												
Cambel and Kupco (1953)	K	19	X	X	X		X	X	X		X	X	X	X	X	Ba, Cr, Mo, Sr, all X
Carstens (1941a)	Q	1		X					—							
Carstens (1943)	K	?											X	—		
Edwards and Carlos (1954)	Q	11														Se X
Erametsa (1939)	Q	10														In —
Fryklund and Harnér (1955)	Q, S	10		X	X		X	X	X		X					Ba X
Gavelin and Gabrielson (1947)	Q, K	100		X				X	X			X				Bi X
Goldschmidt and Peters (1931)	Q	3														Ga —
Goldschmidt and Peters (1932)	Q	1				X				—	X					
Goldschmidt and Strock (1935)	Q	10														Se X
Hartley and Ramage (1897)	K	2			X		X	X	X		X					In X

pyrrhotite are given by Hawley, Lewis, and Wark (81), Hawley and Rimsaite (82), and Hawley, Rimsaite, and Lord (83). They found in pyrrhotite from nickeliferous sulfides platinum in traces up to 56.9 (only 2 samples had more than 5 ppm), Pd 0.1 to 34.3 ppm. (only 4 samples had more than 5 ppm), Rh up to 0.58 ppm, Ru up to 2.12 ppm, Ir up to 1.03 ppm, and Os up to 1.1 ppm. The average of 33 samples from Falconbridge, Sudbury district, excluding one sample with very high content, was 0.72 ppm Pt and 0.27 ppm Pd. The ratio Pt/Pd was highly variable, the extremes reported being 26:1 and 1:20. The variability was taken to indicate that probably the platinum metals are present largely as discrete minerals, and not in solid solution in the pyrrhotite.

TABLE 11
SUMMARY OF QUANTITATIVE DATA ON MINOR ELEMENTS IN PYRRHOTITE (P)
AND TROILITE (T)

Element	Max. concn. ppm	Type of sample	No. of samples in each concentration range										Total No. of samples	Sensitivity ppm
			1% or more	5,000-9,999 ppm	1,000-4,999 ppm	500-999 ppm	200-499 ppm	100-199 ppm	50-99 ppm	10-49 ppm	<10 ppm	Not found		
Co	8,500	P	—	4	35	18	57	21	11	18	1	87	252	10-15
Cu	7,000	P	—	1	1	5	4	10	4	1	—	—	26	2-10
Cu	800	T	—	—	—	1	1	1	—	—	—	—	3	?
Mn	3,000	P	—	—	21	18	32	15	1	10	4	14	115	10-100
Ni	7.47%	P	10	8	30	13	39	42	29	30	34	9	244	10-15
Se	63	P	—	—	—	—	—	—	3	11	6	—	20	1-5?
Se	132	T	—	—	—	—	—	1	1	—	—	—	2	1-5?
Ag	100	P	—	—	—	—	—	1	1	1	11	6	20	5-30
Ag	60	T	—	—	—	—	—	—	1	—	1	1	3	?

The analyses by Schneiderhöhn (166, 167) (1) Schneiderhöhn and Moritz (170) (2), and by Noddack and Noddack (136) (3 pyrrhotites and 3 troilites from meteorites) all fall within the ranges reported by Hawley and co-workers, except that Noddack and Noddack reported 20, 9, and 0 ppm Ru and 10, 6, and 0 ppm Os in the troilites.

Hawley and Rimsaite (82) analyzed 6 pyrrhotites from nonnickeliferous ores. These had much lower contents of platinum metals than the pyrrhotites from nickeliferous ores; the maximum contents found being Pt trace, Pd 0.056 ppm, and Rh 0.06 ppm.

Rhenium.—Noddack and Noddack (136) reported 0.02, 0.02, and 0.03 ppm Re in 3 pyrrhotites, 0.004, 0.01, and 0.04 ppm Re in 3 troilites from meteorites.

Selenium.—The quantitative data are summarized in Table 11.

Silver.—The few quantitative data are summarized in Table 11. Auger (7) gives data in terms of relative intensities for the variation of silver content with depth in two deposits at Noranda, Quebec. The silver content increased with depth in the lower deposit.

Thallium.—Shaw (179) reported 0.074 ppm Tl in a sample from Sudbury.

