METALLOGENIC PROVINCES OF THE SOUTHWESTERN UNITED STATES

AND NORTHERN MEXICO

Thesis by

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ABSTRACT

Some of the metallogenic provinces of the southwestern United States and northern Mexico are defined by the geographic distribution of trace elements in the primary sulfide minerals chalcopyrite and sphalerite. The elements investigated include antimony, arsenic, bismuth, cadmium, cobalt, gallium, germanium, indium, manganese, molybdenum, nickel, silver, tellurium, thallium, and tin. Of these elements, cobalt, gallium, germanium, indium, nickel, silver, and tin exhibit the best defined geographic distribution.

The data indicate that chalcopyrite is the preferred host for tin and perhaps molybdenum; sphalerite is the preferred host for cadmium, gallium, germanium, indium, and manganese; galena is the preferred host for antimony, bismuth, silver, tellurium, and thallium; and pyrite is the preferred host for cobalt, nickel, and perhaps arsenic. With respect to the two minerals chalcopyrite and sphalerite, antimony, arsenic, molybdenum, nickel, silver, and tin prefer chalcopyrite; and bismuth, cadmium, cobalt, gallium, germanium, indium, manganese, and thallium prefer sphalerite. This distribution probably is the result of the inter-action of several factors, among which are these: the various radii of the elements, the association due to chemical similarities of the major and trace elements, and the degree of ionic versus covalent and metallic character of the metal-sulfur bonds in chalcopyrite and sphalerite. The type of deposit, according to a temperature classification, appears to be of minor importance in determining the trace element content of chalcopyrite and sphalerite.

A preliminary investigation of large single crystals of sphalerite and chalcopyrite indicates that the distribution within a single crystal

of some elements such as cadmium in sphalerite and indium and silver in
chalcopyrite is relatively uniform, whereas the distribution of some
other elements such as cobalt and manganese in sphalerite is somewhat
less uniform and the distribution of tin in sphalerite is extremely
erratic. The variations in trace element content probably are due
largely to variations in the composition of the fluids during the growth
of the crystals, but the erratic behavior of tin in sphalerite perhaps is
related to the presence of numerous cavities and inclusions in the crystal
studied.

Maps of the geographic distribution of trace elements in chalcopyrite
and sphalerite exhibit three main belts of greater than average trace
element content, which are called the Eastern, Central, and Western belts.
These belts are consistent in trend and position with a beltlike distribu-
tion of copper, gold, lead, zinc, silver, and tungsten deposits and with
most of the major tectonic features. However, there appear to be no
definite time relationships, for as many as four metallogenic epochs,
from Precambrian to late Tertiary, are represented by ore deposits within
the Central belt.

The evidence suggests that the beltlike features have a deep seated
origin, perhaps in the sub-crust or outer parts of the mantle, and that
the deposits within each belt might be genetically related through a
beltlike compositional heterogeneity in the source regions of the ores.
Hence, the belts are regarded as metallogenic provinces.

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INTRODUCTION

The concept of metallogenic provinces appears to have been first expressed by De Launay and Urbain (1910), and it was later developed by De Launay (1913). De Launay used the term to designate certain geographic areas which are metalliferous, but which also are characterized by specific combinations of metallogenic epochs and of presumably related tectonic conditions. In other words, certain metallized regions of the earth can be distinguished from others by unique combinations of metallogenic epochs and of tectonic and erosional conditions. The provinces thus defined tend to be large, commonly of continental dimensions, and hence tend to include many ore deposits that are only superficially related. Consequently, De Launay's concept of metallogenic provinces is of limited value in the study of actual genetic relationships.

As early as 1902, Spurr (1902, p.336) proposed the term metalliferous provinces to describe those regions that are "...characterized by special combinations or amounts of the rarer, especially the commercially valuable, metals...". Spurr (1905) later changed the term to metallographic province in order to conform to the generally accepted usage of the terms petrographic province and physiographic province. Spurr appears to have had specific areas in mind when he proposed these terms, particularly the so-called Arizona copper province. However, within this province he recognized four distinct metallogenic epochs, the oldest pre-Cambrian and the youngest late Tertiary, each of which is characterized by ore deposits abnormally rich in copper.

There is, therefore, a fundamental difference between De Launay's concept of a metallogenic province and Spurr's concept of a metallographic province. The metallogenic province includes, as one of its more important elements, a time dependence factor, the metallogenic epoch, whereas the metallographic province involves only concentration phenomena, and apparently is independent of time, at least as far back as the geologic record is accurately decipherable.

Lindgren (1933) apparently either did not recognize the difference in these concepts or did not accept Spurr's concept, for on page 878 he states:

> "Over larger or smaller areas the conditions may at a given time be favorable for the deposition of useful minerals. Such areas are called minerogenetic or metallogenetic provinces."

Lindgren's conception of metallogenic (metallogenetic) provinces, therefore, appears to have been similar to De Launay's, but somewhat more vague. In fact, it is of little practical value.

Bateman (1950) more recently has recognized the differences between the two concepts and the confusion that has existed in the use of the terms, and has completely separated the metallogenic epochs (periods of widespread deposition of metals separated by long periods of non-deposition) from the metallogenetic provinces (regions characterized by relatively abundant mineralization that is dominantly of one type). However, in doing this, he has applied De Launay's term metallogenetic province to the concept for which Spurr used the term metallographic province. Although Bateman's discussion

has not aided in the clarification of the terminology, it has
served to put these two independent concepts into their proper
perspectives.

On the other hand, there are certain objections to the use
of the term metallogenic (metallogenetic) to describe features
for which there is yet little evidence of genetic relation-
ship. Therefore, what Bateman calls metallogenetic provinces
perhaps should be more aptly called metallographic provinces,
as originally proposed by Spurr. The term metallogenic
province then could be defined as a region of the earth which
is characterized by greater than average concentrations of
a particular metal or group of metals, and in which the metal-
liferous deposits are genetically related. The requirement of
a genetic relationship is important, for without it the terms
metallogenic and metallographic become synonymous.

Although there are numerous discussions in the literature
concerning metallogenic or metallogenetic provinces, in terms
of groups of ore deposits or mining districts that possess
some genetic feature in common, very few of them have resulted
in concrete expressions, such as maps of the provinces. Spurr
(1923) was one of the first to attempt such an expression in
the publication of maps (pp. 459-462) that show "The Great
Silver Channel". He concluded that all the silver deposits
along the "channel" have a common genetic element; namely,
an underlying source which possesses a compositional hetero-
geneity with a configuration that corresponds to the config-
uration of the "channel". About 10 years later, Butler (1933,
p. 233) published a map which indicates that the important

mining districts of the western United States tend to be concentrated around the margins of the Colorado and Columbia plateaus. This distribution had previously prompted Butler (1930) to suggest a possible genetic relationship between the ore deposits and these "positive" tectonic elements. More recently Billingsley and Locke (1941, p. 52) have published a map of the orogenic belts of the United States (reproduced in part as plate 20 of this paper), and have attempted to show that the more important ore deposits tend to cluster around intersections of these orogenic belts (the "crossroads") and other tectonic features that extend to great depths. If this relationship were true, perhaps each of these clusters could be considered as a metallogenic province, in the present sense of the term, inasmuch as all of the deposits in a cluster presumably would be genetically related through the structural feature that was responsible for the cluster.

Kerr (1946) has outlined three "tungsten arcs" in the western United States, based on the geographic distribution of tungsten deposits. Furthermore, he finds certain features in the deposits of one "arc" which in general serve to distinguish these deposits from those in the other "arcs". Hence, there is a suggestion of a genetic relationship among the various deposits within each "arc".

The foregoing summary of ideas concerning metallographic and metallogenic provinces is not intended as a comprehensive survey of the literature on the subject, but as an illustration of the fact that although the basic concepts have been in existence for nearly half a century, our knowledge of

metallogenic provinces amounts to little more than specula-
tion. This is somewhat surprising in view of the importance
of such knowledge in the exploration for new ore deposits and
in the attack on problems of ore genesis.

The present investigations were undertaken to obtain
factual information that perhaps would shed some light on
these general problems. Specifically, they have been aimed
at two questions. First, do metallogenic provinces exist?
Second, if they do exist, what is their general appearance?

These problems are approached through a detailed study
of the distribution of some of the sulfophile trace elements
in certain primary sulfide ore minerals, chiefly because of
the following considerations. First, in order for two or more
ore deposits to be genetically related, their ores either must
have come from common or related sources or must have arisen
through the same causal processes. If they have come from
common or related sources, about the only property of the ores
that could reflect their common heritage would be certain
compositional characteristics. Consequently, a study of the
compositional variations in the primary sulfide ores of a
region might reveal which of the deposits could be genetically
related, although these variations must be consistent to be of
genetic significance. The demonstration of a consistent
regional difference in the content of one metal, particularly
if it is one of the major metals such as copper, is not
sufficient for the establishment of a metallogenic province,
for it is readily conceivable that two unrelated sources
might be rich in the same metal. But if a group of major and

minor sulfophile elements exhibits a consistent regional distribution, a genetic relationship is more firmly indicated.

Another factor that prompted the choice of the trace element approach is the recording by earlier workers, especially Stoiber (1940) and Warren and Thompson (1945), of large regional differences in the content of certain trace elements in sphalerite, which they related to the metallogenic provinces in which the sphalerite occurs. These findings were influential in the undertaking of the present study, the immediate objective of which is to determine whether there are significant regional differences in the trace element content of certain primary sulfide minerals.

Chalcopyrite was selected for the initial study mainly because one of the most obvious metallographic provinces in North America is the Arizona copper province, and a comparative study of the principal primary ore mineral of copper, chalcopyrite, in this and the surrounding regions was believed most likely to reveal an associated metallogenic province, if such exists. Other factors that were influential in the selection of chalcopyrite are: (1) its fairly widespread occurrence, (2) its nearly universal occurrence as a hypogene mineral, and (3) its common occurrence in fairly coarse grained crystalline masses that are relatively free of intergrowths with other minerals. The main disadvantage in its use is its high iron content, which has necessitated the development of special spectrographic techniques in order to obtain the desired sensitivities with very small samples.

Sphalerite eventually was included in the study with the hope that its trace element content would be sufficiently similar to that of chalcopyrite to permit its use in some areas where chalcopyrite is unavailable. Despite the fact that definite relationships exist between the two minerals with respect to trace element distributions, the relationships unfortunately are not precise enough to permit prediction of the amounts of trace elements contained in chalcopyrite from a knowledge of their content in sphalerite. Therefore, sphalerite was investigated with the same objectives in mind as for chalcopyrite, but as an independent system.

The principal factor in the choice of sphalerite is the fact that considerable spectrochemical work has been done on it by several workers, and some of the results indicate a "provincial" dependence of its trace element content. Other influential factors include the three enumerated above for chalcopyrite, and the fact that sphalerite commonly contains a large variety of "impurity" elements. Disadvantages to the use of sphalerite include: (1) its highly variable iron content, (2) its tendency to contain abundant cavities and inclusions, and, apparently related to this, (3) an erratic behavior of certain trace elements.

The general abundance and widespread occurrence of pyrite are important factors in favor of its use in studies such as this, but the common occurrence of more than one generation of pyrite in many ore deposits, together with the technical difficulties attending its very high iron content, originally were regarded as serious objections to its use. However, a

reconnaissance investigation of ten samples of pyrite, after the technical difficulties were solved in the development of the analytical method for chalcopyrite, indicate that pyrite is very suitable for the purposes at hand. Actually, it may prove to be more suitable than sphalerite.

An examination of 15 samples of galena indicates that this mineral also is an indicator of the geographic distribution of trace elements in the sulfides. The chief value of galena, however, lies in an assemblage of trace elements that is different from those in the other common sulfides. The principal disadvantage to its use, as with sphalerite, is an erratic behavior of some of the elements.

In order for the results of a study of the trace element distribution in sulfides to have genetic significance, the assemblage of elements investigated must include the so-called sulfophile or chalcophile elements. That is, the elements investigated must have accompanied the metal sulfide-bearing solutions from their sources, and must not have been introduced in appreciable quantities from extraneous sources such as the wall rocks. The elements that in general satisfy this requirement are antimony, arsenic, bismuth, cadmium, cobalt, copper, gallium, germanium, gold, indium, iron, lead, mercury, molybdenum, nickel, selenium, silver, sulfur, tellurium, tin, and zinc. Of these, copper, iron, lead, sulfur, and zinc are major constituents of the ores and therefore are generally unsuitable. Furthermore, the poor spectrographic sensitivities do not allow accurate evaluations of the distributions of antimony, arsenic, gold, mercury, selenium, and tellurium.

The enlargement of the area included in the present studies has been mainly in the directions indicated by the results of the preliminary investigations on the Arizona copper province. The area now includes parts of Arizona, California, Colorado, Nevada, New Mexico, Utah, and northern Mexico. The coverage is by no means complete, and in some of these places, especially in Colorado, it is insufficient as a basis for definite conclusions.

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SAMPLING METHODS

It was necessary at the outset of these investigations to determine the variations in the trace element content of chalcopyrite within an ore deposit, within a mining district, and between mining districts. To this end, samples were collected personally from several of the large copper mines of the Southwest. A special effort was made in doing this to obtain clean fresh material from as widely separated parts of the deposits as possible.

When favorable results were obtained from a preliminary investigation of this material, the problem arose of obtaining the maximum geographic coverage of samples in the time available. A majority of the mines and prospects that have yielded suitable material in the past have been abandoned, and the time required to visit all these places personally was considered prohibitive. Hence, samples were accepted and utilized from every available source. It is realized that in adopting this practice the chances for errors in location of samples are great, but the large amount of material thus made readily available is considered worth the sacrifice. However, in a few cases where there is good reason to doubt the accuracy of location of the sample as labeled, the sample either was discarded or the analysis was not considered in the final interpretation.

A polished section was made from the most suitable part of each hand specimen preparatory to obtaining the spectrographic sample. A small block about 10x15x20 mm was sawed from the hand specimen and mounted in a polystyrene ester

plastic. One sawed surface of the mounted specimen was ground on agate and cast iron laps, with silicon carbide and crushed corundum as abrasives. The cast iron lap is made of "gray iron" which contains one percent each of copper and molybdenum. A preliminary polish was obtained with levigated alumina and diamond powder on a lap coated with cellulose acetate and levigated alumina. Diamond powder in mineral oil (Nujol) was used as an abrasive for the final polish on a lap coated with cellulose acetate and cerium oxide.

The samples for spectrographic analysis were obtained as drill cuttings from the surfaces of the polished sections. The drilling equipment consists of a laboratory model dental machine fitted with S. S. White No. 2 "carbide" dental burrs. These burrs are approximately one millimeter in diameter and therefore are suitable for the sampling of relatively small areas of the polished section under the microscope. This method of sampling, by drilling the sample from a polished section under the mineragraphic microscope, is regarded as superior to the commonly employed method of selecting "clean" fragments of crushed material under a binocular microscope.

The chief advantages of the polished section method of sampling are: (1) samples can be obtained from a very small amount of initial material; (2) microscopic intergrowths of other minerals, which ordinarily cannot be seen in rough fragments under the binocular microscope, can be avoided, thus assuring a purer sample; and (3) the other minerals that commonly are associated with the sample mineral can be identified and reckoned as potential contaminants. The

principal disadvantages of the polished section method are:
(1) the implicit but necessary assumption that the material
is homogeneous and monomineralic to the depth penetrated by
the drill (ordinarily about one millimeter), and (2) the
increased chances of contamination during preparation of the
polished section and during the drilling process.

Although it is necessary to assume that the sample is
homogeneous to the depth penetrated by the drill, the uncer-
tainty introduced by such an assumption may be minimized by
noting the other minerals present in the polished section and
regarding them as possible contaminants. Furthermore, from
a knowledge of the distribution of the trace elements among
the more common sulfides, which are more likely to be contam-
inants, it is commonly possible to evaluate semi-quantita-
tively the contribution of the contaminant mineral to the
total trace element content of the sample.

The possibility that contamination occurs in the prepa-
ration of the polished sections and in the drilling process
was tested by analysing two samples that were taken from the
same part of a specimen by two different methods. One sample
(JER-36HSP) was chipped with a diamond-tipped probe from an
unprepared specimen of chalcopyrite. No other minerals could
be seen in the specimen under the binocular microscope.
A second sample (JER-36) was obtained by the regular drilling
procedure from a polished section of the same part of the
specimen, after the first sample was obtained. It is evident
from the analyses of these samples presented in table 1 that
the preparation of the polished sections and the drilling

process do not introduce any systematic contamination effects.

Table 1

Tests for Contamination in the Preparation of Samples
(In parts per million)

Sample No.:	Ag	As	Bi	Cd	Co	Ge	In	Mn	Mo	Ni	Sb	Sn	Te
JER-36HSP	30	-	30	-	4	-	100	30	-	-	-	300	-
JER-36	30	-	30	-	-	-	100	20	-	-	-	100	-

After the general distribution of trace elements in the four most common primary sulfides (chalcopyrite, sphalerite, pyrite, and galena) had been determined, some samples that were known to be contaminated by one or another of these minerals were utilized for certain elements. The purpose of this was to obtain some idea of the distribution of the trace elements in those areas from which no other material was a-vailable at the time.

ANALYTICAL METHODS

Equipment and Instrumental Conditions

The trace element contents of chalcopyrite and sphaler-
ite, and of a few samples of pyrite and galena, were deter-
mined spectrographically with the equipment and under the
conditions described below.

Spectrograph - A Jarrel-Ash 21 foot Wadsworth mounted
grating-type instrument that has a dis-
persion of 5.2 Angstroms per millimeter
in the first order. The grating, a
Johns Hopkins original, has 15,000 lines
per inch.

Electrodes - The anodes are shaped from 1/4 inch graph-
ite rods according to the specifications
of Myers (1951). The cathodes are two
inch long pieces of 1/8 inch graphite rods
that are pointed on one end.

Photographic plates - 4x10 inch Eastman Kodak, emulsion
number III-0, developed four
minutes at 20°C in DK-50 devel-
oper.

Wavelength range - 2300 to 4800 Angstroms in the first
order.

Excitation - A 10 ampere DC arc is used throughout.
The analytical gap is four millimeters,
of which the central half millimeter is
used. The arc is magnified five times and
focused on the slit.

Exposure - A slit width of 25 microns is maintained
throughout. Neutral density quartz filters
are used to reduce the amount of light
transmitted to 40 percent for the chalco-
pyrite samples and to 64 percent for the
sphalerite samples.

Densitometer - Applied Research Laboratories, model
2250.

The Analysis of Chalcopyrite

The spectrographic method for the analysis of chalco-

pyrite that is used here was developed specifically to over-
come the difficulties that are connected with the high iron
content of the mineral ($CuFeS_2$). The aim in this development
has been to combine fair precision and high sensitivity with
speed of analysis.

Previously described methods for the quantitative analy-
sis of sulfides are few, especially for iron-rich sulfides,
and most of them are of about the same general nature (Strock,
1945). The most common procedure has been to mix the sample
with an excess of powdered carbon, and to burn the mixture to
completion. This procedure is unsatisfactory for the present
purposes because: (1) the background on the photographic plate
is so intense, owing to the high iron content, that the
general sensitivity is lowered to an undesirable level;
(2) an iron-rich bead forms during arcing and tends to
"spatter" from the arc, and (3) the consequent loss of sample
results in relatively poor reproducibility of analysis.
Oftedal (1941) encountered similar difficulties in the analy-
sis of iron-rich sphalerite.

In attempts to improve the arcing characteristics, repro-
ducibility, sensitivity, selective volatilization, and to add
an internal standard, considerable experimentation was done
with various mixtures of Na_2CO_3, SiO_2 (quartz), ZnO, and CuO,
in place of the powdered carbon. The best results were
obtained with a mixture that consists of 50 percent SiO_2,
40 percent ZnO, and 10 percent Na_2CO_3. The SiO_2 forms a bead
that burns smoothly. The ZnO is added as an internal stand-
ard and to promote selective volatilization of the non-ferrous

elements. The Na_2CO_3 acts to stabilize the arc and as a flux in the formation of the silica-rich bead. Despite the improvements that resulted from the use of this mixture, the background was still objectionably intense. This objection was overcome, however, by arcing the sample in two stages.

A moving plate study indicated that after the sample mixture is arced for 50 seconds at 10 amperes, the elements of interest, except cobalt, iron, manganese, molybdenum, and nickel are nearly completely volatilized. Furthermore, even enough of these five elements are volatilized in this period of time to yield acceptable sensitivities. Therefore, the procedure finally adopted is to arc the sample mixture for 50 seconds, then advance the camera, without breaking the arc, and burn the sample to completion (altogether about 90 to 110 seconds). Nearly all the iron is effectively held in the silica-rich bead until after the camera is advanced; hence, there is no longer an objectionably intense background in the first, most important exposure. The second and iron-rich exposure, with its intense background, could be used for the determination of cobalt, manganese, molybdenum, and nickel, but the results obtained for these elements from the first exposure are nearly as reproducible as those from the second and are more expeditiously obtained. The second exposure is now used mainly to evaluate iron, manganese, and cobalt interference.

Inasmuch as it was commonly possible to obtain only 15 or 20 milligrams of sample altogether, all the experimentation was done using only five milligrams of sample. This sample

was mixed with 15 milligrams of the SiO_2-ZnO-Na_2CO_3 mixture to make a total electrode charge of 20 milligrams. The use of the small 5 milligram sample permitted about 95 percent of the analyses to be made in duplicate. Moreover, the samples are still large enough to yield fairly good sensitivities, as shown in figure 1A.

The method of internal standardization used in these studies differs somewhat from standard procedures. Ordinarily the internal standard element is added in very small amounts, but in the present work no suitable internal standard could be found that would not be expected to occur as a minor or trace constituent of the samples. Therefore, zinc was used as an internal standard for the less refractory elements by adding a large enough quantity (30 percent of the total mixture in the form of ZnO) to "swamp out" the effects of small amounts of zinc (less than one percent) that might be present as a contaminant from admixed sphalerite. Similarly, inasmuch as the iron content of chalcopyrite is essentially constant, iron was used as an internal standard for cobalt, nickel, and manganese.