Tin.—Noddack and Noddack (136) reported 60, 500, and 1,000 ppm Sn in 3 pyrrhotites, 60, 500, and 1,000 ppm Sn in 3 troilites from meteorites. Auger (7) analyzed and reported 60, 500, and 1,000 ppm Sn in 3 pyrrhotites, 60, 500, and 1,000 ppm Sn in 3 troilites from meteorites. He did not contain of

Titanium.—Noddack and Noddack (136) reported 0.02, 0.02, and 0.03 ppm Ti in 3 pyrrhotites, 0.004, 0.01, and 0.04 ppm Ti in 3 troilites from meteorites. Auger (7) analyzed and reported 0.02, 0.02, and 0.03 ppm Ti in 3 pyrrhotites, 0.004, 0.01, and 0.04 ppm Ti in 3 troilites from meteorites. He did not contain of

Tungsten.—Noddack and Noddack (136) reported 0.02, 0.02, and 0.03 ppm W in 3 pyrrhotites, 0.004, 0.01, and 0.04 ppm W in 3 troilites from meteorites. Auger (7) analyzed and reported 0.02, 0.02, and 0.03 ppm W in 3 pyrrhotites, 0.004, 0.01, and 0.04 ppm W in 3 troilites from meteorites. He did not contain of

Vanadium.—Noddack and Noddack (136) reported 0.02, 0.02, and 0.03 ppm V in 3 pyrrhotites, 0.004, 0.01, and 0.04 ppm V in 3 troilites from meteorites. Auger (7) analyzed and reported 0.02, 0.02, and 0.03 ppm V in 3 pyrrhotites, 0.004, 0.01, and 0.04 ppm V in 3 troilites from meteorites. He did not contain of

Zinc.—Rosenthal (180) reported 0 (sensitivity 5 ppm) Zn in 3 pyrrhotites, 0 (sensitivity 5 ppm) Zn in 3 troilites from meteorites. Auger (7) analyzed and reported 0 (sensitivity 5 ppm) Zn in 3 pyrrhotites, 0 (sensitivity 5 ppm) Zn in 3 troilites from meteorites. He showed less zinc than the pyrrhotites, roughly constant

The type of pyrrhotite and the quantity of manganese, iron, and Tanakaite in the arsenopyrite glaucodot. Only a few of the pyrrhotites

Determined by Noddack (136) are as follows:

Copper—

Germanium—

Gold—

Lead—

Molybdenum—

Platinum—

Rhenium—

Selenium—

Silver—

Tantalum—

Zinc—

Data from

Vark (81), Hawley and Rimsaite (1967) (1) Schneiderhöhn and Noddack (136) (3 pyrrhotites and 3 troilites) and the ranges reported by Hawley and Noddack reported 20, 9, and 0 ppm Pt in 3 pyrrhotites from nonnickeliferous meteorites. The platinum metals found being Pt trace, Pd 0.056 ppm, and Os 0.03 ppm. The silver content reported 0.02, 0.02, and 0.03 ppm in 3 troilites from Sudbury district, Ontario, Canada, Quebec. The silver content reported 0.02, 0.02, and 0.03 ppm in 3 troilites from Sudbury district, Ontario, Canada, Quebec. The silver content reported 0.02, 0.02, and 0.03 ppm in 3 troilites from Sudbury district, Ontario, Canada, Quebec.

MINOR ELEMENTS IN PYRRHOTITE (P)
(T)

Concentration range	Concentration range				Total No. of samples	Sensitivity ppm
	0-99 ppm	10-99 ppm	10-49 ppm	<10 ppm		
0-99 ppm	11	18	1	87	252	10-15
10-99 ppm	4	1	—	—	26	2-10
100-999 ppm	—	—	—	—	3	?
1000-9999 ppm	1	10	4	14	115	10-100
10000-99999 ppm	29	30	34	9	244	10-15
100000-999999 ppm	3	11	6	—	20	1-5?
1000000-9999999 ppm	1	—	—	—	2	1-5?
10000000-99999999 ppm	1	1	11	6	20	5-30
100000000-999999999 ppm	1	—	1	1	3	?

Tin.—Noddack and Noddack (136) found 80, 5, and 0 ppm Sn in 3 pyrrhotites, 60, 500, and 900 ppm in 3 troilites from meteorites. Gavelin and Gabrielson (61) found that tin was present in 13.5 percent of the pyrrhotites analyzed and occurred particularly in pyrrhotite (and pyrite) from ores that did not contain chalcopyrite.