Another practice that was adopted in this work, but which is not recommended for the highest precision, is the use of only one zinc line (2670.5 Å) and one iron line (2791.5 Å) as internal standard lines, instead of the general practice of using neighboring line pairs. The considerably increased speed of analysis is considered worth the slight sacrifice in precision.

Figure 1. The spectrographic sensitivities of the elements
           in chalcopyrite (A) and sphalerite (B).
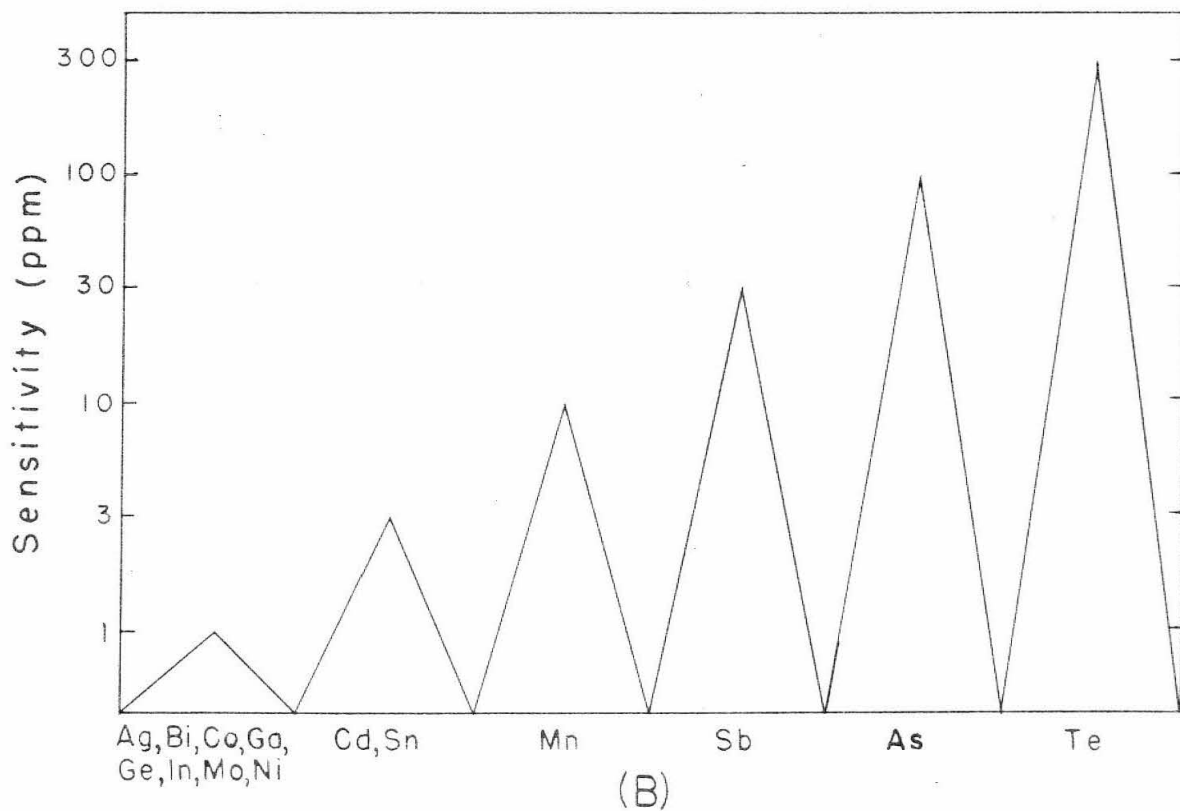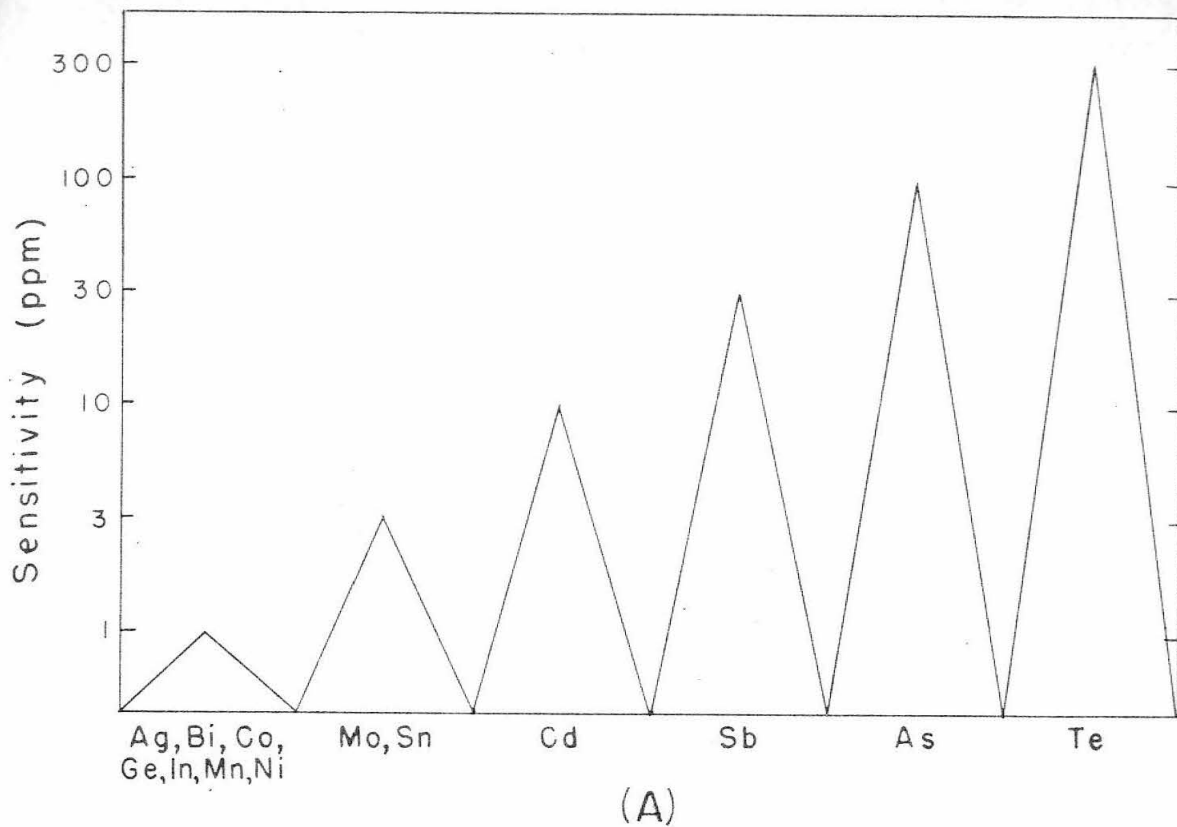
Figure 1

The chalcopyrite standards were prepared by adding, as
spectrographically pure oxides, the elements antimony, arsenic,
bismuth, cadmium, cobalt, germanium, indium, manganese, molyb-
denum, nickel, silver, tin, and tellurium to a base of nearly
pure natural chalcopyrite from Ajo, Arizona (AJ-40, table 4).
Blank corrections were made for the small amounts of bismuth,
cobalt, indium, manganese, silver and tin that were present
in the base. A mixture that contains 5.0 percent by weight of
the elements in the chalcopyrite base was prepared first and
then diluted to 1.0 percent with the base. Further dilutions
from an aliquot of the 1.0 percent standard were made in steps
that differed from each other by a logarithmic factor of 5.
The result is the series of standards, 1, 3.2, 10, 32, 100,
320, 1000, 3200, 10000 parts per million.

The standards are exposed with each group of samples,
and the working curves are reconstructed each time. The
actual construction of the working curves, examples of which
are shown in figures 2 and 3, consisted of plotting on loga-
rithmic coordinates the concentrations versus the element line
to internal standard line intensity ratios. The intensities,
in turn, are obtained from the photographic emulsion calibra-
tion curves, which are constructed according to the method of
Diecke and Crosswhite (1943).

The reproducibility of the method was determined by
analyzing a sample of chalcopyrite (BOR-1, table 4) 14 times
during a period of six months. The results of these tests are
summarized in table 2. Among the six elements that were de-
tected in the test sample, the best reproducibility is

Figure 2. Working curve for the determination of the amount
        of tin in chalcopyrite. The lengths of the vertical
        bars represent the ranges in the results of 13
        analyses of the standard mixtures.

Figure 3. Working curve for the determination of the amount
        of nickel in chalcopyrite. The lengths of the vertical
        bars represent the ranges in the results of 13 analyses
        of the standard mixtures.

Figure 2

Figure 3
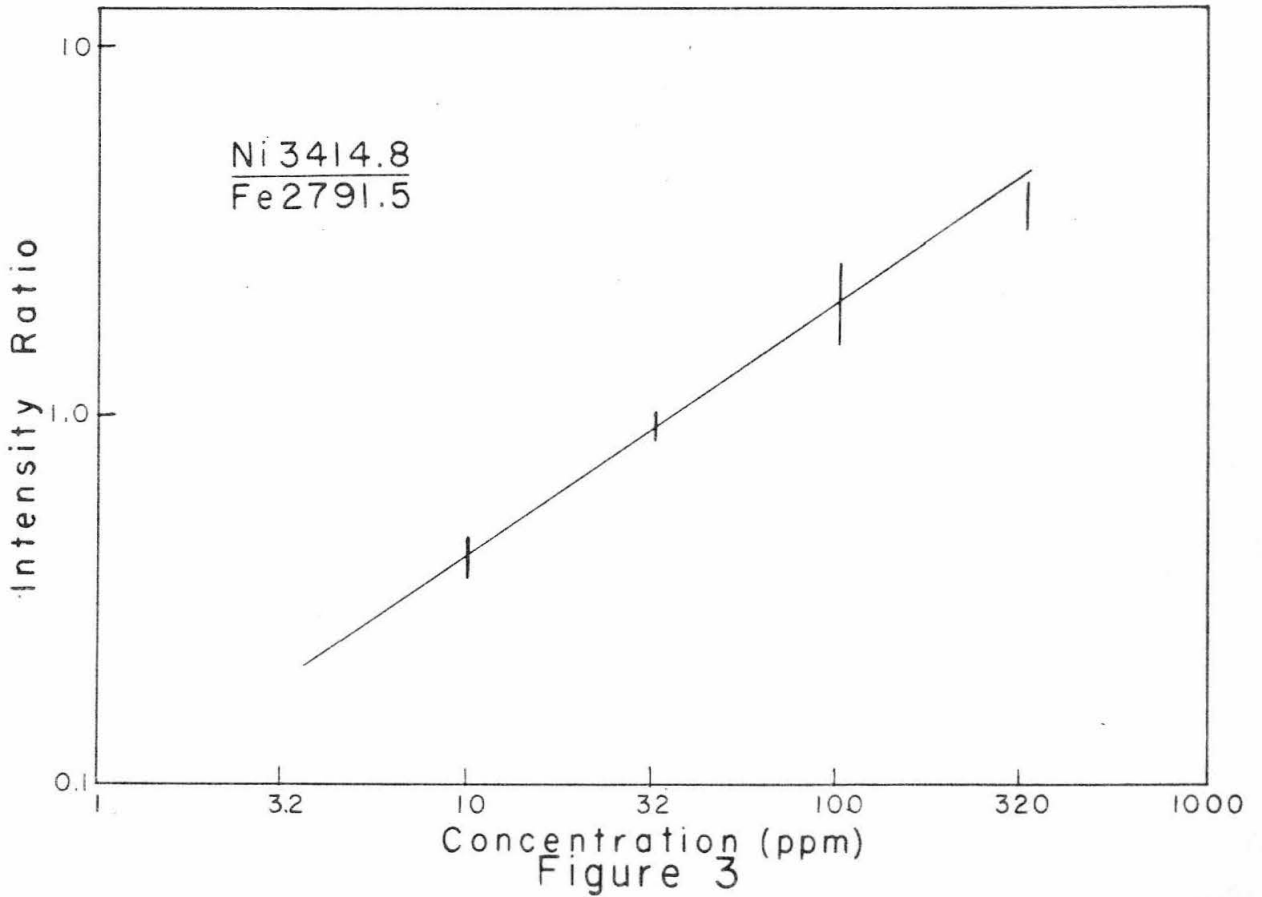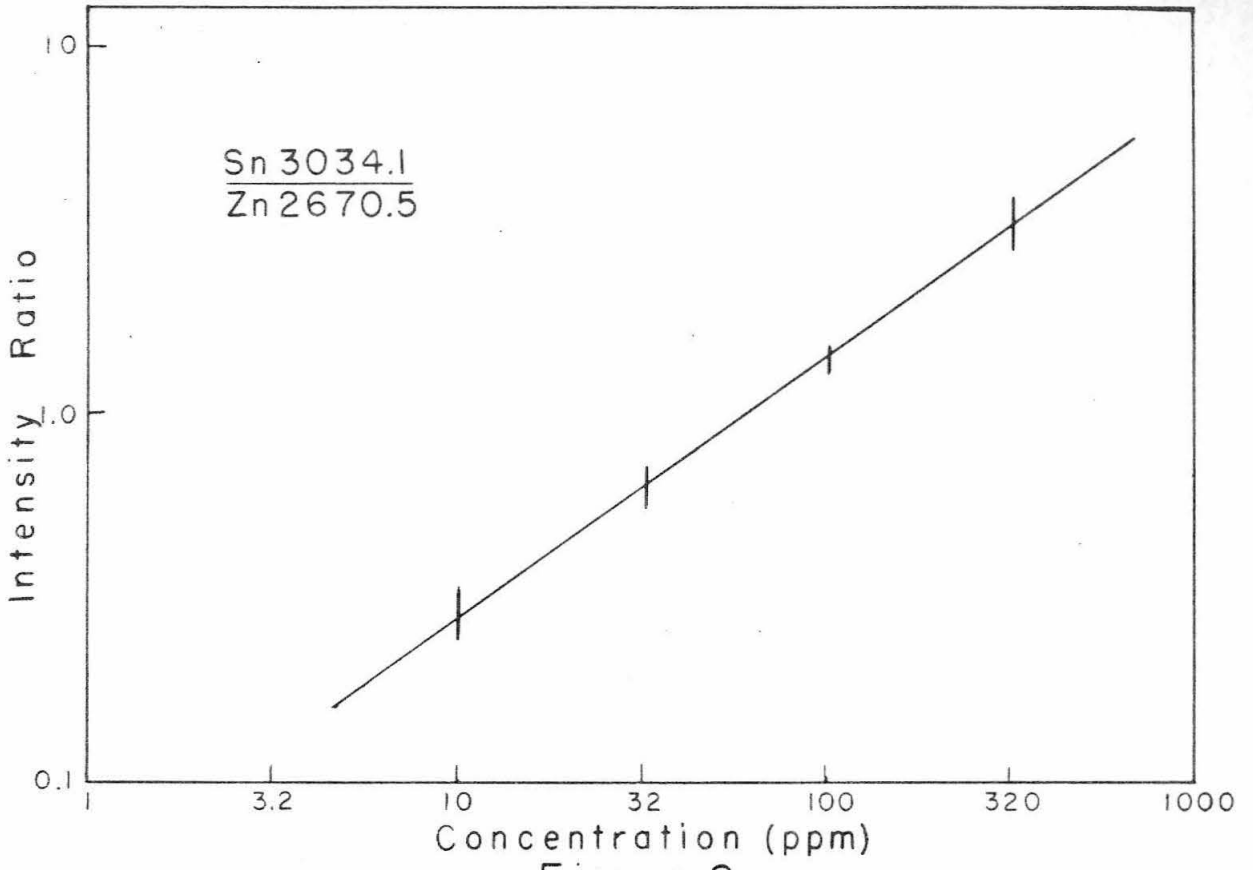
Table 2

Reproducibility of Chalcopyrite Analyses

Element	:	Mean (ppm)	:	Mean Deviation (percent)	:	Standard Deviation (percent)
Cadmium	:	50	:	15	:	19
Indium	:	76	:	23	:	29
Manganese	:	7	:	20	:	25
Nickel	:	18	:	23	:	29
Silver	:	640	:	17	:	21
Tin	:	2000	:	13	:	16

obtained with tin, and the poorest is obtained with nickel. The method of internal standardization is thought to be largely responsible for the poor reproducibility of the nickel value. The data indicate that in general the analytical method for chalcopyrite gives results that are reproducible to one significant figure with a standard deviation of about 25 percent.

The Analysis of Sphalerite

The method that has just been described for the analysis of chalcopyrite was used, with only minor modifications, for the analysis of sphalerite after considerable experimentation failed to produce an equally satisfactory method that was simpler or less time consuming. The more or less standard procedure of mixing the sample with excess carbon and arcing the mixture to completion gave fair but not wholly

satisfactory results for iron-poor sphalerite, and for the more iron-rich types the method was entirely unsatisfactory.

Inasmuch as sphalerite commonly contains large and variable amounts of iron in substitution for zinc, iron cannot be used for an internal standard, as it is in chalcopyrite. Therefore, 15 percent of CuO was added to the SiO_2-ZnO-Na_2CO_3 mixture in place of part of the ZnO and the copper is used as an internal standard for cobalt, manganese, molybdenum, and nickel. This amount of CuO is believed sufficient to "swamp out" the effects of one percent or less of copper that might be present as a contaminant from admixed chalcopyrite. The copper line at 2998.4 Å is used as an internal standard line, together with the zinc line at 2670.5 Å. The effects on internal standardization of the variable zinc content of sphalerite are minimized by the presence of 25 percent ZnO in the SiO_2-ZnO-CuO-Na_2CO_3 mixture.

The only change that was made in the exposure conditions that were established for chalcopyrite is an increase from 40 to 64 percent in the amount of light transmitted to the slit. This change apparently is responsible for the slight increase in the sensitivities of some of the elements in sphalerite, as shown in figure 1B.

The sphalerite standards were prepared by adding, as spectrographically pure oxides, the elements antimony, arsenic, bismuth, cadmium, cobalt, gallium, germanium, indium, manganese, molybdenum, nickel, silver, tin, tellurium, and thallium to a base of synthetic phosphorescent (green) zinc sulfide manufactured by Hammer Laboratories, Denver, Colorado.

Blank corrections were made for 30 ppm cadmium and 10 ppm
manganese. The procedure for dilution of this standard mix-
ture and the method of construction of the working curves are
the same as described previously for chalcopyrite.

The reproducibility of the method was determined by ana-
lyzing a sample of sphalerite (PEW-8, table 5) nine times
during a period of six months. A summary of the results for
the elements detected in the sample is presented in table 3.

Table 3

Reproducibility of Sphalerite Analyses

Elements	:	Mean (ppm)	:	Mean Deviation (percent)	:	Standard Deviation (percent)
Bismuth	:	5.7	:	13	:	16
Cadmium	:	1400	:	10	:	13
Cobalt	:	175	:	25	:	31
Indium	:	11	:	15	:	19
Manganese	:	1900	:	19	:	24
Nickel	:	5.3	:	30	:	37
Silver	:	25	:	20	:	25

Although there appears to be a greater range of reproducibili-
ties for the elements in sphalerite than in chalcopyrite, the
average standard deviation, again, is approximately 25 percent.
The working curves for cadmium, which gives the most reprodúc-
ible results, and for manganese, the reproducibility of which
is average, are shown in figures 4 and 5.

The Analysis of Pyrite and Galena

The analyses of the ten pyrite samples were made using the method and standards that are used for the analysis of chalcopyrite. However, it was necessary to use zinc as the internal standard for all elements because there is a considerable difference in the iron contents of pyrite and chalcopyrite. Similarly, the 15 galena samples were analyzed by the method and standards used in the analysis of sphalerite.

The errors involved in this practice arise chiefly from differences in composition between pyrite and chalcopyrite, on the one hand, and between galena and sphalerite, on the other. The lack of zinc in galena might be expected to result in a weakened intensity of the zinc internal standard line, but the effect apparently is too slight to be detected by the present method. The reason factors such as this are not very influential is that the "matrix" is dominated by the standard mixture of constant composition. It is doubtful, therefore, that the analyses reported for pyrite and galena are significantly in error.

Figure 4. Working curve for the determination of the amount
    of cadmium in sphalerite. The lengths of the vertical
    bars represent the ranges in the results of 14 analyses
    of the standard mixtures.