Titanium.—No quantitative data are available. Auger (7) reported that the titanium content of pyrrhotite at Noranad, Quebec, increased with depth from approximately 0.1 to 0.5 percent. Presumably the titanium is present as an admixture.

Tungsten.—Noddack and Noddack (136) reported 5, 2, and 0 ppm W in 3 pyrrhotites, 4, 0, and 0 ppm W in 3 troilites from meteorites.

Vanadium.—Noddack and Noddack (136) reported 100, 20, and 0 ppm V in 3 pyrrhotites, 150, 30, and 0 ppm V in 3 troilites from meteorites. Auger (7) found that the vanadium content increased with depth at the Noranda Mine, Quebec, the ranges reported being approximately 70 to 400 ppm, as read from his curve.

Zinc.—Rost (161) found 1.5% Zn in one sample, a trace in another, and 0 (sensitivity 500 ppm) in 13 samples. No other quantitative data are available. Hegemann (86) states that zinc was found in very few of the 110 samples analyzed, the maximum amount being 500 ppm, and that these generally showed less zinc after purification. Auger (7) found the zinc content to be roughly constant with depth at about 0.1% at Noranda, Quebec.

Arsenopyrite

The type of data available on arsenopyrite are summarized in Table 12, and the quantitative determinations are summarized in Table 13 for cobalt, manganese, and nickel, mainly from the data of Gavelin and Gabrielson (61) and Tanaka (192). Cobalt is present in appreciable percentages in most of the arsenopyrites analyzed and there is probably a complete series to glaucodot, CoAsS.³ The content of cobalt exceeds that of nickel in all but a few of the analyses.

Determinations of other elements are few, mainly by Noddack and Noddack (136) (N) and by Rost (161) (R), each on one sample. They were as follows:

- Copper—200 ppm (R), very high (N).
- Germanium—30 ppm (105).
- Gold—8 ppm (N), 0.5 ppm (65).
- Lead—50 ppm (N), much (R).
- Molybdenum—60 ppm (N).
- Platinum—0.4 ppm (N).
- Rhenium—0.01 ppm (N).
- Selenium—42, 47, and 57 ppm (52).
- Silver—90 ppm (N), 25 ppm (R), 10 ppm (65).
- Vanadium—300 ppm (N);
- Zinc—400 ppm (R).

³ Dana's System of Mineralogy, 7th Ed., vol. 1, p. 319-324, 1944.

TABLE 12
SUMMARY OF REFERENCES ON ARSENOPYRITE

Under Type of Data, Q means quantitative analysis, S means semi-quantitative analysis, K means qualitative analysis. Under the elements listed, the symbol X means that the element was present, the symbol — means that the element was looked for, but not found.

Reference	Type of data	No. of samples	Sb	Bi	Cd	Co	Cu	Ge	In	Pb	Mn	Ni	Ag	Sn	Zn	Others
Anderson (1953)	K	2	—		—			—	—					—	X	
Bernard (1953)	K	4	X	X	X		X		X	X			X	X		
Bernard (1954)	K	2				X	X			X						Ga —
Borovik, Lizunov, and Shcherbina (1941)	K	4														
Borovik and Prokopenko (1938)	K	4						—	X							
Brewer and Baker (1936)	K	1							X?							Sc X?, Y X
Eberhard (1910)	K	4														Se X
Edwards and Carlos (1954)	Q	3														
Erametsa (1934)	Q	6							—		X	X				
Gavelin and Gabrielson (1947)	Q	39				X										Au X, Pt metals —
Goldschmidt and Peters (1932)	Q	1											X			
Goldschmidt and Peters (1933)	Q	3							—							
Haberlandt and Schiener (1951)	S	1				X						X				
Hoehne (1934)	Q	1	—											—		
Kimura, Nagashima, et al. (1952)	Q	2						X								
Kinoshita and Muta (1950)	K	2	X				X	—	—	X			X	X	X	Au X, Te —
Kutina (1949)	K	1				X	X			X			X	X	X	
Kutina (1953c)	K	2	X	X		X	X			X	X	X	X		X	Ti X, Ga X, Hg X, Ru X?
Noddack and Noddack (1931)	Q	1	—	—	—		X	—		X			X	—		Au X, V X, Mo X, Pt X, Re X, Hg —, W —, Pd —
Prokopenko (1941c)	K	?							X						X	
Rost (1939)	Q	1				—	X			X	—	X	X			
Tanaka (1943)	Q	10				X	X			X	X	X				
Tasaka (1954)	Q	1				X	X			X	X	X				
Williams and Byers (1911)	Q	1				X	X			X	X	X				

In addition to the quantitative analysis of the ore mineral, known among the in extractions empirical investigations of the ore mineral.

Offered although stances.

Element

Co Ni

galena: amount was not also certain manium that each and the in the sphalerite of the galena. preferred galena. Offer the indi the data Anders than a tended

	Au, X, Pt metals -	Au X, Te -	Ti X, Ga X, Hg X, Ru X?	Au X, V X, Mo X, Pt X,	Re X, Hg -, W -, Pd -	Au -	Se X
		X X X				X	-
		X					
X		X X X X				X	-
	X	X				X X X	
		X				-	X
		X X X X K				X	
						X	
	X						
		X X X X K				X	
	X	X X				- X X	
			X -				-
		X X					
1	3						
Q	Q	S	Q Q	K K	K K	K Q	Q Q S Q
Goldschmidt and Peters (1932)	Goldschmidt and Peters (1933)	Haberlandt and Schiener (1951)	Hoehe (1934)	Kimura, Nagashima, et al. (1952)	Kinoshita and Muta (1950)	Kutina (1949)	Kutina (1953c)
Noddack and Noddack (1931)	Prokopenko (1941c)	Rost (1939)	Tanaka (1943)	Tassel (1954)	Williams and Byers (1934)		

In addition, antimony, bismuth, cadmium, indium, and tin have been reported qualitatively (Table 12).

DISTRIBUTION OF ELEMENTS AMONG CO-EXISTING MINERALS

Knowledge of the manner in which the minor elements are distributed among the co-existing mineral phases of an ore deposit is extremely important in extractive metallurgy as well as theoretically, and there is a good deal of empirical information available from smelting practice. Comparatively few investigators have made painstaking separations and analyses of co-existing ore minerals; these are summarized below.

Galena-Sphalerite

Oftedal (138) analyzed both galena and sphalerite from 40 localities, although the minerals were not separated from the same sample in many instances. He found that lead, antimony, and bismuth occurred only in the

TABLE 13
SUMMARY OF QUANTITATIVE DATA ON MINOR ELEMENTS IN ARSENOPYRITE

Element	Max. concn. ppm.	No. of samples in each concentration range										Total No. of samples	Sensitivity ppm
		1% or more	5,000-9,999 ppm	1,000-4,999 ppm	500-999 ppm	200-499 ppm	100-199 ppm	50-99 ppm	10-49 ppm	<10 ppm	Not found		
Co	3.36%	12	4	17	4	4	2	-	4	-	7	54	10-22
Mn	3,000	-	-	5	-	5	4	3	11	11	1	40	10
Ni	3,000	-	-	9	4	17	4	1	6	5	8	54	10-100

galena; silver was commonly present in galena and only rarely found in small amounts in sphalerite free from galena inclusions; thallium, present in galena, was not found in pure sphalerites, but was present in "schalenblende" that also contained lead and arsenic. Oftedal found that cobalt, gallium, germanium, indium, mercury, nickel, and zinc occurred only in the sphalerite and that cadmium was found in only two samples of zinc-free galena. Arsenic and tin were found in both minerals; the arsenic content was much higher in the galena; Tornquist (196) however, reported higher arsenic contents in sphalerite than in galena for samples from five localities. The distribution of tin was somewhat erratic, but generally the content was higher in the galena. Oftedal concluded that in deposits containing both minerals, tin is preferentially taken up by sphalerite in very low-temperature deposits and by galena at higher temperatures.

Oftedal's conclusions are in general agreement with the data reported on the individual minerals. McLellan (121) stated, however, without giving the data, that in lead-zinc ores, indium is present mainly in the galena. Anderson (5) found that galena might be either richer or poorer in indium than associated sphalerite; in both minerals, the concentration of indium tended to be greater in samples from high temperature deposits.

Zvyagintzev and Fillipov (215) reported that galena, sphalerite, and pyrite separated from the same sample contained 5, 1.5, and 0.5 ppm Pt, respectively.