Figure 5. Working curve for the determination of the amount
    of manganese in sphalerite. The lengths of the vertical
    bars represent the ranges in the results of 14 analyses
    of the standard mixtures.
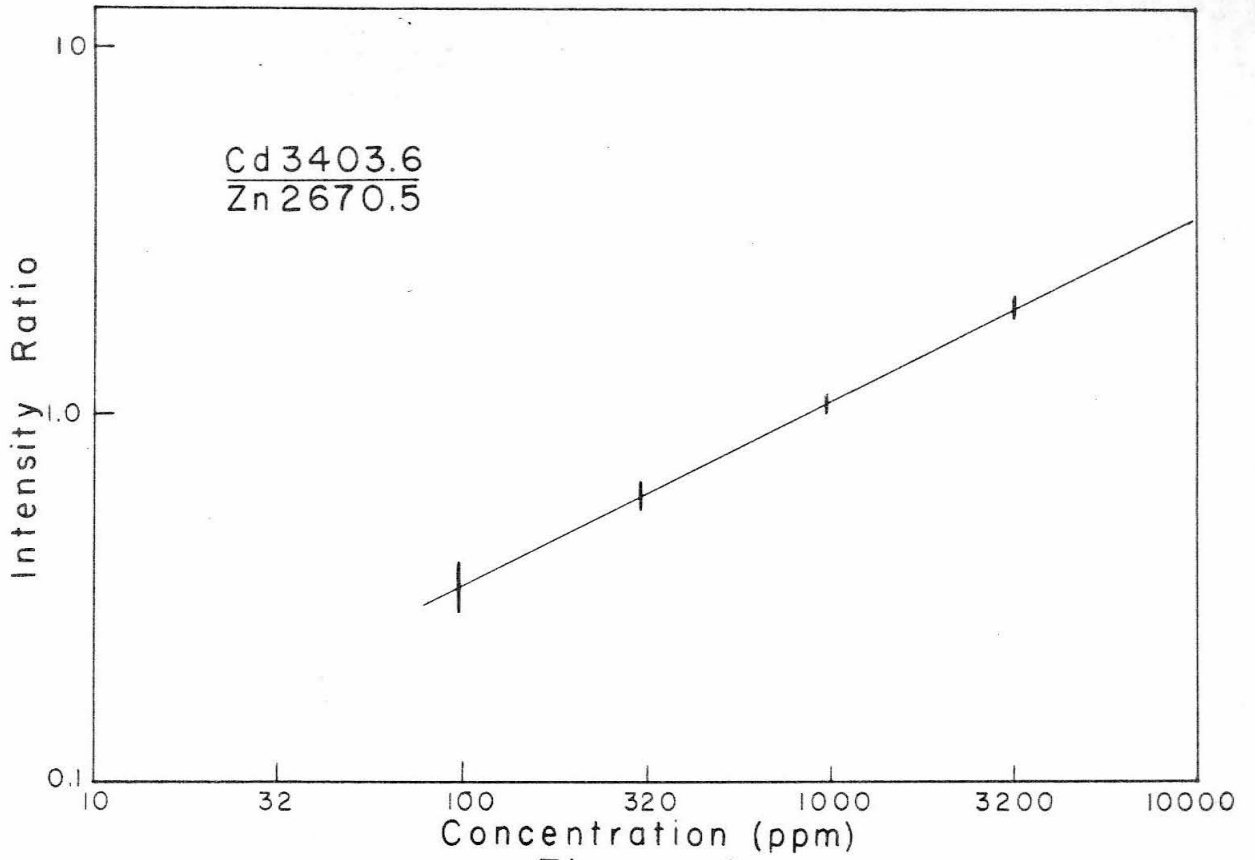
Figure 4
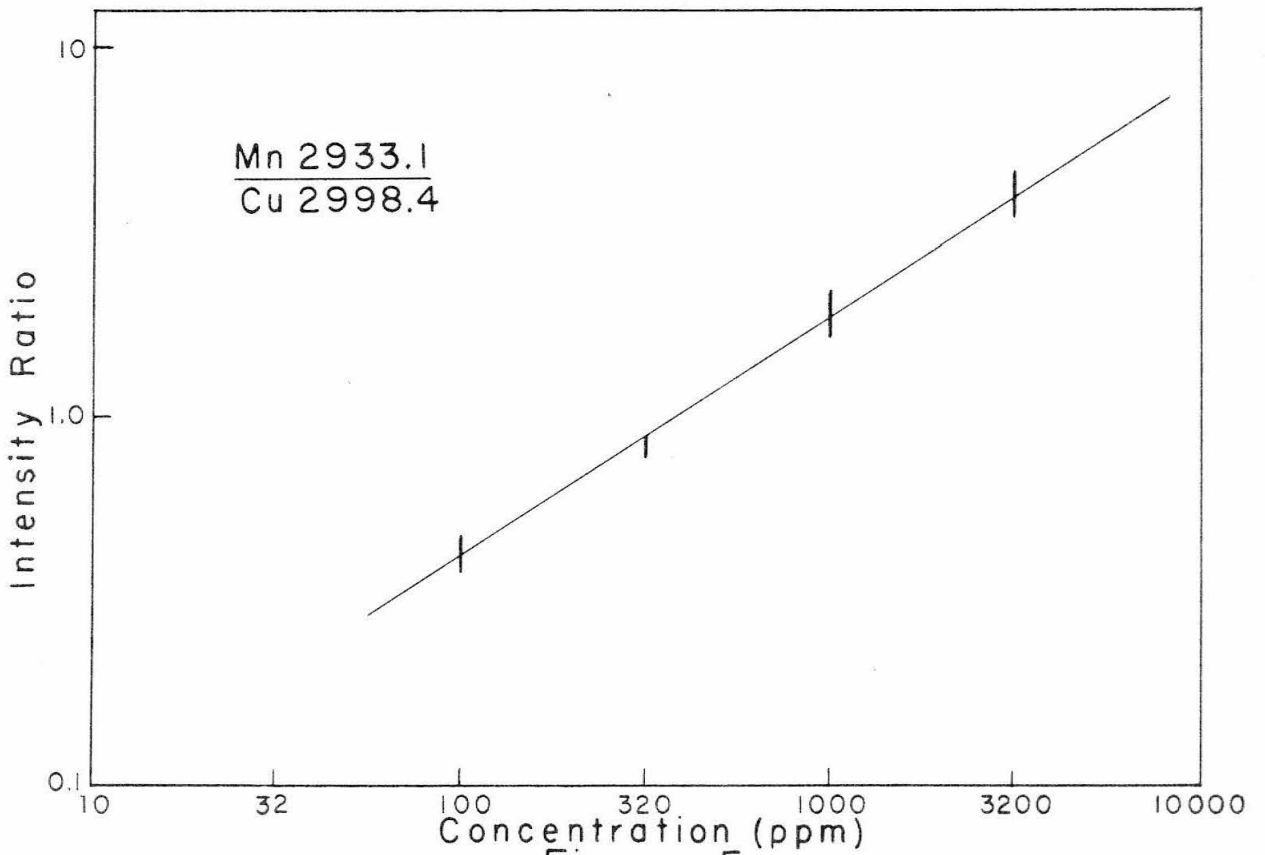
Figure 5

THE ANALYTICAL DATA

All the samples of chalcopyrite, sphalerite, pyrite, and galena that were analyzed in connection with the present study are represented in tables 4 - 7. Each entry in the tables is an average of duplicate determinations on the same sample in about 95 percent of the cases. Insufficient material was available in the other five percent to permit duplicate determinations. These data form the bases for the ensuing discussions and are the main evidence for the conclusions that are drawn.

The arrangement in each of the four tables is essentially the same. The analyses are grouped according to the mining districts from which the samples came, and the samples are located within each district as accurately as the available information permits. The data thus grouped are averaged for certain of the elements in chalcopyrite and sphalerite, and these district averages are presented in the legends of the maps of plates 1 - 12. Each district is indicated on these maps by a number which corresponds to the district number in the tables.

Near the ends of tables 4 and 5 are several groups of analyses that are given letter designations instead of district numbers. These analyses are not represented on the maps (plates 1 - 12) for one reason or another. Some have been obtained from districts that are outside the areas covered by the maps, for some others the exact localities are not known, and others represent series of analyses from single crystals or individual specimens.

A short dash (-) in the tables indicates that the element was not detected in either analysis of the sample. A "less than" symbol (<) in the silver analyses indicates that silver was detected, but in amounts less than one part per million, the lower limit of the standards. A "greater than" symbol (>) indicates that the element is present in such large amounts that the analysis line is too dense to microphotometer accurately (less than two percent transmission). A query (?) indicates one of two things: either slight contamination from the preceding sample during weighing is suspected, or a potentially interfering element is present in abnormally high concentrations. Both situations are relatively easy to detect, but neither is easy to evaluate.

Although tellurium was sought in all samples analysed, it was not detected in any sample of pyrite, and in only one each of chalcopyrite and sphalerite*, both of which are suspected of being contaminated. Therefore, tellurium is omitted from tables 4 - 6 to conserve space. For the same reason, gallium is omitted from table 7.

---

* The chalcopyrite sample, N-116, contains 800 ppm tellurium, and the sphalerite sample, ARI-58, contains 300 ppm tellurium.

Table 4

Trace Elements in Chalcopyrite
(In parts per million)

Dist. No.	Sample No.	Locality	Ag	As	Bi	Cd	Co	Ge	In	Mn	Mo	Ni	Sb	Sn
		ARIZONA												
1		Wallapai District												
	CHL-11	Keystone Mine	900	-	100	-	-	-	200	90	-	-	-	200
2		Cedar Valley Dist.												
	AN-1	Antler Mine	40	-	70	-	3	-	10	40	4	-	-	500
	CW-1	Copper World Mine	100	-	-	-	-	5	4	10	90	5	-	600
	CW-2	"	100	-	-	-	-	-	4	5	300	3	-	600
	BOR-1	Boriana Mine	600	-	-	50	-	-	80	7	-	20	-	2000
	BOR-2	"	700	-	-	30	2	-	50	70	-	20	-	1000
	BOR-3	"	1000	-	-	80	-	-	80	20	-	5	-	700
3		Eureka District												
	BAG-4	Bagdad	<1	-	-	-	-	-	4	1	-	-	-	60
	BAG-21	Bagdad Pit	3	-	-	-	1	-	1	1	-	-	-	70
	BAG-22	"	6	-	-	-	1	-	10	-	500	-	-	80
	BAG-23	Old Dick Mine	30	-	-	-	-	-	-	50	20	-	-	8
	BAG-25	Copper King Mine	20	-	-	-	-	-	20	200	-	-	-	2000
4		Verde District												
	JER-30	United Verde Mine	10	-	-	-	-	-	30	40	-	10	-	50
	JER-32	"	50	-	-	-	20	-	70	20	30	-	-	200
	JER-33	"	50	-	-	-	-	-	200	40	-	20	-	200
	JER-34	"	40	-	-	-	-	-	300	70	-	-	-	300
	JER-35	"	70	-	-	-	-	-	60	100	-	-	-	100
	JER-36	"	30	-	30	-	-	-	100	20	-	-	-	100
5		Peck District												
	ARI-98	Crown King Mine	4000	300	3	20	2	-	5	20	-	5	-	100
6		Bradshaw District												
	ARI-99	Money Metals Mine	600	300	-	100	40	-	10	1	-	4	-	30
7		Minnehaha District												
	ARI-103A	12 miles SW of Mayer	20	-	-	-	-	-	6	-	-	-	-	-

Table 4 (cont.)

Dist. No.	Sample No.	Locality	Ag	As	Bi	Cd	Co	Ge	In	Mn	Mo	Ni	Sb	Sn
8		Swansea District												
	ARI-66	Swansea	3	-	-	-	2	-	2	-	5	-	-	-
	ARI-67	"	1	-	-	-	8	-	3	-	-	-	-	-
9		Green Valley Dist.												
	MAZ-15	E. foot of N. Peak, Mazatzal Mtns.	2000	20000	2000	400	-	-	200	20	30	-	>10000	8000
10		Miami District												
	MIA-12	Inspiration Shaft	40	-	-	-	2	-	-	1	3	40	-	200
	MIA-13	Live Oak Pit	50	-	-	-	3	-	-	-	1000	30	-	90
	MIA-14	Inspiration Mine	40	-	-	-	-	-	-	-	30	-	-	200
11		Globe District												
	OD-3	Old Dominion Mine	10	-	-	-	2	-	7	3	5	5	-	200
12		Summit District												
	MIA-4	Castle Dome Mine	70	-	-	-	-	-	-	4	6	-	-	4
	MIA-6	"	100	-	-	-	60	-	-	6	6	9	-	100
13		Pioneer District												
	MAG-27	Magma Mine	8	-	8	-	2	-	8	600	3	6	-	10
	MAG-32	"	100	1000	900	-	6	6	3	8	7	20	100	70
	MAG-46	"	30	6000	500	-	3	-	3	2	-	-	100	20
	MAG-76	"	10	-	20	-	-	-	20	20	-	-	-	30
14		Copper Mountain Dist.												
	MCI-9	Ariz. Central Mine	50	-	-	40	-	-	-	-	-	-	-	3
15		Mineral Creek Dist.												
	RAY-12	Ray Pit	70	-	20	-	-	-	9	10	100	-	-	30
	RAY-14	"	40	-	-	-	2	-	30	200	-	-	-	20
	RAY-15	Ray (surface)	50	-	-	-	-	-	10	10	-	-	-	20
	RAY-16	Ray, No. 4 well	50	-	8	-	-	-	50	20	-	-	-	80
16		Banner District												
	CHR-3	Christmas Mine	10	-	-	-	20	-	10	400	60	40	-	30
17		Stanley District												
	ARI-113	Unnamed prospect	2	-	200	-	4	-	-	60	200	70	-	10
	ARI-114	"	<1	-	60	-	1	-	-	200	20	100?	-	-

Table 4 (cont.)

Dist. No.	Sample No.	Locality	Ag	As	Bi	Cd	Co	Ge	In	Mn	Mo	Ni	Sb	Sn
18		Bunker Hill Dist.												
	CHA-1	Childs-Aldwinkle Mine	3	2000	-	-	3	-	-	-	5	6	-	100
	CHA-10	"	9	-	400	-	-	-	3	3	6	-	-	20
	CHA-12	"	5	-	-	-	-	-	-	-	4	-	-	30
	CHA-27	"	<1	-	-	-	30	-	-	30	5	3	-	-
	CHA-40	"	2	-	-	-	6	-	7	1	4	-	-	200
19		Mammoth, San Manuel District												
	SM-7	San Manuel Mine	30	-	-	-	-	-	-	300	-	-	-	30
	SM-8	"	20	-	-	-	4	-	-	-	8	3	-	30
20		Silver Bell Dist.												
	AT-1	Atlas Mine	50	-	40	-	10	-	10	10	-	10	-	40
	AT-2	"	60	-	20	80	50	-	30	400	80	20	-	4
	AT-3	"	200	-	30	-	30	-	10	30	9	70	-	8
	AT-4	"	100	-	10	-	20	-	10	7	-	8	-	5
21		Ajo District												
	AJ-36	New Cornelia Mine	40	-	-	-	6	-	-	1	-	-	-	40
	AJ-37	"	40	-	-	-	50	-	-	-	-	-	-	4
	AJ-38	"	40	-	-	-	-	-	-	6	-	-	-	8
	AJ-40	"	50	-	20	-	7	-	7	2	-	-	-	5
	AJ-41	"	100	-	-	-	2	-	-	100	7	-	-	40
22		Gunsight District												
	CM-1	Copper Mtn. Mine	200	400	500	-	70	-	7	4	-	7	-	10
23		Amole District												
	ARI-108A	Mile Wide Mine	6	-	30	-	-	-	9	100	10	-	-	-
24		Cochise District												
	JO-1+2	Johnson Camp	6	-	5	-	9	-	20	500	20	30	-	20
27		Pima District												
	PIM-2	San Xavier Ext. Mine	60	-	50	-	6	-	-	6	3	4	-	-
	PIM-3	Pima Mine	400	2000	30	-	100	-	70	20	400	20	-	70
	PIM-4	"	40	-	20	-	30	-	100	300	10	5	-	40
	PIM-6	"	60	-	6	-	30	-	50	200	-	6	-	50
28		Helvetia District												
	ARI-107	McClary's Mine	400	-	9	-	200	-	20	-	100	10	-	200

Table 4 (cont.)

Dist. No.	Sample No.	Locality	Ag	As	Bi	Cd	Co	Ge	In	Mn	Mo	Ni	Sb	Sn
33	ARI-110	Exile and King Mine	200	-	-	-	10	-	30	500	20	3	-	40
		Warren District												
	BI-52	Junction Shaft	40	-	20	-	-	-	400	80	-	20	-	200
	BI-53	"	70	-	20	-	-	-	400	300	10	-	-	200
	BI-54	"	30	-	-	-	-	-	400	30	-	-	-	100
	BI-56	Campbell Shaft	60	-	-	-	-	-	-1000	90	10	-	-	200
35		Patagonia, Duquesne District												
	ARI-85	Santa Nino Mine	60	-	9	-	20	-	-	20	600	-	-	40
	SN-1	"	40	-	-	-	40	-	70	20	-	20	-	40
	SN-4	"	100	-	-	-	-	-	10	2	-	-	-	50
	ARI-108B	Morning Glory Mine	30	-	-	-	-	-	80	700	-	-	-	30
		CALIFORNIA												
36		Afterthought Dist.												
37	AFT-3	Afterthought Mine	1	400	-	10	4	2	-	2	-	20	-	-
		Lights Canyon Dist.												
38	SUP-13	Superior Mine	1000	-	-	-	2	-	9	600	-	-	-	20
		Nevada City Dist.												
40	IMM-56	Idaho Maryland Mine	<1	-	-	200	1	-	3	-	-	6	-	-
		Fairplay District												
41	C-229	Consumnes Mine	40	-	100	-	1	-	-	2	-	10	-	20
		Pine Creek Dist.												
44	C-220	Pine Creek	<1	500	3	-	-	-	3	10	-	-	-	70
		Argus Range												
45	MS-17	Mtn. Springs Canyon	100	-	4	40	2	-	1	7	-	-	-	-
		Woody District												
47	C-257	Greenback Mine	20	-	-	-	20	-	10	-	-	70	-	100
		Cima District												
48	C-151	Evening Star Mine	30	-	-	70	-	-	400	6	-	10	-	1000
		Ord District												
	C-256	Painsville Mine	7	-	4	-	3	-	10	30	-	10	-	-
		Tujunga District												
50	C-263	Pacoima Canyon	2000	-	-	60	8	-	9	30	-	10	-	30

Table 4 (cont.)

Dist. No.	Sample No.	Locality	Ag	As	Bi	Cd	Co	Ge	In	Mn	Mo	Ni	Sb	Sn
51		Crestmore District												
	C-261	Crestmore Mine	800	-	300	10	1	-	20	-	-	200	-	40
52		Julian District												
	C-260	Friday Mine	3	-	-	-	100	-	-	20	→1000	→1000	-	10
53		Cargo Muchacho Dist.												
	CMU-29	Cargo Muchacho	1000	-	1	20	-	-	20	300	-	-	100	-
		COLORADO												
54		Ward District												
	COL-102	Albion Mine	3000	5000	-	20	1	-	2	600	90	9	500	50
55		Kremmling District												
	COL-80	Kremmling	30	100	40	-	-	-	5	-	-	-	-	-
	COL-81	"	70	300	-	-	-	-	-	3	-	-	600	-
56		Central City Dist.												
	COL-100	Bobtail Incline	30	700	100	-	-	-	200	9	10	-	-	100
57		Idaho Springs Dist.												
	COL-94	Plutus Mine	80	100	-	-	-	-	200	-	-	7	-	7
	COL-95	Bride Mine	2000	8000	-	90	2	-	3	20	20	-	9000	20
58		Griffith District												
	COL-91	Georgetown	2000	1000	9	-	<1	-	200	-	10	20	1000	-
60		Red Cliff District												
	COL-106	Gilman	70	-	-	-	-	-	40	2	-	4	-	2000
	COL-107	Rocky Pt. Horizon	200	-	-	-	1	40	200	2	-	-	-	900
62		Fremont Pass Dist.												
	CL-14	Climax Molybdenum Mine	60	-	9	-	50	-	200	700	10	5	-	800
65		Roaring Fork Dist.												
	COL-101	Aspen	200	-	-	-	10	-	10	2000	70	9	-	-
67		Cebolla District												
	COL-83	Red Top Mine	70	2000	-	-	6	-	60	1	-	-	-	2000
69		Uncompahgre Dist.												
	OU-1	Des Ouray Ore Chute	1000	9000	80	30	-	-	7	200	-	-	800	40
	OU-2	Benack Tunnel	500	-	5	300	-	-	40	600	8	-	300	200
70		Sneffels District												
	COL-113	Camp Bird Mine	7	-	20	7	7	-	6	50	-	-	-	-

Table 4 (cont.)

Dist. No.	Sample No.	Locality	Ag	As	Bi	Cd	Co	Ge	In	Mn	Mo	Ni	Sb	Sn
72		Iron Springs Dist.												
	COL-108	Alta Mine	300	-	1000	80	1	20	?	8000	-	5	-	-
74		Animas District												
	COL-110	Green Mtn. Mine	200	-	2	600	10	-	2	100	-	6	-	-
75		Pioneer District												
	COL-104	Blackhawk Mine	30	-	200	20	1	-	300	50	-	4	-	2000
		NEW MEXICO												
76		Willow Creek Dist.												
	PEC-2	Pecos Mine	50	-	-	30	-	-	2	20	-	20	-	4
	PEC-3	"	20	-	-	-	-	-	2	-	-	4	-	8
78		San Pedro District												
	NM-60	San Pedro District	400	-	10	-	2	-	7	200	20	40	-	-
	NM-69	San Pedro Mine	200	-	5	20	70	-	7	8	-	500	-	-
79		Magdalena District												
	MG-1	Magdalena District	600	-	2000	40	-	-	3	20	-	-	-	-
80		Nogal District												
	NM-74	Tommy LeMay Claim	9	-	-	200	1	-	-	3	-	50	-	-
	NM-75	"	60	-	-	-	<1	-	-	200	-	5	-	-
82		Hermosa District												
	HE-5	Nana Mine	2000	-	-	30	-	-	-	40	6	-	600	4
	HE-6	"	20000	-	-	50	4	-	-	200	400	10	500	-
83		Fierro-Hanover Dist.												
	BH-14	Black Hawk Cons. Mines	20	-	20	-	10	-	-	200	-	4	-	-
84														
	OS-1	Oswaldo No. 1 Mine	100	-	-	-	6	-	-	400	-	-	-	-
		Steeple Rock Dist.												
	NM-25	Carlisle Mine	9	-	-	-	-	-	-	-	-	-	-	-
	NM-70	"	200	-	-	500	2	-	-	30	-	-	-	4
	NM-71	Gold-Silver Mine	70	-	-	10	-	-	-	20	-	-	-	3
85		Santa Rita District												
	G-3	Groundhog Mine	40	-	-	-	3	-	10	7	3	9	-	-
	G-4	"	20	-	-	-	4	-	-	10	-	3	-	4
	G-6	"	20	-	-	-	-	-	-	6	4	2	-	3

Table 4 (cont.)

Dist. No.	Sample No.	Locality	Ag	As	Bi	Cd	Co	Ge	In	Mn	Mo	Ni	Sb	Sn
	G-11	Groundhog Mine	100	-	60	-	20	-	2	300	-	-	-	8
	SR-15	Ivanhoe Lease	1000	-	-	100	20	-	-	100	-	-	-	-
	SR-16	Chino Mine	40	-	-	-	20	-	-	400	4	6	-	6
	SR-17	"	1	-	-	-	1	-	2	10	4	6	-	30
88		Orogrande District												
	NM-79	Jim Mine	20	-	4	-	-	-	10	40	-	3	-	-
	NM-80	Lucky Mine	40	-	-	-	5	-	10	30	20	30	-	5
89		Organ District												
	NM-57	Stevenson Bennett Mine	90	-	-	-	-	-	7	2	-	10	-	-
90		Lordsburg District												
	CAM-11	85 Mine	300	-	600	-	-	-	20	-	8	-	-	-
	CAM-21	"	200	-	20	-	-	-	10	200	-	6	-	8
	CAM-22	"	60	-	-	-	-	-	10	-	-	-	-	-
	CAM-24	"	5	-	40	-	-	-	8	10	2	60	-	6
	CAM-25	"	7	-	10	-	-	-	30	6	-	-	-	-
	CAM-27	"	80	-	-	-	-	-	10	2	-	6	-	-
	NM-30	"	70	-	7	-	3	-	10	100	-	4	-	-
	NM-28	Banner Mine	100	-	-	-	-	-	2	5	4	20	-	-
	NM-32	"	50	-	-	-	-	-	3	-	4	3	-	-
	NM-62	Lordsburg District	20	-	-	-	-	-	8	-	-	-	-	-
91		Eureka District												
	NM-76	Little Hatchet Mtns.	90	-	90	-	2	-	2	200	-	30	-	-
	NM-77	"	90	-	600	20	1	-	50	4	10	8	-	-
		NEVADA												
92		Mountain City Dist.												
	N-168	Mtn. City Copper	6	-	5	-	20	-	-	20	30	8	-	30
93		Jackson Creek Dist.												
	N-159	Humboldt King Claims	2	-	8	-	80	2	-	1	-	90	-	-
94		Tuscarora District												
	N-86	Independence Mine	400	-	-	70	1	-	3	5	-	-	300	40
98		Safford District												
	N-138	Safford District	700	1000	-	-	50	-	1	100	20	100	-	6

Table 4 (cont.)

Dist. No.	Sample No.	Locality	Ag	As	Bi	Cd	Co	Ge	In	Mn	Mo	Ni	Sb	Sn
99	N-140	Safford District	3000	–	–	100	3	–	5	2000	–	3	–	–
	N-142	Railroad District	100	–	10	300	10	–	10	3000	–	9	–	400
102		Bullion District												
	N-148	Elder Creek	1000	200	3	200	80	–	8	20	–	200	–	200
103		Dolly Varden Dist.												
	N-162	Victoria Mine	100	–	–	–	10	–	4	3	–	80	–	–
	N-163	"	200	–	–	–	4	–	5	2	–	50	–	8
110		Reese River Dist.												
	N-146	Austin	100	600	–	–	2	7	2	200	–	–	–	200
112	COM-1	Comstock District	4000	–	–	–	–	–	–	30	–	–	–	–
	VI-1	Comstock District Cons. Calif. and Virginia Mine	2000	–	–	10	–	–	–	40	70	–	–	–
113		Ely District												
	ELY-13	Emma-Nevada Mine	20	–	–	–	300	–	–	7	–	8	–	100
	ELY-18	Ruth Mine	70	–	–	–	40	–	–	200	–	7	–	20
	ELY-19	"	70	–	–	–	70	–	–	100	–	40	–	30
	ELY-23	Morris Mine	50	–	–	–	2	–	–	10	10	7	–	40
	ELY-24	"	50	–	–	–	2	–	–	5	3	7	–	30
115	N-128	Buckskin District	500	–	3	20	7	–	5	70	–	6	–	8
116		Yerington District												
	YER-2	Yerington Copper Co.	<1	–	2	–	–	–	2	2	–	–	–	–
	YER-4	Ludwig Mine	30	–	–	–	5	3	–	1	–	400	–	–
	YER-5	Mason Valley Mines	2	–	–	–	100	–	–	7	–	100	–	–
117		Gardnerville Dist.												
	N-154	Ruby Hill Mine	100	–	–	80	–	–	2	30	–	10	–	40
	N-157	"	60	–	–	20	3	–	–	10	6	–	–	10
	N-158	"	50	–	–	10	6	–	–	20	5	–	–	40
120		Santa Fe District												
	N-87	8 mi. N. of Luning	200	200	–	10	200	–	10	10	–	–	–	10
	N-97	Emma Mine	100	–	7	10	100	–	4	90	10	40	–	30

Table 4 (cont.)

Dist. No.	Sample No.	Locality	Ag	As	Bi	Cd	Co	Ge	In	Mn	Mo	Ni	Sb	Sn
123	N-100	Champion Mine	30	-	-	30	-	-	1	300	40	-	-	6
		Silver Star Dist.												
	N-95	Gold Range District	90	-	30	60	1	-	10	1	-	-	-	5
125		Tonopah District												
	TON-78	Montana Tonopah Mine	20	-	-	-	-	-	-	-	-	-	-	8
	TON-79	"	2000	-	20	-	-	2	-	6	-	-	-	80
	TON-85	MacNamara Mine	2000	-	-	-	-	5	-	6	-	-	300	-
126		Jack Rabbit Dist.												
	N-114	Bristol District	300	-	-	-	-	-	-	20	2	-	-	6
129		Tem Piute Dist.												
	N-164	Lincoln Mine	100	-	-	20	-	-	3	400	-	10	-	100
130		Bullfrog District												
	N-160	Beatty	40	-	-	-	-	-	<1	<1	-	-	-	-
	N-161	"	60	-	-	-	40	-	20	2	-	200	-	40
131		Copper King Dist.												
	KW-1	Key West Mine	10	-	-	-	-	-	5	7	-	300	-	7
	KW-3	"	20	100	4	-	-	-	-	7	-	70	-	6
133		Eldorado District												
	N-116	Callahan & Averal Property	3000	400	600	-	40	-	-	200	2	200	-	-
		UTAH												
135		Uinta District												
	PC-12	New Park Mine	500	-	-	-	-	-	1	4	-	-	-	-
	PC-16	"	500	-	500	-	-	-	70	40	-	-	-	-
	PC-17	"	100	-	20	-	-	-	50	3	-	-	-	-
136		Bingham District												
	BIN-7	Utah Apex Mine	30	-	8	7	-	-	50	70	-	-	-	200
	BIN-8	Highland Boy Mine	200	-	2000	20	-	-	100	300	-	-	-	900
	BIN-12	Utah Apex Mine	200	-	200	-	-	-	40	20	-	-	-	400
	BIN-14	Bingham Mine (Pit)	100	-	20	-	10	-	6	8	-	20	-	40
137		American Fork Dist.												
	UT-31	Silver Wave Min. Co.	20	-	-	-	7	-	1	80	60	-	-	10
	UT-41	American Fork Dist.	20	-	-	-	-	-	30	-	-	30	-	80

Table 4 (cont.)

Dist. No.	Sample No.	Locality	Ag	As	Bi	Cd	Co	Ge	In	Mn	Mo	Ni	Sb	Sn
138		Ophir District												
	UT-42	Hidden Treasure Mine	800	-	-	100	5	3	-	200	-	20	-	100
139		Gold Hill District												
	UT-45A	Gold Hill	200	-	-	-	6	-	20	2	80	-	-	40
141		San Rafael District												
	UT-38	Lucky Strike Mine	1	4000	-	100	3000	200	-	-	300	1000	-	-
142		Frisco District												
	UT-43	O.K. Mine	10	-	20	-	1	-	2	-	-	-	-	7
143		White Canyon Dist.												
	UT-44	Happy Jack Mine	200	700	-	-	300	20	-	400	90	100	-	-
		MONTANA												
172		Butte District												
	BU-36	Mountain Con Mine	30	4000	40	-	-	40	1	3	-	-	800	50
	BU-45	"	200	-	100	-	-	4	-	4	-	-	-	-
		MEXICO												
		CHIHUAHUA												
145		Temosachic, Guerrero District												
	CA-7	Calera Mine	400	-	-	30	4	-	2	500	10	-	-	-
146		Magistral, Iturbide District												
	MEX-47	Magistral Mine	20	-	-	-	90	-	9	<1	-	60	-	-
147		San Diego, Iturbide District												
	SE-94	San Antonio Mine	200	-	-	40	1	-	1	400	-	-	-	5000
	SE-95	"	50	-	-	30	1	-	1	300	-	5	-	5000
149		Guerrero, Guerrero District												
	MEX-48	Guadalupe Mine	30	-	30	-	20	-	7	4	-	10	-	-
152		Los Reyes, Jimenez District												
	MEX-45	Los Reyes Mine	60	-	-	-	100	-	10	1	-	50	-	-

Table 4 (cont.)

Dist. No.	Sample No.	Locality	Ag	As	Bi	Cd	Co	Ge	In	Mn	Mo	Ni	Sb	Sn
153		El Parral, Hidalgo District												
	PAR-3	Parral Unit	200	-	-	30	30	-	-	2	-	3	200	-
154		Alisos, Andres del Rio District												
	MEX-35	El Carmen Mine	<1	-	-	-	-	-	2	1	-	-	-	-
	MEX-36	"	<1	-	-	-	-	-	3	1	-	-	-	-
		DURANGO												
159		Reina de Cobre, Cuencame District												
	VEL-1	Reina de Cobre Mine	60	200	-	30	400	-	-	50	-	30	-	8
	VEL-2	"	200	100	-	20	90	-	<1	60	-	30	-	9
160		San Lucas, San Juan del Rio District												
	MEX-37	Santa Cruz Mine	60	-	-	-	-	-	200	1	-	4	500	-
	MEX-38	"	100	-	-	-	-	-	100	1	-	6	300	-
	MEX-39	"	600	-	1000	50	-	-	200	300	-	7	2000	-
162		Tayoltita, San Dimas District												
	TAY-1	Tayoltita	50	-	-	20	4	-	50	10	-	4	-	300
		SAN LUIS POTOSI												
163		Matehuala, Catorce District												
	MAT-1	Dolores Unit	60	-	50	200	30	-	60	20	-	10	-	1000
	MAT-2	"	60	-	5	300	10	-	20	100	-	-	-	2000
		SONORA												
165		Cananea, Arispe Dist.												
	CN-20	Puertocitos Open Cut	40	-	-	-	-	-	-	10	3	-	-	-
	CN-33	Colorado Mine	60	-	4	-	4	-	-	2	20	20	-	20
	CN-35	"	40	-	50	-	3	-	-	20	-	20	-	10
	CN-37	"	20	-	20	-	20	-	-	2	-	-	-	50
	CN-38	Cananea Duluth Mine	90	-	90	-	2	-	-	60	-	-	-	4

Table 4 (cont.)

Dist. No.	Sample No.	Locality	Ag	As	Bi	Cd	Co	Ge	In	Mn	Mo	Ni	Sb	Sn
166		Nacozari, Arispe District												
	NAC-6	Pilares Mine	50	-	-	-	-	-	70	5	40	-	-	90
	NAC-7	"	40	-	-	-	-	-	80	-	20	-	-	40
	NAC-9	"	70	-	-	-	-	-	80	-	30	-	-	50
	NAC-18	"	9	-	-	-	-	-	40	10	20	-	-	200
167		Santa Domingo, Arispe District												
	NAC-21	Santa Domingo Mine	7	-	-	-	1	-	20	600	-	4	-	80
168		Santa Barbara, Hermosillo District												
	MEX-29	Alaska Mine	<1	-	2000	-	-	3	10	800	-	-	-	20
	MEX-30	"	2	-	4	-	-	2	10	200	-	-	-	10
	MEX-31	"	6	-	2	-	-	-	6	50	-	-	-	6
169		San Javier, Hermosillo District												
	MEX-26	Cerro Verde Prop.	<1	-	4	-	-	-	4	900	-	-	-	30
		ZACATECAS												
170		Sain Alto, Sombrerete District												
	MEX-52	San Martin Mine	2000	200	10	100	9	-	1	100	-	30	300	2000
171		Sombrerete, Sombrerete District												
	MEX-49	Tocayos Mine	2000	-	-	40	1	-	-	<1	-	-	7000	60
		Ducktown, Tennessee												
A	DT-28	Ducktown	90	-	-	-	-	-	4	100	4	7	-	70
	DT-29	"	100	-	-	-	3	-	70	600	-	10	-	500
	DT-34	"	100	-	-	30	-	-	70	200	-	5	-	500
	DT-39	"	60	-	-	-	-	-	10	100	-	30	-	200
	DT-43	"	50	-	-	-	-	-	15	300	-	30	-	300
B	PAC-17	Pachuca, Hidalgo Real del Monte	2000	-	-	-	-	-	-	-	-	-	-	10

Table 4 (Cont.)

Dist. No.	Sample No.	Locality	Ag	As	Bi	Cd	Co	Ge	In	Mn	Mo	Ni	Sb	Sn
C		Glacier Peak, Wash.												
	WA-16	Glacier Peak	200	600	-	90	80	-	5	9	-	20	-	90
	WA-17	" "	400	-	-	90	10	-	3	9	-	30	-	90
D		Exact locality unknown												
	C-54	Calif. Mines (?), San Bernardino Co., California	50	-	3	50	100	-	-	20	20	600	-	9
	C-253	Amer. Golden Eagle Mine, California	<1	-	4	-	5	-	1	1	-	-	-	-
	CAM-12	Calumet and Arizona Mines, Bisbee, Ariz. (?)	50	-	-	-	-	-	100	200	-	-	-	-
	CHL-9	Chloride, Ariz. (?)	20	3000	-	-	-	-	1	-	-	-	-	-
	IMM-47	Idaho Maryland Mine, Grass Valley, Calif.(?)	200	-	-	30	-	-	-	-	-	200	-	-
	N-82	Mtn. City, Nev. (?) (From ore bins, Elko)	30	-	-	-	10	-	-	4	6	-	-	-
	N-99	Lost Indian Mine, Toiyabe Range, Nev.	500	-	-	-	1	-	-	60	-	-	200	8
	N-122	Stone Mine, Pershing Co., Nevada	8	-	-	-	-	-	-	200	30	80	-	-
E		Alisos, Chihuahua (Single Crystal)												
	MEX-35A	El Carmen Mine	3	-	-	-	-	-	1	-	-	-	-	60
	MEX-35B	" "	<1	-	-	-	-	-	1	-	-	-	-	-
	MEX-35C	" "	<1	-	-	-	-	-	1	-	-	-	-	9
	MEX-35D	" "	<1	-	-	-	-	-	2	-	-	-	-	-
	MEX-35E	" "	<1	-	-	-	-	-	2	-	-	-	-	-
	MEX-35F	" "	<1	-	-	-	-	-	2	-	-	-	-	6
	MEX-35G	" "	<1	-	-	-	-	-	1	-	-	-	-	30
F		Ellenville, N. Y., (Single Crystal)												
	NY-4A	Ellenville	800	-	-	-	-	-	10	-	-	-	200	-

Table 4 (cont.)

Dist. No.	Sample No.	Locality	Ag	As	Bi	Cd	Co	Ge	In	Mn	Mo	Ni	Sb	Sn
	NY-4B	Ellenville	600	-	-	-	-	-	10	-	-	-	-	-
	NY-4C	"	500	-	-	-	-	-	10	-	-	-	-	-
	NY-4D	"	500	-	-	4	-	-	9	-	-	-	-	-
	NY-4E	"	500	-	-	-	-	-	10	-	-	-	-	-
	NY-4F	"	500	-	-	-	-	-	10	-	-	-	-	-
	NY-4G	"	300	-	-	-	-	-	9	-	-	-	-	-
G		Miscellaneous												
	CN-35bn	Colorado Mine, Cananea, Sonora (Bornite)	700	-	1000	-	8	-	-	50	-	-	-	20
	JER-36HSP	United Verde Mine, Jerome, Ariz., (Hand Spec.)	30	-	30	-	4	-	100	30	-	-	-	300
	SR-16HSP	Chino Mine, Santa Rita, N. Mex.(Hand Spec.)	5	-	-	-	4	-	-	80	-	-	-	-

Table 5

Trace Elements in Sphalerite
(In parts per million)

Dist. No.	Sample No.	Locality	Ag	As	Bi	Cd	Co	Ga	Ge	In	Mn	Mo	Ni	Sb	Sn	Tl
		ARIZONA														
1		Wallapai District														
	CHL-10	Towne Mine	200	-	10	5000	10	6	-	200	900	-	-	-	-	-
	CHL-11	Keystone Mine	200	-	3	2000	4	10	-	600	2000	-	-	-	-	-
2		Cedar Valley Dist.														
	CW-1	Copper World Mine	8	-	2	2000	5	20	2	10	400	-	-	-	10	-
3		Eureka District														
	BAG-24	Copper Queen Mine	1	-	-	2000	40	20	20	-	400	10	-	-	30	-
	BAG-28	"	<1	100	-	2000	10	10	7	3	200	6	-	-	100	-
	BAG-29	Copper King Mine	2	200	-	3000	30	20	3	5	500	-	-	-	200	-
4		Verde District														
	JER-37	United Verde Mine	40	800	-	5000	40	200	90	300	200	-	10	-	1000	-
	JER-361	"	4	-	-	4000	10	90	-	200	700	50	-	-	800	-
5		Peck District														
	ARI-98	Crown King Mine	100	-	-	3000	200	20	-	40	1000	-	-	-	10	-
6		Bradshaw District														
	ARI-99	Money Metals Mine	20	-	6	5000	400	9	-	200	800	-	-	-	-	-
12		Summit District														
	MIA-4	Castle Dome Mine	20	-	-	3000	80	-	-	50	400	20	8	-	8	-
	MIA-6	"	20	-	-	4000	-	-	-	20	800	-	-	-	-	-
13		Pioneer District														
	MAG-27	Magma Mine	300	-	9	3000	10	-	-	100	2000	-	10	-	10	-
	MAG-75	"	300	-	100	2000	5	200	8	300	2000	-	-	-	9	-
14		Copper Mtn. Dist.														
	MCl-9	Ariz. Central Mine	90	-	2	20000	30	9	-	-	200	-	-	-	-	-
19		Mammoth, Tiger, San Manuel District														
	MAM-6	Mammoth Mine	200	-	4	4000	-	50	-	-	50	-	-	200	500	-
	MAM-9	"	40	-	1	8000	60	10	-	20	600	-	-	-	-	-
	MAM-11	"	40	-	2	9000	20	6	-	-	300	-	-	-	-	-

Table 5 (cont.)

Dist. No.	Sample No.	Locality	Ag	As	Bi	Cd	Co	Ga	Ge	In	Mn	Mo	Ni	Sb	Sn	Tl
20		Silver Bell District														
	ARI-104	Stump Mine	2	-	3	6000	200	-	-	-	100	-	-	-	-	-
	AT-1	Atlas Mine	10	-	70	4000	800	2	-	80	2000	-	70	-	-	-
	AT-5	"	2	-	3	4000	400	8	-	200	2000	-	80	-	-	-
	AT-6	"	2	-	100	4000	400	-	-	70	2000	-	40	-	-	-
	AT-7	"	4	-	3	3000	300	-	-	40	5000	-	50	-	-	-
25		Dragoon District														
	AB-1	Abril Mine	100	-	4000	3000	200	-	-	-	3000	-	20	-	-	-
	AB-2	"	30	-	500	4000	300	-	-	-	1000	-	30	-	-	-
	ARI-100	Senecia Mine	2	-	-	4000	10	-	-	50	4000	-	-	-	-	-
	SJ-1	San Juan Mine	20	-	30	5000	200	10	-	20	2000	2	3	-	-	-
	SJ-2	"	200	-	2000	4000	200	-	-	10	1000	20	-	-	-	-
	SJ-3	"	3	-	10	4000	100	-	-	-	2000	-	3	-	-	-
26		California District														
	ARI-112	Hilltop Mine	3	-	-	4000	10	30	-	-	1000	200	3	-	8	-
27		Pima District														
	PIM-2	San Xavier Ext. Mine	30	-	-	5000	300	-	-	40	3000	-	10	-	-	-
	PIM-7	"	2	-	-	3000	60	-	-	-	3000	-	-	-	-	-
	PIM-8	"	20	-	80	3000	100	-	-	10	2000	-	3	-	4	-
29		Tombstone District														
	TB-12	Ingersoll Mine	200	-	1	5000	-	200	3	2	4000	-	-	90	40	-
	TB-14	Silver Thread Mine	300	2000	-	5000	100	20	-	-	2000	7	20	400	-	-
	TB-15	Toughnut Mine	1	-	10	6000	60	-	-	-	1000	-	-	-	-	-
30		Tyndall District														
	TY-1	Tyndall District	20	-	5	3000	400	20	-	-	1000	-	-	-	20	-
	TY-2	"	200	-	400	3000	300	2	-	-	2000	-	-	-	6	-
31		Harshaw District														
	ARI-106	Trench Mine	30	-	-	4000	-	30	20	-	30	-	-	-	-	-
32		Oro Blanco District														
	MON-2	Montana Mine	300	-	-	8000	50	-	-	3	2000	-	-	100	-	-
	MON-3	"	60	-	-	9000	30	-	-	-	500	-	-	60	-	-
33		Warren District														
	BI-58	Sacramento Mine	30	-	100	4000	-	9	-	100	2000	-	-	-	20	-
	BI-59	Junction Mine	3	-	2	3000	-	2	-	10	3000	-	-	-	-	-

Table 5 (cont.)