For data on selenium, see below under pyrite-chalcopyrite. Compare also the sections above on galena and sphalerite.

Pyrite-Pyrrhotite

The distribution of cobalt and nickel between pyrite and pyrrhotite in the same hand specimens was studied by Rost (161) on 12 samples and by Hege-mann (87) on 27 samples. Although the contents of cobalt and nickel and the Co:Ni ratios were highly variable from sample to sample, both found that cobalt tends to concentrate in pyrite, and nickel in pyrrhotite. Only in a few samples did the pyrite contain more nickel or less cobalt than the pyrrhotite. A few chemical analyses by Bjørlykke and Jarp (18) give results in accord with these. Gavelin and Gabrielson (61) confirmed these conclusions in a study of Swedish ores, but their analyses showed, in general, lower ratios of Co(pyrite)/Co(pyrrhotite) and Ni(pyrrhotite)/Ni(pyrite). They also extended the data to include arsenopyrite and chalcopyrite. They found the order of decreasing cobalt content to be arsenopyrite-pyrite-pyrrhotite-chalcopyrite, of decreasing nickel content to be arsenopyrite-pyrrhotite-pyrite-chalcopyrite. Their data for manganese show about equal amounts in pyrite and pyrrhotite and slightly smaller amounts in arsenopyrite and chalcopyrite.

Data on selenium and the platinum metals are given below under Pyrite-Chalcopyrite; compare also the sections above on pyrite and pyrrhotite.

Pyrite-Chalcopyrite and Associated Minerals

The distribution of cobalt, nickel, and manganese between pyrite and chalcopyrite has been discussed above under Pyrite-Pyrrhotite. Data are also available on the platinum metals and on selenium.

Platinum Metals.—Hawley and co-workers (Hawley, Lewis, and Wark, 81; Hawley and Rimsaite, 82; Hawley, Rimsaite, and Lord, 83) have determined the content of platinum metals in pyrite, chalcopyrite, pyrrhotite, pentlandite, and in mixed arsenides (maucherite, gersdorffite, and niccolite) from various mines, but it is not clear whether any of the analyses were made on minerals separated from the same ore sample. Their results show considerable variation for a single mineral from a single mine, and the following generalizations by me are very tentative. Chalcopyrite seems to have generally the highest concentration of total platinum metals. For palladium, the order of decreasing content may be arsenides, chalcopyrite, pyrrhotite, pentlandite, pyrite; for platinum, it may be pentlandite, chalcopyrite, pyrrhotite, pyrite, arsenides; the contents in pyrite are very much lower than those of the other minerals listed. Zvyagintzev and Filippov (215) determined platinum in minerals from a single deposit and found galena 5, sphalerite 1.5, pyrite 0.5 ppm respectively.

Selenium.—The data of Bergenfelt (12) on ores from northern Sweden indicate that for minerals from the same mines the order of decreasing selenium

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smaller amounts in arsenopyrite

are given below under Pyrite-
on pyrite and pyrrhotite.

Associated Minerals

manganese between pyrite and
Pyrite-Pyrrhotite. Data are
selenium.
(Hawley, Lewis, and Wark,
saite, and Lord, 83) have de-
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ite, gersdorffite, and niccolite)
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single mine, and the following
chalcopyrite seems to have gen-
m metals. For palladium, the
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content is galena, chalcopyrite, arsenopyrite, sphalerite, pyrite, and pyrrhotite, the selenium content of the last three being very much lower than that of the others. Analyses by Carstens (35) of pyrite and chalcopyrite concentrates from Norwegian mines also show much higher concentrations of selenium in the chalcopyrite. Determinations by Edwards and Carlos (52) on Australian samples show considerable variation of the selenium content of the minerals, but give in general the order chalcopyrite, arsenopyrite, pyrite (hydrothermal), pyrrhotite, sphalerite, galena, thus differing from Bergenfelt's order in the much lower selenium content in galena.

CONCLUDING REMARKS

I hope that this summary has made evident some of the large gaps in our knowledge and that it will encourage research aimed at answering some of the unsolved problems. It should be emphasized that qualitative analyses on dubious material are not of much use, nor are quantitative analyses of pure material of unknown geological history very enlightening. The great need now is for careful analyses of material of known purity and known paragenetic history, supplemented by equilibrium studies such as the pioneering work of Kullerud (110).

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Abstract
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