Dist. No.	Sample No.	Locality	Ag	As	Bi	Cd	Co	Ga	Ge	In	Mn	Mo	Ni	Sb	Sn	Tl
	BI-60	Bisbee	5	-	-	5000	20	-	-	200	30	-	-	-	-	-
34		Hereford District														
	ARI-115	Hereford	7	-	-	10000	30	-	-	-	80	-	20	200	-	-
35		Patagonia, Duquesne District														
	ARI-105	Duquesne Mine	<1	-	-	3000	100	-	-	30	6000	-	-	-	-	-
		CALIFORNIA														
39		Ophir District														
	C-153	Hathaway Mine	900	-	-	9000	7	-	-	9	40	-	7	-	-	-
42		Cerro Gordo Dist.														
	C-171	Estelle Mine	90	-	-	6000	-	200	40	20	500	-	5	-	30	-
43		Darwin District														
	DA-13	Thompson Tunnel	20	-	-	7000	10	70	-	20	6000	-	10	-	30	-
	DA-20	Defiance Mine	50	-	4	6000	5	200	-	40	3000	-	10	-	200	-
46		Saratoga District														
	C-258	Shoshone Mine	200	-	-	4000	3	20	-	40	100	-	-	90	100	-
	C-259	"	70	-	-	4000	-	6	-	200	90	-	-	50	90	-
49		Oro Grande District														
	AD-14	Adelanto District	<1	-	-	5000	20	30	-	20	5000	-	-	-	-	-
51		Crestmore District														
	C-175	Crestmore Mine	3	3000	-	10000	-	-	-	9	1000	2	-	-	-	-
	C-261	"	50	-	20	10000	50	10	-	70	200	-	10	-	60	-
		COLORADO														
54		Ward District														
	COL-102	Albion Mine	300	700	-	2000	-	4	-	20	3000	20	-	-	5	-
55		Kremmling District														
	COL-80	Kremmling	900	-	1000	3000	-	30	-	90	50	-	-	-	-	-
	COL-81	"	10	-	4	3000	-	20	-	100	60	-	-	-	-	-
57		Idaho Sprgs. Dist.														
	COL-95	Bride Mine	400	1000	-	6000	-	60	50	20	2000	-	-	2000	6	-
	COL-96	"	100	600	-	6000	7	30	8	100	3000	-	-	-	6	-
58		Griffith District														
	COL-92	Silver Plume Mine	60	-	-	5000	70	5	-	-	200	3	-	-	-	-
	COL-93	Molini Tunnel	<1	-	-	4000	90	-	-	10	400	-	20	-	-	-

Table 5 (cont.)

Dist. No.	Sample No.	Locality	Ag	As	Bi	Cd	Co	Ga	Ge	In	Mn	Mo	Ni	Sb	Sn	Tl
	COL-117	Jo Reynolds Vein	200	-	-	4000	-	-	-	-	100	-	-	-	20	-
59		Montezuma District														
	COL-111	Fisherman Vein	80	-	-	4000	10	60	20	-	200	-	-	-	20	-
60		Red Cliff District														
	COL-105	Gilman	40	-	-	4000	-	80	-	50	500	-	-	-	1000	-
61		Tenmile District														
	COL-82	Sheep Mountain	400	-	-	5000	-	30	-	80	700	-	-	-	30	-
63		Leadville District														
	COL-85	Little Ellen Hill	100	-	10	5000	20	-	-	200	2000	5	8	-	10	-
	COL-86	"	30	-	-	4000	-	-	-	40	1000	3	-	-	8	-
64		Buckskin District														
	COL-115	Russia Mine	2000	-	-	6000	30	-	-	-	300	3	-	2000	-	-
	COL-116	"	7000	-	-	7000	30	-	-	-	40	8	-	300?	-	-
66		Elk Mtn. District														
	COL-84	Crested Butte Dist.	200	-	-	7000	200	8	-	300	2000	-	-	-	10	-
68		Kerber Creek Dist.														
	COL-88	Blue Moon Lode	200	-	-	7000	-	400	50	300	2000	-	-	-	-	20
	COL-90	Pawley Mine	100	-	-	6000	-	300	40	60	800	-	-	-	-	40
69		Uncompahgre Dist.														
	OU-2	Benack Tunnel	50	-	3	3000	3	10	-	100	600	4	-	-	50	-
	OU-3	"	60	-	-	3000	6	9	-	-	400	-	-	-	7	-
70		Sneffels District														
	COL-113	Camp Bird Mine	7	-	5	5000	100	-	-	60	900	-	-	-	-	-
71		Eureka District														
	COL-118	Sunnyside Mine	40	-	4	4000	-	-	-	20	3000	-	-	-	2	-
72		Iron Springs Dist.														
	COL-109	Alta Mine	300	-	20	4000	6	9	-	-	2000	-	-	400	4	-
73		Creede District														
	COL-114	Amethyst Mine	3	-	-	8000	90	-	-	-	200	-	-	-	-	-
74		Animas District														
	COL-110	Green Mtn. Mine	500	-	5	8000	60	4	-	9	1000	7	-	100	-	-
75		Pioneer District														
	COL-103	Enterprise Mine	100	-	-	9000	-	20	-	-	3000	-	-	-	5	-

Table 5 (cont.)

Dist. No.	Sample No.	Locality	Ag	As	Bi	Cd	Co	Ga	Ge	In	Mn	Mo	Ni	Sb	Sn	Tl
		NEW MEXICO														
76		Willow Creek Dist.														
	NM-58	Willow Creek Dist.	800	-	100	3000	9	100	-	10	400	2	2	500	40	-
77		Cerrillos District														
	NM-65	Cerrillos District	9	-	-	5000	40	30	-	20	50	-	-	-	4	-
	NM-66	Pennsylvania Mine	3	-	-	3000	-	10	3	-	3000	-	-	-	-	-
79		Magdalena District														
	MG-1	Magdalena District	200	-	500	4000	30	-	-	60	600	-	-	-	-	-
	MG-2	"	20	-	100	4000	100	-	-	50	800	-	-	-	-	-
	MG-3	"	60	-	-	5000	4	-	-	-	2000	-	-	-	-	-
80		Nogal District														
	NM-74	Tommy LeMay Claim	40	-	-	10000	30	4	-	-	60	-	40	-	2	-
81		Mogollon District														
	NM-67	Mogollon District	30	-	-	3000	7	-	-	-	3000	-	-	-	-	-
	NM-68	Mogollon District	20	-	300	1000	200	-	-	8	2000	-	300	-	-	-
82		Hermosa District														
	HE-1	Day Tunnel	30	-	-	5000	60	-	-	-	70	5	-	-	-	-
	HE-3	"	30	-	-	5000	30	2	-	-	200	10	-	-	200	-
	HE-5	Nana Mine	1000	-	1	5000	40	20	-	-	300	-	-	-	5	-
83		Fierro-Hanover Dist.														
	BH-6	Black Hawk Mine	200	-	80	2000	100	-	-	30	4000	-	8	-	-	-
	BH-9	"	30	-	80	2000	200	-	-	30	2000	-	20	-	-	-
	HAN-5	N. J. Zinc Co. Mine	50	-	3	2000	20	-	-	20	2000	-	7	-	-	-
	HAN-6	"	80	-	3	2000	60	-	-	-	600	-	-	-	-	-
	HAN-16	"	50	-	4	1000	40	-	-	30	3000	-	-	-	-	-
	HAN-19	Surface outcrop	90	-	50	4000	-	-	-	100	7000	-	-	-	-	-
	HAN-20	Empire Zinc Mine	2	-	2	2000	30	-	-	-	20000	-	1	-	100	-
	NM-54	Shingle Canyon Mine	400	-	7	2000	10	-	-	200	4000	-	20	-	-	-
	NM-55	"	20	-	40	3000	40	10	-	200	400	-	-	-	20	-
	OS-1	Oswaldo No. 1 Mine	70	-	60	2000	100	-	-	40	2000	-	-	-	-	-
	PEW-8	Pewabic Mine	20	-	4	1000	300	20	-	60	1000	30	20	-	-	-
	PEW-9	"	40	-	2	2000	200	10	-	60	2000	-	10	-	-	-
	PEW-12	"	30	-	3	2000	200	-	-	60	1000	-	20	-	-	-
	PEW-13	"	200	-	700	1000	200	-	-	50	3000	-	9	-	-	-

Table 5 (cont.)

Dist. No.	Sample No.	Locality	Ag	As	Bi	Cd	Co	Ga	Ge	In	Mn	Mo	Ni	Sb	Sn	Tl
84		Steeple Rock Dist.														
	NM-25	Carlisle Mine	20	-	2	20000	100	8	-	-	300	-	-	-	7	-
	NM-70	"	300	-	-	7000	50	9	-	-	500	-	-	-	20	-
85		Santa Rita District														
	G-3	Groundhog Mine	30	-	2	4000	7	-	-	-	300	-	-	-	-	-
	G-4	"	200	-	2	2000	60	-	-	100	2000	-	5	-	-	-
	G-11	"	100	-	40	800	60	-	-	20	2000	-	-	-	-	-
	G-18	"	70	-	7	3000	30	-	-	-	2000	-	-	-	-	-
	OS-2	Oswaldo No. 2 Mine	100	-	4	3000	6	-	-	30	500	-	-	-	10	-
	OS-4	"	90	-	8	3000	5	-	-	100	1000	-	-	-	8	-
	SR-15	Ivanhoe Lease	100	-	20	3000	60	-	-	20	1000	-	-	-	-	-
86		Burro Mtns. Dist.														
	NM-59	Little Burro Mtns.	500	200	-	4000	60	5	-	-	300	-	-	40	20	-
87		Cooks Peak District														
	NM-63	Cooks Peak District	80	-	-	4000	-	-	-	20	600	5	-	-	-	-
	NM-64	"	20	-	-	3000	-	-	-	100	300	7	-	-	90	-
89		Organ District														
	ORG-2	Merrimac Mine	20	-	200	1000	200	-	-	8	2000	-	30	-	-	-
	ORG-4	"	60	-	>4000	1000	100	2	-	7	1000	-	20	20	10	-
90		Lordsburg District														
	CAM-23	85 Mine	30	-	-	4000	80	-	-	-	100	-	-	-	-	-
	CAM-26	"	4	-	-	6000	20	10	-	10	40	-	-	-	-	-
95		NEVADA Donnelly District														
	N-111	Comrade Mine	10	-	-	5000	8	8	-	10	1000	-	4	200	40?	-
96		Sierra District														
	N-124	Dun Glen Mine	200	-	50	8000	-	3	-	40	70	-	-	400	-	-
97		Imlay District														
	N-125	Nr. Betty LaVerne Mine	100	-	30	5000	-	-	-	100	600	-	->7000	-	-	-
98		Safford District														
	N-140	Safford District	200	-	10	4000	90	-	-	-	2000	3	4	-	-	-
100		Lewis District														
	N-93	Eagle Mine	4000	300	4	7000	-	20	-	30	7000	-	->7000	-	20	-

Table 5 (cont.)

Dist. No.	Sample No.	Locality	Ag	As	Bi	Cd	Co	Ga	Ge	In	Mn	Mo	Ni	Sb	Sn	Tl
101		Kennedy District														
	N-121	Kennedy District	20	-	-	7000	-	20	-	10	4000	-	-	50	-	-
	N-155	"	100	6000	-	6000	5	50	-	20	2000	-	-	200	-	-
102		Bullion District														
	N-143	Julius Mine	8000	300	90	3000	-	7	-	30	200	20	-	20000	5	-
	N-147	Buckingham Mine Consolidated Mines	500	200	7	7000	-	90	-	30	10000	-	-	1000	-	-
	N-149	Gray Eagle Mine	400	20000	6	7000	6	30	-	30	3000	-	-	2000	-	-
104		Mineral Hill Dist.														
	MH-2	Mineral Hill Mine	500	-	-	3000	-	20	300	-	200	-	3	-	-	-
	MH-3	"	300	200	-	2000	-	40	>500	-	300	-	-	-	-	-
	MH-4	"	300	-	-	3000	-	40	300	-	70	-	-	-	8	20
105		Pyramid District														
	PYR-1	Frank Blandin Claims	600	700	2	4000	-	40	80	80	300	-	-	2000	10	-
	PYR-2	"	100	200	6	4000	-	100	6	20	70	30	-	1000	2	-
	PYR-3	"	900	300	2	7000	-	20	20	10	30	-	4	2000	-	-
106		Roberts District														
	N-139	Jameson, Fletcher, and Carletti prop.	100	900	2	4000	-	300	1000	-	70	-	-	-	40	100
107		Cherry Creek Dist.														
	N-126	Cherry Creek Dist.	70	-	-	6000	60	10	-	-	2000	-	3	-	300	-
	N-129	Star Mine Cherry Creek Dist.	900	-	-	6000	20	-	-	-	2000	-	-	400	70	-
108		Wedekind District														
	WED-1	Wedekind District	1	-	1	5000	-	30	3	2	2000	-	-	-	3	-
	WED-2	Wedekind District	40	-	-	8000	-	60	-	10	1000	-	-	-	-	-
109		Peavine District														
	N-156	Votero Zinc Mine	4	-	-	5000	9	100	200	-	40	-	-	-	-	-
111		Eureka District														
	EU-1	Albion Mine	700	-	-	6000	6	30	-	100	2000	-	1	800	100	-
114		Antelope District														
	N-141	Keystone Lode	200	-	-	3000	90	-	7	6	3000	2	10	-	-	-
117		Gardnerville Dist.														
	N-158	Ruby Hill Mine	200	-	-	8000	100	10	80	7	80	-	10	-	4	-

Table 5 (cont.)

Dist. No.	Sample No.	Locality	Ag	As	Bi	Cd	Co	Ga	Ge	In	Mn	Mo	Ni	Sb	Sn	Tl
118		Duckwater District														
	N-85	Duckwater	1	-	-	6000	-	8	-	-	700	-	-	-	-	-
119		Garfield District														
	N-131	West of Luning	500	-	3000	7000	7	9	-	40	2000	80	-	-	-	-
	N-135	Mabel Mine	70	-	20	9000	5	10	-	5	100	-	-	-	-	-
121		Cedar Mtn. District														
	SIM-2	Simon Mine	40	100	100	9000	400	-	-	40	2000	-	30	-	-	-
	SIM-7	Simon (Mina)	400	-	10	4000	100	4	-	-	4000	-	4	100	4	-
	SIM-8	"	100	-	1	4000	200	1	-	-	6000	-	3	20	3	-
122		Belmont District														
	BEL-3	Belmont	1000	-	9	4000	-	10	-	20	400	-	4	2000	-	-
124		Tybo District														
	N-152	Tybo	30	300	-	5000	-	-	-	80	1000	-	-	-	-	-
127		Pioche District														
	N-21	Comb. Metals Mine	60	-	-	4000	-	60	20	30	500	-	7	-	300	-
	PIO-2	"	200	200	-	6000	10	90	100	40	500	-	8	-	300	-
	PIO-9	Pioche	90	100	-	5000	-	80	300	-	400	-	9	-	600	-
	PIO-12	Black Ledge, Pioche Mines	300	200	8	3000	-	8	>500	-	90	20	10	20	3	-
128		Goldfield District														
	GFD-37	White Rock Shaft	400	200	70	9000	-	500	70	700	20	-	-	1000	-	-
129		Tem Piute District														
	N-165	Lincoln Mine	<1	-	-	4000	10	-	-	100	5000	-	6	-	-	-
	N-166	"	1	-	-	3000	20	-	6	80	9000	-	10	-	-	-
132		Yellow Pine Dist.														
	GS-34	Potosi Mine	600	700	1	10000	-	4	700	-		-	8	200	-	-
	GS-43	"	700	100	1	6000	-	4	600	-		-	6	40	-	-
	GS-44	"	500	300	2	7000	6	30	700	-		200	10	-	6	-
	GS-45	"	100	400	1	8000	3	10	700	-		30	30	300	-	-
		UTAH														
134		Big Cottonwood Dist.														
	UT-46	Cottonwood Canyon	50	1000	3	6000	-	>700	40	10	4000	-	6	60	3	-
135		Uinta District														
	PC-1	Ontario Mine	2	-	-	6000	-	10	-	-	7000	-	-	-	100	-

Table 5 (cont.)

Dist. No.	Sample No.	Locality	Ag	As	Bi	Cd	Co	Ga	Ge	In	Mn	Mo	Ni	Sb	Sn	Tl
	PC-3	Daly-Judge Mine	6	-	-	5000	-	20	-	-	2000	-	-	-	-	-
	PC-10	"	40	-	-	7000	7	50	-	20	3000	-	-	100	-	-
	PC-12	New Park Mine	30	-	-	10000	-	10	-	30	2000	-	-	-	-	-
	PC-13	"	5	-	-	8000	-	-	-	-	1000	-	-	-	10	-
	PC-16	"	4	-	-	10000	-	-	-	30	700	-	-	-	-	-
	PC-28	Ontario Mine	1	-	-	5000	-	7	-	20	100	-	-	-	100	-
	PC-34	"	1	-	-	5000	-	9	-	20	500	-	-	-	60	-
136		Bingham District														
	BIN-9	Lark Mine	<1	-	-	6000	-	40	-	-	5000	-	-	-	5	-
	BIN-11	Butterfield Mine	5	-	-	4000	4	60	-	20	500	3	-	200	20	-
138		Ophir District														
	UT-37	Ophir District	20	-	-	10000	30	20	-	200	4000	-	-	-	-	-
	UT-42	Hidden Treasure Mine	60	-	2	7000	8	8	-	-	4000	-	-	-	20	-
140		Tintic District														
	EUR-46	North Lilly Mine	20	600	-	6000	-	1	6	5	80	-	-	40	3	10
	UT-29	Chief Cons. Mines	600	200	2	8000	8	>400	30	80	90	-	-	-2000	-	-
142		Frisco District														
	UT-1	Lincoln Mine	40	-	-	5000	-	-	-	200	900	-	-	-	-	-
	UT-14	"	30	-	-	3000	-	-	-	500	1000	300	-	-	-	-
	UT-33	Milford	30	-	60	5000	100	4	-	60	7000	-	-	-	3	-
144		BAJA CALIFORNIA														
		El Triunfo, San Antonio District														
	MEX-32	Humboldt Mine	400	-	-	6000	-	100	-	200	200	-	-	-3000	4000	-
		CHIHUAHUA														
147		San Diego, Iturbide District														
	SE-94	San Antonio Mine	10	-	-	4000	20	-	-	-	2000	-	-	-	4	-
	SE-95	"	60	-	8	4000	10	-	-	-	3000	-	-	-	20	-
148		Santa Eulalia, Iturbide District														
	SE-96	Potosi Mine	10	-	-	9000	-	20	-	8	4000	-	-	-	-	-
	SE-98	Santo Domingo Mine	20	-	-	5000	10	20	-	10	3000	-	-	-	-	-

Table 5 (cont.)

Dist. No.	Sample No.	Locality	Ag	As	Bi	Cd	Co	Ga	Ge	In	Mn	Mo	Ni	Sb	Sn	Tl
149		Guerrero, Guerrero District														
	CA-4	Calera Mine	80	-	-	5000	100	-	-	-	2000	20	-	50	-	-
150		Meoqui, Camargo Dist.														
	MEX-28	Las Plomosas Mine	100	-	-	3000	-	30	100	-	700	-	-	-	9	-
	MEX-33	Las Plomosas Mine	40	-	-	3000	-	10	200	-	200	-	-	-	-	-
151		Naica, Camargo Dist.														
	MEX-53	Naica	200	-	-	7000	50	-	-	5	6000	-	-	-	10	-
	MEX-54	Naica	200	-	30	8000	70	-	-	9	5000	10	-	-	-	-
152		Los Reyes, Jimenez District														
	MEX-46	Josefina y Anexas Mine	200	-	-	5000	30	-	-	100	3000	-	-	-	-	-
153		El Parral, Hidalgo District														
	PAR-1	Parral Unit	500	-	-	8000	200	8	-	-	1000	-	-	-400	-	-
	PAR-2	"	3000	200	-	4000	70	9	-	-	1000	4	-1000	-1000	200	-
	PAR-4	"	80	-	-	7000	100	10	-	-	3000	1	-	-	-	-
155		Sta. Barbara, Hidalgo District														
	SAF-1	San Francisco del Oro	100	-	-	9000	200	8	-	-	1000	-	5	-	-	-
	SAN-1	Hidalgo Vein	30	1000	5	4000	70	-	5?	-	1000	-	-	-	-	-
	SAN-3	La Paz Vein	40	-	-	5000	200	20	-	6	2000	3	1	-	-	-
		DURANGO														
156		Penoles, Mapimi Dist.														
	OJ-37	Ojuela Mine	200	-	-	6000	-	-	-	30	6000	-	-	-300	10	-
	OJ-40	"	10	-	-	10000	-	9	-	10	3000	-	-	-	-	-
157		Las Vacas, Nombre de Dios District														
	MEX-44	La Fortuna Mine	700	-	-	8000	5	10	-	8	300	-	-1000	-1000	-	-
158		Teneras, Cuencame Dist.														
	VEL-3	Teneras Mine	300	900	-	8000	10	50	-	-	2000	-	-4000	-4000	40	-
	VEL-4	"	30	-	-	8000	8	60	-	-	1000	-	-400	-400	20	-

Table 5 (cont.)

Dist. No.	Sample No.	Locality	Ag	As	Bi	Cd	Co	Ga	Ge	In	Mn	Mo	Ni	Sb	Sn	Tl
159		Reina de Cobre, Cuencame District														
	VEL-1	Reina de Cobre Mine	6	-	-	3000	600	7	-	10	2000	-	20	-	-	-
	VEL-2	"	20	-	-	4000	600	2	-	20	2000	-	20	-	-	-
160		San Lucas, San Juan del Rio District														
	MEX-40	Santa Cruz Mine	7	-	3	8000	-	-	-	5	1000	-	-	-	20	-
	MEX-41	"	700	-	-	8000	5	10	-	8	300	-	-1000	-	-	-
161		Panuco de Coronado, San Juan del Rio dist.														
	MEX-42	Guadalupe Victoria	800	3000	-	9000	200	-	-	30	3000	-	-3000	-	10	-
	MEX-43	"	200	200	-	9000	20	-	-	40	3000	-	-3000	-	8	-
		SAN LUIS POTOSI														
164		Charcas, Venado Dist.														
	MEX-34	Charcas	90	-	-	10000	-	-	-	-	3000	-	-	60	10	-
		SONORA														
165		Cananea, Arispe Dist.														
	CN-38	Cananea Duluth Mine	200	-	100	2000	300	10	-	80	5000	-	6	-	-	-
	CN-39	"	100	400	30	2000	200	-	-	50	700	30	10	500	7	-
	CN-40	Democrata Mine	70	200	70	2000	400	-	-	100	1000	-	10	-	-	-
166		Nacozari, Arispe Dist.														
	ELT-3	El Tigre Mine	200	-	-	10000	-	300	-	300	2000	-	-	300	200	-
	ELT-7	"	70	-	-	5000	7	100	-	-	6000	-	-	200	20	-
	ELT-8	"	200	-	-	9000	-	100	-	300	3000	-	-	500	300	-
		ZACATECAS														
170		Sain Alto, Sombrerete District														
	MEX-52	San Martin Mine	300	-	8	4000	-	-	-	-	600	-	-	-	40	-
171		Sombrerete, Sombrerete District														
	MEX-50	Tocayos Mine	200	-	-	10000	5	-	-	4	800	70	10	300	10	-
	MEX-51	"	20	-	-	10000	-	-	-	3	900	3	-	-	100	-

Table 5 (cont.)

Dist. No.	Sample No.	Locality	Ag	As	Bi	Cd	Co	Ga	Ge	In	Mn	Mo	Ni	Sb	Sn	Tl
A	PAC-12	Pachuca, Hidalgo Dios te Guie Vein	100	–	–	6000	4	50	–	–	800	–	–	–	–	–
B	ARI-58	Exact Locality Unknown Mammoth St. Anthony Mine(?), Arizona	200	–	2	9000	20	10	–	–	300	–	–	–	–	–
	ARI-88	Sta. Cruz Co.,Ariz. Keystone Mill,	2000	–	1000	10000	80	–	–	50	500	–	–	–	–	–
	CHL-1	Chloride, Arizona	200	–	2	4000	–	8	–	40	1000	–	–	–	8	–
	COL-99	Castleton Mine	10	–	–	6000	–	90	–	50	700	–	–	–	60	–
	MEX-27	Baja California	2	–	–	4000	–	7	100	–	2000	–	–	–	–	–
	N-102	More Mine, Mineral Co., Nevada	600	4000	–	3000	–	20	6?	8	20000	–	→8000	>8000	10000	–
C		Fierro-Hanover Dist., N.M.(Single Crystal)														
	HAN-20A	Empire Zinc Mine	3	–	4	2000	10	–	–	–	20000	–	2	–	80	–
	HAN-20B	"	1	–	–	2000	20	–	–	–	20000	–	2	–	6	–
	HAN-20C	"	1	–	–	2000	30	–	–	–	30000	–	2	–	300	–
	HAN-20D	"	1	–	–	2000	10	–	–	–	30000	–	2	–	10	–
	HAN-20E	"	2	–	4	2000	70	–	–	–	20000	–	1	–	100	–
	HAN-20F	"	1	–	–	2000	60	–	–	–	20000	–	1	–	7	–
	HAN-20G	"	1	–	2	2000	10	–	–	–	3000	–	1	–	20	–
	HAN-20H	"	1	–	2	2000	10	–	–	–	1000	–	–	–	60	–
	HAN-20U	"	1	–	3	2000	30	–	–	–	20000	–	–	–	70	–
	HAN-20V	"	3	–	3	2000	20	–	–	–	20000	–	–	–	2000	–
	HAN-20W	"	2	–	2	2000	10	–	–	–	20000	–	–	–	20	–
	HAN-20X	"	2	–	3	2000	10	–	–	–	30000	–	–	–	5	–
	HAN-20Y	"	1	–	2	2000	60	–	–	–	10000	–	–	–	30	–
	HAN-20Z	"	1	–	1	2000	40	–	–	–	10000	–	–	–	300	–
D		Tintic District, Utah (Sgle. layered sample)														
	EUR-46A	North Lilly Mine	200	900	–	9000	–	20	4	>400	90	–	–	200	3	7
	EUR-46B	"	80	400	–	8000	8	10	4	100	40	–	–	100	–	7
	EUR-46C	"	10	700	–	5000	–	1	7	5	50	–	7	30	–	20
	EUR-46D	"	10	600	–	5000	–	2	4	4	80	–	–	30	–	10

Table 5 (cont.)

Dist. No.	Sample No.	Locality	Ag	As	Bi	Cd	Co	Ga	Ge	In	Mn	Mo	Ni	Sb	Sn	Tl
	EUR-46E	North Lilly Mine	20	300	-	5000	6	2	4	3	30	-	-	40	-	8
	EUR-46F	"	10	200	-	200	-	2	50	2	40	-	-	20	2	10
	EUR-46G	"	20	1000	-	2000	-	10	60	3	60	-	-	20	3	70
	EUR-46H	"	50	1000	-	2000	-	50	30	200	60	-	-	300	9	20
E		Miscellaneous														
	COL-97	Lamartine Mine, Near Idaho Springs, Colo.	1	-	-	10000	-	7	-	-	2000	-	-	-	-	-
	PC-7	Silver King-Coalition Mine, Park City, Utah	600	4000	-	8000	-	80	20	-	5000	-	30	2000	20	100

Table 6

Trace Elements in Pyrite
(In parts per million)

Dist. No.	Sample No.	Locality	Ag	As	Bi	Cd	Co	Ge	In	Mn	Mo	Ni	Sb	Sn
		ARIZONA												
1		Wallapai District												
	CHL-11	Keystone Mine	1000	600	30	-	60	-	20	90	-	20	-	9
8		Swansea District												
	ARI-67	Swansea	<1	-	-	-	1000	-	-	20	-	200	-	-
11		Globe District												
	OD-3	Old Dominion Mine	<1	-	-	-	90	-	-	10	-	40	-	30
15		Mineral Creek District												
	RAY-14	Ray Pit	9	-	-	-	2000	-	-	20	7	900	-	-
18		Bunker Hill District												
	CHA-1	Childs Aldwinkle Mine	<1	400	-	-	10	-	-	10	-	40	-	-
21		Ajo District												
	AJ-40	New Cornelia Mine	300	-	70	-	80	-	-	30	-	60	-	-
33		Warren (Bisbee) District												
	BI-53	Junction Shaft	200	-	200	-	40	-	30	300	-	30	-	30
		COLORADO												
62		Fremont Pass District												
	CL-14	Climax Molybdenum Mine	300	-	500	-	20	-	30	300	20	200	-	-1000
		NEW MEXICO												
83		Fierro-Hanover District												
	HAN-19	Surface Outcrop	3	-	-	70	40	-	20	3000	-	100	-	-
85		Santa Rita District												
	SR-17	Chino Mine	<1	-	-	-	400	-	-	10	40	400	-	-

Table 7

Trace Elements in Galena
(In parts per million)

Dist. No.	Sample No.	Locality	Ag	As	Bi	Cd	Co	Ge	In	Mn	Mo	Ni	Sb	Sn	Te	Tl
		ARIZONA														
6		Bradshaw District														
	ARI-99	Money Metals Mine	4000	–	7000	100	40	–	–	60	–	–	300	–	–	–
12		Summit District														
	MIA-6	Castle Dome Mine	600	–	100	200	–	–	–	50	–	–	300	–	–	–
29		Tombstone District														
	TB-9	Tombstone	>100000	–	10	20	–	–	–	20	–	–	3000	5	300	–
	TB-14	Silver Thread Mine	30000	900	100	400	10	–	–	1000	10	–	2000	6	1000	–
	TB-15	Toughnut Mine	2000	–	–	60	–	–	–	10	20	–	1000	–	100	–
33		Warren District														
	BI-52	Junction Shaft	8000	–	>10000	10	–	–	–	600	–	–	–	–	100	–
		NEW MEXICO														
82		Hermosa District														
	HE-4	Hummingbird Mine	700	–	20	6	–	–	–	10	10	–	300	–	–	–
84		Steeple Rock Dist.														
	NM-25	Carlisle Mine	500	–	–	50	–	–	–	4	–	–	40	–	100	–
85		Santa Rita District														
	G-11	Groundhog Mine	1000	–	3000	7	7	–	–	80	–	–	40	–	100	–
		NEVADA														
98		Safford District														
	N-140	Safford District	4000	–	300	100	10	–	–	500	30	–	1000	10	300	–
106		Roberts District														
	N-139	Jameson, Fletcher and Carletti Prop.	200	10000	30	90	–	50	–	–	20	–	4000	–	–	600
111		Eureka District														
	EU-1	Albion Mine	>100000	–	–	50	–	–	–	20	–	–	4000	300	–	–
		SONORA														
165		Cananea, Arispe District														
	CN-38	Cananea Duluth Mine	70000	300	>10000	9	20	–	–	300	–	–	200	–	200	–

Table 7 (cont.)

Dist. No.	Sample No	Locality	Ag	As	Bi	Cd	Co	Ge	In	Mn	Mo	Ni	Sb	Sn	Te	Tl
166		Nacozari, Arispe District														
	ELT-3	El Tigre Mine	50000	-	-	20	5	-	-	20	-	-	2000	9	-	-
	ELT-8	" "	9000	-	90	200	-	-	-	200	-	-	2000	20	-	-

SOME ASPECTS OF THE CRYSTAL CHEMISTRY AND GEOCHEMISTRY
OF CHALCOPYRITE AND SPHALERITE

The Variations in Trace Element Content
Within Single Crystals and Specimens

Sphalerite

An examination of table 5 reveals that the trace element content of sphalerite from various parts of a mine, or, in many places, an entire mining district, is relatively constant with respect to some elements, and highly variable with respect to others. For example, the cadmium content of sphalerite is remarkably constant throughout a mine or district, but the tin content commonly varies within wide limits. In contrast to this, the tin content of chalcopyrite from a given mine tends strongly to vary within relatively narrow limits, and, on this basis, tin is regarded as exhibiting a well defined geographic distribution. It is important, therefore, to determine if possible whether the large variations in the tin content of sphalerite are dependent upon the site of crystallization or upon other factors.

The approach to this problem has been to determine the variations in the trace element content within a single crystal of sphalerite, and by comparison to determine whether these variations could account for the variations observed between different specimens from the same mine. It is realized that the properties of a large well-formed crystal of sphalerite, which obviously grew in an open space, are not necessarily representative of the bulk of the sphalerite samples studied here, most of which occur as relatively fine-grained

replacements. In fact, the open space fillings very probably exhibit a much greater variability than other modes of occurrence, owing to the wide range in conditions, especially of pressure, that must exist in an open space during the growth of a large crystal.

The large crystal that was selected for analysis occurred as a partial filling of a vug in andradite-rich rock at the Empire Zinc Mine, Hanover, New Mexico. An examination of the sawed surface of the interior of this crystal revealed that it is twinned; hence care was taken to obtain samples from only one individual of the twin. As shown in figure 6, the samples were taken at three to four millimeter intervals, from the base (where the crystal was attached to the wall of the vug) to the terminal faces. About a centimeter from the termination the crystal undergoes a color change, from dark brown inward to greenish-gray outward. This color change is faintly visible in figure 6 and is indicated in figure 7 by the vertical line very near sample Z.

The analyses of the 14 samples that were obtained from this crystal (HAN-20) are presented in table 5 (district C), and are represented graphically in figure 7*. The results, as they are shown in figure 7, clearly indicate the source of the variations in trace element content that were noted above.

The cadmium content remains remarkably constant throughout the crystal, whereas the tin content is extremely erratic. The manganese content, on the other hand, is approximately

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*The data are plotted to two significant figures in figure 7, but are reported to only one significant figure in table 5.

Figure 6. Section of a large crystal of sphalerite (HAN-20)
showing the locations of the samples, the analyses of
which are reported in table 5, district C, and repre-
sented graphically in figure 7. The twinned crystal
occurred in a vug in andradite-rich contact rock and
was attached to the wall of the vug along the surface
indicated as the "base" in the photograph.
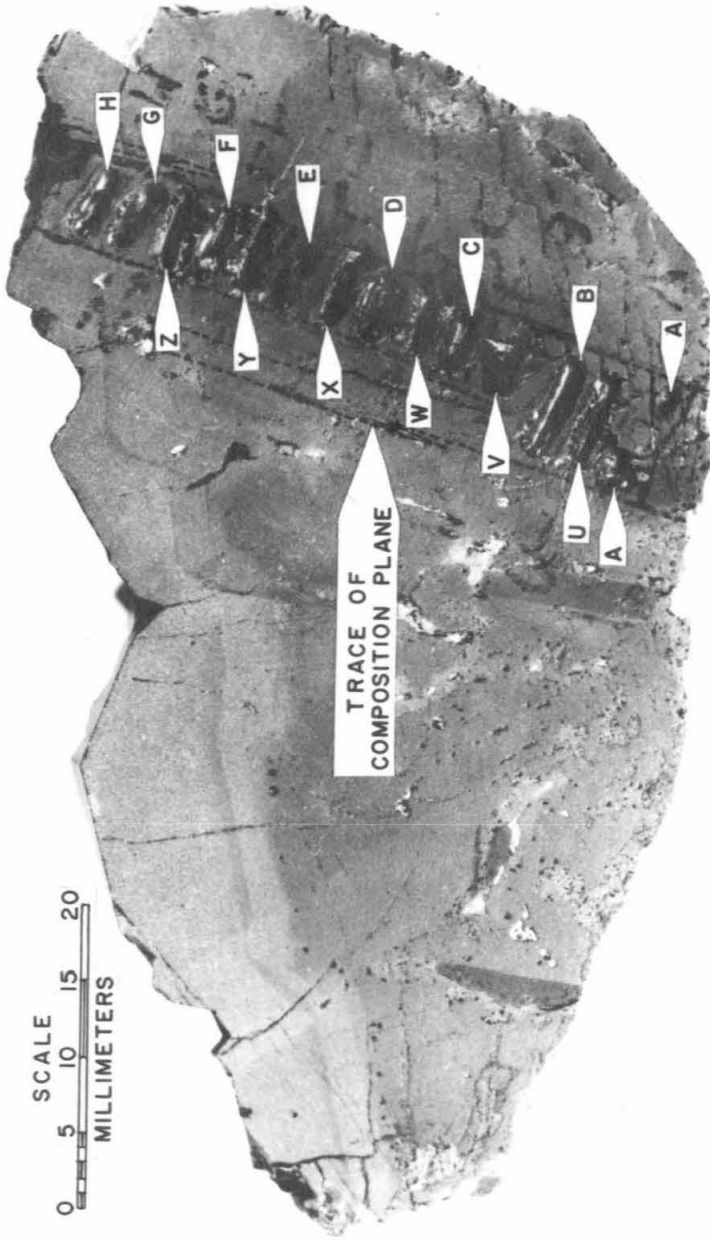
HAN-20

Figure 6

Figure 7. Variations in the trace element content of the
           large crystal of sphalerite shown in figure 6. The
           left-hand border of the figure represents the "base"
           of the crystal, where it was attached to the wall of
           the vug, and the right-hand border represents the
           terminal face of the crystal.

Figure 7
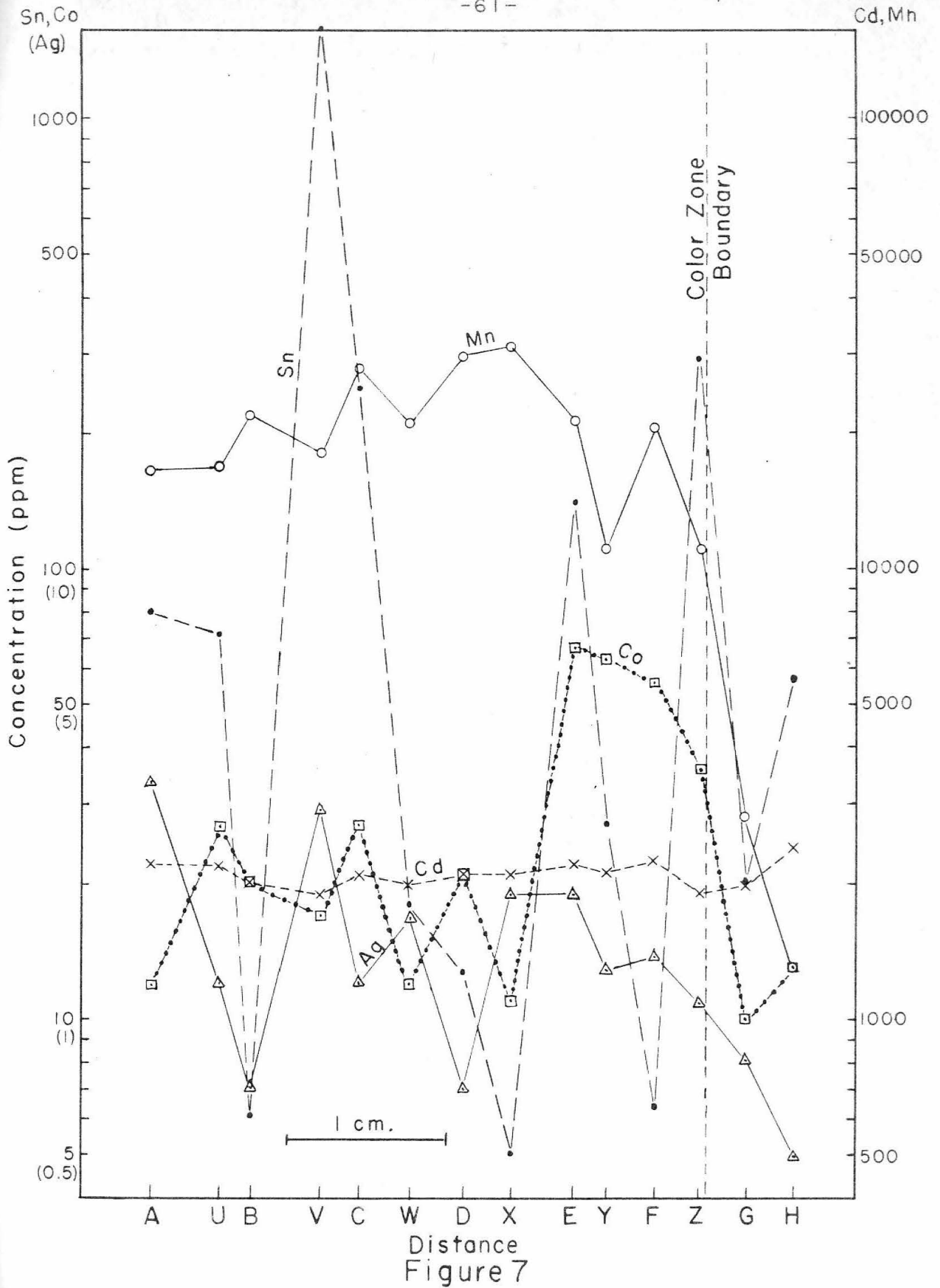
constant within the brown part of the crystal, but undergoes
about a tenfold decrease across the color zone boundary into
the greenish-gray part. Similarly, a comparison of intensity
ratios for iron indicates that the amount of this element also
decreases by a factor of approximately ten across the color
zone boundary; and the decrease doubtless is largely respon-
sible for the change in color. Hence it would appear that the
same or closely related factors govern the distribution of both
iron and manganese in sphalerite. Silver also appears to de-
crease in amount toward the outer part of the crystal, but the
decrease, if real, is slight. Although the cobalt content
decreases across the color zone boundary, there is essentially
as much cobalt in the outer greenish-gray zone as there is in
the inner part of the brown zone.

The cause of the erratic behavior of tin is not fully
understood. It probably is not the result of changes in the
composition of the fluids from which the crystal was deposited,
for none of the other elements shows similar or related varia-
tions. However, this does not mean that changes in the compo-
sition of the fluids are not important, for they very likely
are the cause of the changes in the iron, manganese, cobalt,
and silver contents that were described in the foregoing
paragraph.

The fact that the behavior of tin is unique among the
elements present in the crystal suggests that the cause might
lie in some unique property of tin or one of its compounds.
This suggestion becomes a real possibility when it is recog-
nized that tin, in the form of a volatile halide, very well

could be an important constituent of the microscopic white
crustifications that occur on the walls of numerous cavities
that were penetrated by the drill in obtaining samples. The
cavities that occur in the large crystal are of two general
types; angular cavities as much as five millimeters across
that apparently are the result of non-uniform growth of the
crystal, and semi-spherical cavities that are as much as two
millimeters in diameter. The semi-spherical cavities presum-
ably represent bubbles of the vapor phase that became attached
to the surfaces and eventually were incorporated in the growing
crystal. The tin, then is presumed to have been present in the
vapor phase originally, as the fluoride perhaps, and subse-
quently to have precipitated as a constituent of the white
crustifications. Many of the cavities, moreover, contain
small quartz crystals that are "dusty" with minute crystals
of a high refringent and high birefringent mineral that could
be cassiterite.

It is possible that the decrease in the iron and manganese
contents of the crystal near its outer margins indicates a
sharp decrease in the temperature of the system during crys-
tallization. Either this is not the case or cadmium is not
sensitive to such temperature changes, for the cadmium content
remains constant across the color zone boundary. The decrease
more probably represents an impoverishment of the fluids in
iron and manganese.

In summary, it is suggested that the erratic behavior of
tin in the crystal studied is in some way related to the
presence of numerous cavities and inclusions, but that the

more systematic variations are a reflection of the changing nature of the fluids from which the crystal was deposited. Furthermore, the geologic occurrence of the specimen, essentially as an open space filling, is regarded as important not only in the development of such a large crystal, but in the number and nature of the cavities and inclusions, and in the general variability of both the physical and chemical conditions of crystal growth.

The importance of conditions of deposition in the distribution of trace elements is further emphasized by the results of an examination of a specimen of botryoidal sphalerite from the North Lilly Mine, Tintic District, Utah (EUR-46). Samples were obtained from eight successive layers of the specimen as shown in figure 8. The results are presented in table 5 (district D) and are shown graphically in figure 9*. The most striking feature of the trace element content of this sample is its pronounced variability; however, there is a readily discernible pattern to the variations. The general level of concentration is highest in the first sample (A), the earliest, decreases through the middle, and increases toward the last sample (H), the latest. The main exceptions are germanium and thallium, which are enriched in the outer layers. In general, the higher trace element contents are in the darker colored layers, and sample G, which is richest in germanium, is from a distinctly reddish layer.

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*The data are plotted to two significant figures in figure 9, whereas they are reported to only one significant figure in table 5.

Figure 8. A polished section of botryoidal sphal-
    erite (EUR-46) showing the location of samples,
    the analyses of which are reported in table 5,
    district D, and represented graphically in
    figure 9. The specimen is capped by layers
    of botryoidal pyrite.

EUR-46

Figure 8

Figure 9. Variations in the trace element content of the
      specimen of botryoidal sphalerite shown in figure 8.

Figure 9
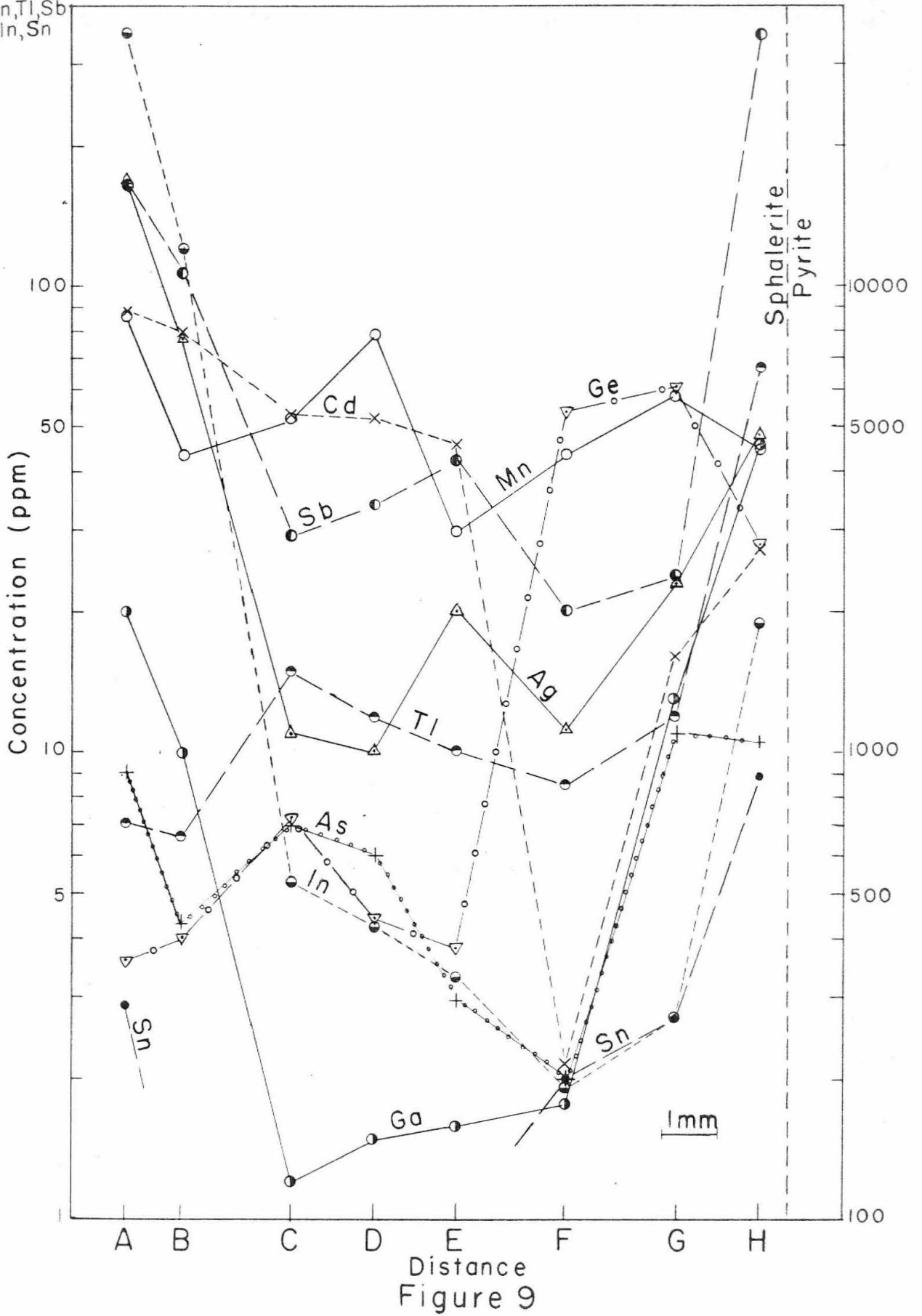
The causes for the behavior of the trace elements in this specimen are not known, especially for the erratic behavior of cadmium. The fact that layers A and H, both of which are rich in trace elements, were near layers of botryoidal pyrite suggests that the gross variations may be the result of variations in the composition of the solutions; that is, the initial supply of solutions may have become impoverished in the trace elements, and then replenished, perhaps by a fresh supply of solutions. Whatever may be the causes for the behavior of the trace elements in this specimen, botryoidal sphalerite is rare in the Southwest and any conclusions based on this specimen are not likely, therefore, to be generally applicable.

Chalcopyrite

Chalcopyrite crystals as large as the sphalerite crystal studied were not available; hence fewer samples could be obtained from each crystal. Furthermore, it was not possible to tell at what point the crystals began their growth, as was possible with the sphalerite crystal.

One fairly large twinned crystal of chalcopyrite was obtained from Ellenville, New York (NY-4), through the courtesy of Professor C. S. Hurlbut of Harvard University. Seven samples were obtained from a polished section of this crystal, as indicated in figure 10. The analyses (table 4, district F) reveal that this crystal is nearly free of trace elements, except for silver and a small amount of indium. Although this is unfortunate for the present purposes, the remarkably slight variations in the silver and indium contents throughout

both individuals of the twin provide convincing evidence that single crystals of chalcopyrite have a much greater tendency toward uniform trace element composition than have sphalerite crystals.

A second chalcopyrite crystal of about the same size as the one just described was obtained from the El Carmen Mine, Alisos, Chihuahua (MEX-35), through the courtesy of Mr. M. B. Nesbitt of the El Potosi Mining Company. The seven analyses of this crystal, which are presented in table 4 (district E), indicate that it is even purer than the first crystal. Despite its purity, however, it exhibits remarkably uniform silver and indium contents throughout.

On the other hand, the tin content of this crystal appears to vary within wide limits. This feature was somewhat puzzling at first because tin was not detected in a composite sample of the interior of an adjacent crystal (table 4, district 154). However, the composite sample does not include the near surface parts of the crystal, whereas the first and last samples (MEX-35A and MEX-35G) not only include the near surface parts on opposite sides of the crystal, but some of the surface tarnish as well. Hence, it is suggested that most of the tin that is in these two samples was contributed either by the tarnish coating or by the near-surface parts of the crystal, and therefore probably was not all an original constituent.

It is probably coincidental that the only available large crystals of chalcopyrite are remarkably pure with respect to most of the trace elements. But it is also conceivable that

Figure 10. A polished section of a twinned crystal
     of chalcopyrite (NY-4) showing the location of
     samples, the analyses of which are reported in
     table 4, district F. The dashed line indicates
     the trace of the composition plane of the twin.

NY-4

Figure 10

the crystals grew to a relatively large size because some elements, which commonly occur in finer grained chalcopyrite and which might act to "poison" the surfaces of the growing crystals and thereby inhibit their growth, were absent from the fluids from which the crystals were deposited.

The distribution of trace elements in single crystals of galena has been studied by Frondel, Newhouse, and Jarrel (1942). The spectrochemical evidence indicated that the octahedral face loci of the galena crystal tend to be slightly richer in trace elements, especially silver, than the cube face loci. In corroboration of this, it was demonstrated by differential staining techniques that the octahedral face loci contain more silver than the cube face loci. However, the evidence from staining is not conclusive for there naturally is more silver per unit area of octahedral surface, even if the silver is randomly distributed through the crystal, owing to the fact that the atomic density is greater in the octahedral planes than in the cube planes.

On the other hand, it is possible that two univalent silver atoms could replace one divalent lead atom in the galena lattice by the substitution of one of the silver atoms for the lead atom and allowing the other silver atom to enter a tetrahedral interstice. The silver atoms do not have to enter the lattice in pairs, just so long as silver occurs in both positions. Such an arrangement would result in a greater effective concentration of silver in the octahedral plane than in the cube plane.

The causes for the behavior of the trace elements in single crystals remain in large part poorly understood. It is suggested that the nature of the solutions from which the crystals were deposited is an important factor, whereas temperature effects generally are of less significance. This is true only so long as the saturation levels of the elements in the particular mineral are not reached; otherwise temperature may be a controlling factor. However, it is believed that the saturation levels rarely have been reached in the examples studied here.

The Distribution of Trace Elements Among the Sulfides

Thirty nine of the polished sections that were made in connection with the present investigations have furnished samples of both chalcopyrite and sphalerite. The analyses of these sample pairs bear the same specimen numbers in tables 4 and 5. Inasmuch as each of these sample pairs has been obtained from the same polished section, all together they should provide a fairly reliable estimate of the distribution coefficients of the various elements between chalcopyrite and sphalerite. Together with nine chalcopyrite-pyrite pairs, one chalcopyrite-sphalerite-pyrite trio, six chalcopyrite-sphalerite-galena trios, one chalcopyrite-galena pair, one sphalerite-pyrite pair, and five sphalerite-galena pairs, the 39 chalcopyrite-sphalerite pairs form the basis for the following discussion. However, it should be mentioned at the outset that although the data are considered adequate to establish the relationships between chalcopyrite and sphalerite,

they are relatively meager for pyrite and galena; hence, the conclusions that are drawn concerning these latter two minerals may, in certain cases, require modification when more data are obtained.

The distribution of the various trace elements among the four sulfides, pyrite, sphalerite, chalcopyrite, and galena, is summarized in figure 11. The preference of a particular element for each of the four minerals is indicated in the figure by the relative lengths of the bars; no other relationship is intended. Thus galena contains very much more silver than the other three minerals, whereas there are only relatively slight differences in the silver contents of pyrite, sphalerite, and chalcopyrite. On the other hand, arsenic is not highly concentrated in any one of the four minerals, although pyrite and chalcopyrite appear to contain slightly more than sphalerite or galena.

The greater amount of data available for chalcopyrite and sphalerite permits a more precise analysis of the distribution of trace elements between these two minerals than is possible with any of the other minerals considered. A series of nine frequency histograms is presented in figure 12, representing the data obtained from the 39 chalcopyrite-sphalerite pairs. In the following pages, this distribution is discussed in considerable detail, particularly with respect to its crystallochemical and geochemical significance.

Figure 11. The distribution of trace elements among the
minerals pyrite, sphalerite, chalcopyrite, and galena.
The relative degree of concentration of a particular
trace element in each of the minerals is indicated by
the lengths of the bars. No relationship is intended
in the relative lengths of the bars vertically within
each column.

-73-

Figure 11

Antimony

Galena very clearly is the most important host mineral for antimony among the four sulfides under consideration. According to Goldschmidt (1954, p. 477), "Antimony, in amounts up to about 0.5 per cent. (or even 1 per cent.) by weight, is a very common constituent of many hydrothermal galena deposits, replacing either sulphur (as does arsenic) or lead (as does bismuth). Possibly both alternatives occur." However, on page 406 he states: "It is certain that Se and Te replace sulphur, and this is most probably also true for As and Sb which are often found as constituents of galena in amounts up to 10,000 p.p.m." It would appear from this that Goldschmidt favors the sulfur over the lead as the element that is replaced by antimony. However, a comparison of the distributions of antimony, arsenic, and bismuth among the four sulfides (figure 11), reveals that antimony very closely resembles bismuth, which generally is believed to substitute for lead in galena, but bears little resemblance to arsenic, which doubtless substitutes for sulfur. Furthermore, the atomic (and ionic) properties of antimony are more similar to those of lead than to those of sulfur. These features, together with the fact that antimony greatly prefers the lead sulfide to the other sulfide minerals, strongly suggest that lead in galena is the element most commonly replaced by anti-mony. However, another factor that might be involved in the high antimony content of galena is the possiblity of increasing concentrations of antimony in the solutions during the sequence of crystallization, which is in general from pyrite to galena

Figure 12. Frequency histograms that represent the distribution of nine trace elements between chalcopyrite and sphalerite. A log concentration ratio greater than unity indicates a preference for chalcopyrite, a ratio less than unity indicates a preference for sphalerite.
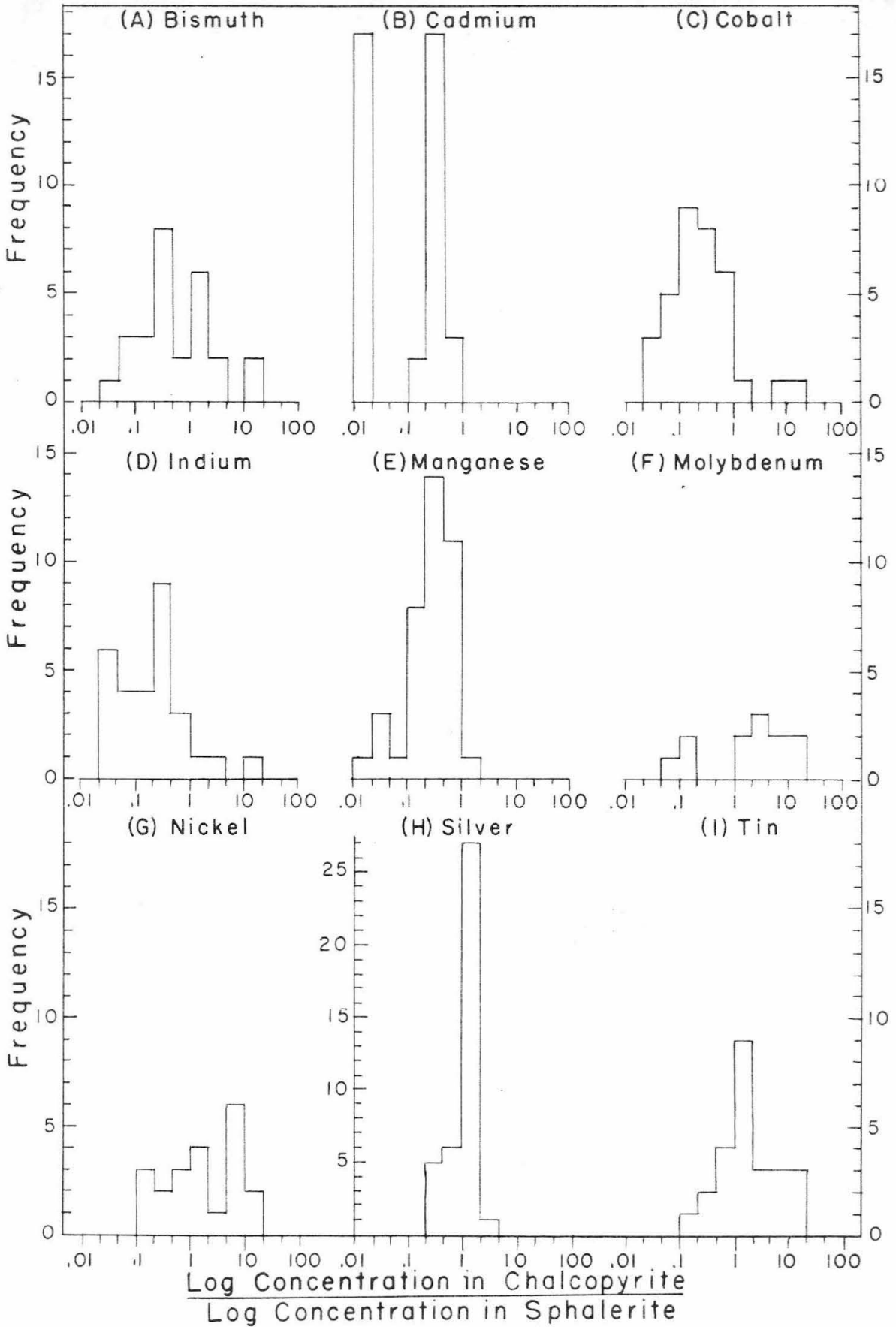
Figure 12

(left to right) in figure 11.

The distribution of antimony between chalcopyrite and sphalerite is not well defined because antimony was detected in only seven of the chalcopyrite-sphalerite pairs. In six of the seven pairs, antimony is concentrated in chalcopyrite; hence, it is assumed that this element has a slight preference for chalcopyrite over sphalerite, although the maximum level of concentration in uncontaminated samples of both minerals is about the same, approximately 500 ppm. Moreover, a comparison of tables 4 and 5 indicates that, in general, antimony is of more common occurrence in sphalerite than in chalcopyrite, despite the fact that a potential antimony contaminant, tetrahedrite, is fully as common in association with chalcopyrite as with sphalerite.

There is little doubt that both chalcopyrite and sphalerite can accept as much as 500 ppm antimony in solid solution, apparently in substitution for the metals rather than for sulfur. That it does not substitute for sulfur is suggested by the large difference in their tetrahedral radii, 1.36 Å for antimony and 1.04 Å for sulfur, which is in excess of the 20 percent limit*. In sphalerite it probably substitutes for zinc, which has a tetrahedral radius of 1.31 Å. On the basis of covalent radii alone, it would appear that the antimony in chalcopyrite has a choice of positions, for the radii of both copper (1.35 Å) and iron (1.24 Å) differ only slightly from

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*It is generally accepted on empirical grounds that isomorphous substitution does not readily occur if the relevant radii of the two elements concerned differ by more than 20 percent of the larger radius.

the radius of antimony. However, an examination of several
analyses of tetrahedrite (Palache, Berman, and Frondel, 1946,
pp. 376-378), a mineral with a tetrahedral structure analogous
to chalcopyrite and sphalerite, indicates that in the reverse
substitution, iron prefers the copper site to the antimony site.
Furthermore, the absence of antimony in the pyrite analyses of
table 6 indicates that antimony does not readily substitute for
iron. Hence, it seems probable that antimony substitutes for
the copper in chalcopyrite. It also is probable that the
similarity in the levels of antimony substitution in both
chalcopyrite and sphalerite is a reflection of the similarities
in atomic positions and general structural features of these
two minerals.

The absence of antimony in the analyses of pyrite in
table 6 and in other published analyses (Auger, 1941, and
Hawley, 1952) perhaps is best explained by the fact that the
antimony atom in either four or six-fold coordination is too
large to substitute for sulfur (four-fold coordination) or
iron (six-fold coordination).

An examination of tables 4 and 5 reveals a relatively
strong tendency for high antimony values to be accompanied by
high silver values. Much of this effect probably is due to
contamination by a silver-bearing sulfo-antimonide such as
tetrahedrite, pyrargyrite, or polybasite; but in some cases
where it can be shown microscopically that the sample is free
of such minerals, there still appears to be a general parallel-
ism between the antimony and silver contents. Perhaps this
association reflects a tendency toward isomorphous substitution

of pyrargyrite or tetrahedrite, or it might indicate an important amount of association* of certain elements in the solutions prior to the deposition of solid phases.

Arsenic

Arsenic, unlike antimony, possesses no strong affinities for any of the four sulfides, although there appears to be some preference for the iron-bearing minerals, pyrite and chalcopyrite. The main reason for the relatively uniform distribution of arsenic, which is in contrast to antimony, is that arsenic substitutes for sulfur, the "common denominator" of all four minerals. The difference in their tetrahedral radii amounts to only 12 percent of the larger arsenic radius (1.18 $\overset{o}{A}$). The apparent preference of arsenic for pyrite is readily understandable in view of the relationship of pyrite to arsenopyrite (FeAsS), but the nearly equal preference for chalcopyrite is not readily understandable on this basis, in that there is no apparent structural reason for arsenic definitely to prefer chalcopyrite over sphalerite. The very strong tendency for arsenic to be associated with the earlier crystallized iron-bearing sulfides suggests again that there may be a significant amount of association of some elements, in this case iron and arsenic, in the hydrothermal solutions at the time of deposition of chalcopyrite and sphalerite. If this is true, chalcopyrite might be expected to be enriched in arsenic as compared with sphalerite.

*Association is used here in a general sense. It does not necessarily mean that the "associated" elements are bonded together in the strict chemical sense, although both of them might be indistinguishably bonded to sulfur, oxygen, etc. in complexes. It is possible that the "association" arises as a consequence of close similarities in chemical behavior and response to various physical conditions.

The maximum amount of arsenic that can be taken into sphalerite and chalcopyrite appears to be in excess of 2000 ppm and to be about the same for each mineral. The data do not permit a reliable estimate of the maximum amounts that may be accepted by pyrite and galena, although it is fairly certain that pyrite may contain more than 600 ppm arsenic and galena more than 900 ppm despite the statements of Palache, Berman, and Frondel (1946, p. 202) to the contrary. The extremely high value of 10,000 ppm arsenic in the sample of galena, N-139 (table 6, district 106), is due to contamination by a mineral that closely resembles jordanite, but which might be a mixture or a solid solution of jordanite and an antimony-bearing mineral with properties similar to jordanite.

Bismuth

Galena is by far the most important host mineral for bismuth of the four species studied, as it commonly contains more than 10,000 ppm. Oftedal (1941) found as much as 30,000 ppm bismuth in galena from southern Norway. Generally it is assumed that bismuth, with an atomic radius of 1.77 Å, substitutes for lead (1.69 Å) in galena, and it was on this basis that the comparison with antimony was made previously. However, Goldschmidt (1954, p. 408) suggests that a mechanism similar to that proposed for the capture of silver by galena might also operate in the capture of bismuth; i.e., the silver (and bismuth?) may be captured in the tetrahedral interstices of the galena structure.

The phenomenon of octahedral cleavage or parting in galena, which Goldschmidt (1954, pp. 406-407) related to bismuth contents approaching 10,000 ppm, was not observed in the bismuth-rich galena studied here. Nor do the results of the present investigations support Goldschmidt's claim (p. 407) that, "...all galena rich in bismuth (about 10,000 p.p.m. Bi) also contains thallium (100 - 500 p.p.m.)...". In fact, the only thallium-bearing galena analyzed in the present work is relatively bismuth-poor. However, there is some support for Goldschmidt's claim that galena rich in bismuth always is rich in silver, although much silver-rich galena is not bismuth-bearing.

The capture of an element in interstices of the crystal lattice also might be invoked to explain the occurrence of as much as 500 ppm bismuth in pyrite. It is conceivable that bismuth might be captured in the tetrahedral interstices in the pyrite structure, which are just about large enough to accommodate the bismuth atom in tetrahedral coordination. No other explanation is offered for this occurrence of bismuth, for the atomic properties of bismuth are much too different from those of iron or sulfur to permit its substitution for either of them.

Bismuth exhibits a slight but noticeable preference for sphalerite over chalcopyrite, as shown in figure 12A, although the maximum concentration in uncontaminated material appears to be about 700 to 1000 ppm in both minerals. A bismuth-bearing mineral, most commonly bismuthinite, is intergrown with chalcopyrite or sphalerite in nearly all the samples of

these minerals that contain 2000 ppm bismuth or more.

A good reason for the slight preference of bismuth for sphalerite is not forthcoming. Its tetrahedral covalent radius (1.46 Å) is such that it could substitute equally well for copper in chalcopyrite or for zinc in sphalerite.

Cadmium

Sphalerite is so predominant as a host for cadmium that when more than 100 ppm of this element appears in an analysis of one of the other minerals, except possibly galena, contamination from sphalerite may be suspected. Oftedal (1941) found as little as 10 ppm cadmium in sphalerite from Kangerluarsuk, Greenland, and as much as 51,000 ppm in a sample of sphalerite from southern Norway. The cadmium contents of the sphalerite samples analyzed in the present studies range from 200 to 20,000 ppm, but more than 95 percent are within the range 2,000 to 10,000 ppm. The regional average cadmium content of sphalerite for the Southwest is about 5,500 ppm. Warren and Thompson (1945) obtained an average of 4,500 ppm cadmium for sphalerite from British Columbia, but considering the difference in spectrographic methods, it is doubtful whether the difference between these averages is significant.

Sandell and Goldich (1943) found that the ratio of cadmium to zinc in some "American igneous rocks" is very near 1:500. Goldschmidt (1954, p. 271) has compared this with a cadmium to zinc ratio between 1:100 and 1:300 for sphalerite, chiefly from Norway, and has interpreted the difference as

confirmation of the more chalcophile nature of cadmium as compared with zinc. Although the regional average for the ratio of cadmium to zinc in sphalerite from the Southwest is about 1:120, the ratio ranges from 1:70 to 1:700, depending upon the geographic location. Furthermore, the 1:500 ratio for the "magmatic rocks" is based on samples that represent relatively small areas of only two states, Minnesota and Texas, and cannot, therefore, be assumed to represent all "magmatic" rocks the world over.

It has been well established that cadmium occurs in solid solution in sphalerite, in substitution for zinc (Kröger, 1939; Kullerud, 1953). Generally it is assumed that this substitution occurs because cadmium and zinc sulfides have identical crystal structures, and because cadmium and zinc are very similar chemically; i.e., they have similar electronic configurations, electronegativities, etc. However, chalcopyrite has the same crystal structure and similar lattice constants, and when associated with sphalerite, it generally contains less than 10 ppm cadmium* (figure 12B). Therefore the behavior of cadmium in these tetrahedral structures cannot be logically explained on crystallochemical grounds alone.

The very strong preference that cadmium shows for sphalerite is readily explained if it is assumed that, because of the very close chemical similarities of cadmium and zinc, the

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*Where no sphalerite is present, as in some of the gold quartz veins of Grass Valley, California, the chalcopyrite contains as much as 200 ppm cadmium.

two elements already are associated in the fluids prior to deposition. This hypothesis of pre-depositional association of some of the elements, which has been suggested before as a possible explanation for the apparent association of antimony with silver, is compatible with the observation that galena, which generally crystallizes later than either sphalerite or chalcopyrite, persistently contains up to 100 ppm cadmium; and Oftedal (1941) has found as much as 1000 ppm cadmium in sphalerite-free galena from Norway. This hypothesis, if correct, also would explain the remarkably constant cadmium content of sphalerite within most mining districts.

The substitution of cadmium for lead in galena is readily understandable strictly from the atomic and ionic size relationships of these two elements. Moreover, the covalent radius of iron (1.24 Å) is close enough to that of cadmium (1.47 Å) to permit a small amount of cadmium to substitute for iron in pyrite. However, because of the possibility of contamination from sphalerite in the only analysis of pyrite in which cadmium was reported, it is doubtful that cadmium commonly occurs in pyrite in amounts greater than 20 or 30 ppm.

Cobalt

Cobalt was found in all four of the sulfides analyzed, although the amount actually present in the galena structure probably does not exceed 20 ppm. Pyrite contains the most cobalt (2000 ppm or more), as might be expected from the close similarities in chemical properties of cobalt and iron, and from the similarities in crystal structures of the sulfides of these two elements. According to Goldschmidt (1954, p. 668),

Gavelin and Gabrielson (1947) found that pyrite and pyrrhotite in copper ores generally contain more cobalt than the same minerals in zinc ores. The data in table 6 are inconclusive in this respect, although it is true that the highest percentages of cobalt are in pyrite from districts in which copper predominates over zinc. If inferences can be drawn from the meager data, a comparison of the zinc-rich deposits associated with the Hanover stock, New Mexico (district 83), with the more zinc-poor, copper-rich deposits associated with the Santa Rita stock (district 85) affords some support for Gavelin and Gabrielson's suggestion. However, even though the more cobalt-poor pyrite appears to be associated with the less copper-rich ores, these ores are not necessarily zinc-rich, as, for example, in the Bunkerville district, Arizona (district 33), a predominantly copper producing district in which the pyrite is relatively poor in cobalt.

Bjørlykke (1945) found the cobalt content of Norwegian pyrite to range from 0.47 to 1.25 percent. From a comparison with table 6, it may be concluded that pyrite from Norway is considerably richer in cobalt than pyrite from the southwestern United States, especially Arizona. A comparison of sphalerite samples from the two regions also reveals a large difference in cobalt contents. Thus, Oftedal (1941) found as much as 3000 ppm cobalt in many Norwegian sphalerite deposits, whereas 800 ppm is the most cobalt found in sphalerite from the Southwest.

Chalcopyrite also is a host for cobalt, but a relatively poor one by comparison with pyrite or sphalerite, as shown in

figure 12C. The amount that occurs in chalcopyrite generally
is less than 400 ppm, except for one sample (UT-38, table 4,
district 141) which very probably is contaminated with
cobaltite.

The very definite enrichment of cobalt in sphalerite, as
compared with chalcopyrite, is difficult to explain by the
crystallochemical principles discussed thus far, unless it is
assumed that small differences in covalent radii are important.
Alternatively, it is possible that the decrease in cobalt con-
tents through the series pyrite - sphalerite - chalcopyrite -
galena is a result of temporally progressive impoverishment
of the solutions in cobalt.

Cobalt occurs in galena in amounts up to 20 ppm. This
relatively small amount is in keeping with crystallochemical
considerations, and with the impoverishment postulate as well.
Regardless of whether the bonding between lead and sulfur in
galena is largely ionic (as suggested by Goldschmidt, 1954),
metallic, covalent, or, more probably, of hybrid character,
the size relationships of the atoms and/or ions involved are
inappropriate for appreciable substitution of cobalt for lead.

Gallium

Gallium was determined only in sphalerite and galena in
the present investigations. However, most of the spectra of
chalcopyrite and pyrite were examined for gallium, but none
was found in amounts greater than about 30 ppm, the approxi-
mate level of interference by iron. Nor was gallium detected
in any of the samples of galena (table 7), an observation in

full agreement with those of Oftedal (1941), who also found no
detectable gallium in sphalerite-free galena from Norway.
Together these facts indicate that sphalerite, which in the
Big Cottonwood district, Utah (district 134) contains more than
700 ppm gallium, contains essentially all the gallium in the
average base-metal sulfide deposit.

The obvious preference of gallium for sphalerite, despite
the lack of quantitative information on its partition between
sphalerite and chalcopyrite, poses the same problems of distri-
bution as do cobalt and cadmium. Explanations based on simple
crystallochemical considerations are not convincing, because
the crystal structures and the sizes of the constituent atoms
of chalcopyrite and sphalerite are too similar. Moreover, the
hypothesis that involves progressive changes in the composition
of the solutions is not very acceptable because the changes in
the gallium content of the minerals are not systematic. Among
the possible explanations that have been proposed thus far,
there remains the one that involves a relatively high degree
of association of some of the elements in the solutions prior
to deposition. This may be particularly applicable to gallium
in sphalerite in view of the close proximity of gallium to zinc
in the periodic table. However, another explanation, which
perhaps might also apply to the distribution of cadmium and
cobalt as well as to gallium, involves a consideration of
differences in the character of the bonds between the various
metals and sulfur--specifically a consideration of the probable
differences in the degree of ionic versus covalent and metallic
bonding associated with the metals in chalcopyrite and

sphalerite.

According to Kullerud (1953), the unit cell dimensions of β(Zn,Fe)S increase with increasing iron content, and he has correlated this phenomenon with a greater ionic character of the Fe-S bonds. Kullerud also found that manganese has a similar, though much greater effect on the M-S bond distance. This finding tends to support his first interpretation, inasmuch as the Mn-S bond is considered to be largely ionic (Pauling, 1948, pp. 186-187)*. If it is true that the presence of iron or manganese in the ZnS structure imparts a more ionic character to the bonds with sulfur, and if it is assumed that metals like iron and manganese, which have a relatively greater tendency toward ionic character in their bonds with sulfur, are preferentially concentrated in the more ionic structures, then an explanation of the partition of some of the metals between sphalerite and chalcopyrite is suggested. Thus a comparison of electronegativities (Pauling, 1948; Green, 1953) and of M-S bond distances** indicates that, in general, the bonds in sphalerite have about twice as much ionic character as the bonds in chalcopyrite. Thus it might be predicted that metals such as gallium, cadmium, and particularly manganese, whose tendencies toward ionic character of their bonds with sulfur are equal to or greater than that of iron, would be concentrated in sphalerite; in contrast, those

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*Cadmium has an even greater effect on the unit cell dimensions of β(Zn,Cd)S than does manganese (Kullerud, 1953, p. 116), but this is most likely due to the much larger tetrahedral radius of cadmium (1.48 Å).

**In sphalerite the Zn-S bond distance is 2.35 Å, and in chalcopyrite the Cu-S and the Fe-S distances are 2.32 Å and 2.20 Å, respectively.

metals with lesser ionic tendencies would be concentrated in
chalcopyrite. For those elements similar to iron in respect
to ionic character, other factors might be decisive. Moreover,
it is doubtful that the degree of ionic character of the M-S
bond is an important factor in the partition of trace elements
between chalcopyrite and sphalerite unless other factors such
as atomic size are favorable.

Germanium

Among the four minerals under consideration, sphalerite
is the principal host for germanium. As much as 1000 ppm
germanium has been found in the sphalerite investigated here,
and similar amounts have been reported from the Mississippi
Valley region (Graton and Harcourt, 1935; Stoiber, 1940;
Warren and Thompson, 1945). Oftedal (1941) found as much as
500 ppm germanium in sphalerite from Norway.

A feature of germanium-rich sphalerite that was noticed
in these investigations is a yellowish-orange to ruby red
color in the more iron-poor varieties. The actual shade of
color appears to depend upon the ratio of germanium to iron,
the darker reds being associated with higher iron contents.
If the iron content exceeds a certain but unknown amount,
however, the reddish color is no longer apparent, and the
germanium-rich sphalerite is then brown.

Chalcopyrite also contains germanium, but in much smaller
amounts than sphalerite. The largest amount found (200 ppm)
is in the chalcopyrite of a pitchblende-bearing specimen from
the San Rafael district, Utah (district 141). Goldschmidt and

Peters (1933) found as much as 50 ppm germanium in chalco-
pyrite from Butte, Montana, and in the present investigations
a similar amount (40 ppm) was found in a sample from the same
district (table 4, district 172).

Germanium was not detected in any of the pyrite samples
analyzed here, and this, together with the similar experiences
of others (Goldschmidt, 1954, pp. 386-387), clearly indicates
that pyrite does not readily accept germanium. Furthermore,
judging from the work of Oftedal (1941) and, except for one
sample, from the present investigations, a similar conclusion
can be drawn for galena. The single exception is the galena
from specimen number N-139 (table 7, district 106), and the
sphalerite from this specimen contains the most germanium
found in the present investigations (greater than 1000 ppm).
Moreover, the galena sample is plainly contaminated with
jordanite(?), the germanium content of which is unknown.

The problems connected with the distribution of germanium
among the four sulfides are essentially the same as those
involved in the distribution of gallium. The fact that germa-
nium, like gallium, tends to form tetrahedral sulfide struc-
tures is the most logical reason for its concentration in
sphalerite and chalcopyrite instead of in minerals with non-
tetrahedral structures like pyrite and galena. However, this
does not explain the definite tendency for germanium, as well
as gallium, to be concentrated in sphalerite in preference to
chalcopyrite. Nor does this preference appear to be explained
by any hypothesis involving changes in the composition of the
solutions. The hypothesis of association of the metals prior

to deposition, in this case germanium with zinc, may be applicable, but it does not appear to be as likely an explanation for germanium as for gallium, owing to the greater difference in chemical properties of germanium and zinc. There remains, then, the possibility, outlined in the discussion of gallium, that the difference in behavior of sphalerite and chalcopyrite as hosts for germanium may be related to differences in the character of the M-S bonds in the two minerals. A comparison of electronegativity values indicates that germanium, in a tetrahedral sulfide, should have about the same or slightly greater tendency toward ionic bonding than gallium, therefore it is more likely to be enriched in sphalerite.

Indium

Erämetsä (1939), in a detailed study of the indium content of many Finnish rocks and minerals, found that among the sulfides indium is concentrated in the following minerals, in order of decreasing amount: Sphalerite, chalcopyrite, bornite, and tetrahedrite. No indium was detected in 10 samples of galena, although in every instance sphalerite from the same mine contained indium in amounts up to 1000 ppm. These findings are in close agreement with those of Oftedal (1941), who detected no indium in 47 samples of galena from various parts of Norway, although 75 percent of the sphalerites from the same region contain as much as 500 ppm indium. However, McLellan (1945, p. 635), without presenting any supporting evidence, attempted to refute these findings by claiming that:

> "In the course of treatment at the smelters and refineries the indium tends to concentrate with the zinc and the cadmium and this, no doubt, has given

rise to the erroneous observation that indium occurs
in nature largely in association with zinc minerals.
Indium is frequently observed in relatively large quan-
tities in primary zinc sulfide ores but its actual
occurrence in them is typically in the galena associated
with these zinc and cadmium minerals."

The only support for McLellan's claim that has been found

to date comes from analyses published by Anderson (1953),

according to which just one of 19 samples of sphalerite,

mostly Australian and Tasmanian, contains an appreciable

amount of indium (in excess of 100 ppm). No indium was de-

tected in the galena analyzed in the present study, although

12 of the 15 galena samples are from polished sections that

also furnished sphalerite samples, and seven of these 12

sphalerite samples contain up to 300 ppm indium. In view of

this and of the statistical fact that only one of 91 analyses

of galena from various parts of the world report an appreciable

amount of indium, it is concluded, despite McLellan's claims

to the contrary, that indium is not concentrated in galena as

compared with sphalerite.

It is evident from table 4 that chalcopyrite also is an

important host for indium, as it contains as much as 1000 ppm

of the element. However, the evidence presented in figure 12D

indicates that chalcopyrite is not as favorable a host for

indium as is sphalerite. It would appear by analogy with

gallium, which has similar crystallochemical properties and

distribution, that the factors which determine the distribution

of indium and gallium between sphalerite and chalcopyrite are

somewhat similar. Hence the arguments presented in attempts

to explain the preference of gallium (and germanium) for

sphalerite probably can be applied to the similar behavior

of indium.

Pyrite also contains indium, but apparently in quantities not much greater than 30 ppm. The relatively slight tendency for indium to occur in the octahedral pyrite structure apparently reflects its very strong preference for the tetrahedral structures, as shown by many of its compounds such as InSb, InAs, InP, and InS (metastable).

Manganese

Manganese occurs in appreciable quantities in all four of the minerals investigated; but sphalerite is by far the best host, for it contains as much as 40,000 ppm (4 percent) manganese. Although this maximum value is about twice the maximum amount of cadmium found in the sphalerite of the Southwest, the regional average manganese content is about 1700 ppm and is therefore somewhat less than the regional average cadmium content (5500 ppm).

Kullerud (1953) has shown that the substitution of manganese for zinc in sphalerite causes a large increase in the unit cell dimension and in the M-S bond distance. Inasmuch as the covalent radius of manganese (1.26 Å) is even smaller than that of zinc (1.31 Å), the increase in the M-S bond distance is interpreted as being probably the result of an increased ionic character imparted to the bonds by manganese. Furthermore, because the increase in bond distance is greater for manganese than for iron, it is probable that the M-S bond in (Zn,Mn)S mixed crystals is more ionic than in (Zn,Fe)S mixed crystals. Such an interpretation finds additional support in a comparison of electronegativity values, for the

electronegativity of manganese (1.4) is considerably less than that of iron (1.65) or zinc (1.5).

It is somewhat surprising to find that galena rather than pyrite or chalcopyrite ranks second as a host for manganese (cf. figure 11). Manganese occurs in all but one of the galena samples analyzed, and in amounts up to 1000 ppm. There is little doubt that it occurs in substitutional solid solution in galena, and the reason becomes apparent when it is realized that alabandite, the stable form of MnS, has the same crystal structure as galena (NaCl type) and a unit cell dimension that differs from galena by only 0.72 Å. This would mean that the effective radius of manganese in the galena structure differs from the lead radius by about 12 percent, well within the range of ready substitution. Another feature common to manganese and lead is a somewhat anomalous behavior in sulfides with respect to bond type. Actually, it is largely because of this anomalous behavior that the sulfides of lead and manganese are so similar and that manganese substitutes for lead in galena so readily.

The present data suggest that manganese shows a slight preference for galena over pyrite, the third ranking host mineral. Manganese occurs in amounts greater than 10 ppm in all 10 of the pyrite samples analyzed, and the largest amount is 3000 ppm. This observation contradicts the statement made by Goldschmidt (1954, p. 624):

"That there is a fundamental difference in the type of bonding between FeS_2 and MnS_2 is also indicated by the fact that manganese never enters into natural iron pyrite crystals, in spite of the rather close similarity of both the metallic radii and ionic

radii of the two elements."

Actually, it is probably just these similarities, as well as a similarity in the electronic configurations of the two elements, that accounts for the presence of the considerable amounts of manganese that are found in pyrite.

Chalcopyrite apparently contains the least manganese of the four minerals under consideration, although the difference between chalcopyrite and pyrite is so slight as to be of little significance. The maximum amount of manganese found in chalcopyrite is 8000 ppm, but there are many samples in which manganese was not detected.

The strong preference of manganese for sphalerite over chalcopyrite (figure 12E) poses nearly as many difficulties of explanation as does the similar behavior of cobalt. The closer similarities in electronic configurations and covalent radii between manganese and iron, as compared with zinc, indicate that the iron-bearing chalcopyrite should be at least as favorable a host as sphalerite for manganese. That it is not may indicate that the more ionic Mn-S bond makes the more ionic sphalerite structure a better host for manganese than the less ionic, more metallic chalcopyrite structure. This is essentially the same explanation that was proposed for the distribution of gallium, germanium, indium, and perhaps cadmium and cobalt.

Molybdenum

Molybdenum shows no great preference for any one of the four minerals under consideration, nor does it tend to occur in large amounts in the sulfides, except in molybdenite.

The largest concentrations of molybdenum that have been found in molybdenite-free material are 400 - 500 ppm in chalcopyrite and 200 - 300 ppm in sphalerite. The largest amounts that have been found in pyrite and galena are 40 ppm and 30 ppm, respectively, but a comparison of sample pairs indicates that there is essentially as much molybdenum in these two minerals as there is in chalcopyrite.

A comparison of the chalcopyrite-sphalerite pairs reveals, as shown in figure 12F, that molybdenum is slightly more concentrated in chalcopyrite than in sphalerite. This is in contrast to the behavior of most of the other elements considered so far, and apparently reflects a different nature of the molybdenum atom, as well as a possible concentration effect in the solutions. Its covalent radius (1.36 Å) is intermediate with respect to the major elements of the minerals concerned and, accordingly, it might be expected to occur in substitution for any one of these elements. Molybdenum has very little tendency to form tetrahedrally directed bonds, so there is no reason to expect its concentration in the tetrahedral sulfides, such as chalcopyrite and sphalerite. However, quadrivalent molybdenum has a strong tendency to form bonds that are directed toward the corners of a trigonal prism, as in molybdenite, and inasmuch as the interbond angles of this arrangement are not greatly different from the octahedral bond angles, as in pyrite, it might be expected that this latter mineral would be a preferred host for molybdenum. Similarly, the octahedral coordination of sulfur about lead in galena would make this mineral an equally good host for molybdenum, but the differences

in covalent and atomic radii of molybdenum and lead are very near the 20 percent limit.

To summarize the behavior of molybdenum in the four minerals, pyrite, sphalerite, chalcopyrite, and galena, it may be said that none of the minerals is a particularly good host. Perhaps this is the reason for the common occurrence of molybdenite in association with these minerals. Of the four minerals, pyrite is a little the better host for molybdenum, probably because of the more compatible coordination properties of molybdenum and iron in combination with sulfur.

Nickel

Nickel is strongly concentrated in pyrite, as shown in figure 11. The maximum amount of nickel in the analyses of pyrite in table 6 is 900 ppm, but this doubtless reflects the incompleteness of the present data. Bannister (1940) has suggested that there is a complete series from bravoite, with a nickel to iron ratio of 1:1, to nickel-free pyrite. The preference that nickel shows for pyrite is readily explained by the similarities in the atomic properties of nickel and iron, and the ability of nickel to form octahedral covalent bonds.

Among the remaining three sulfides, chalcopyrite is slightly preferred to sphalerite as a host for nickel (figure 12G), and galena appears to be free of the element. The slight preference for chalcopyrite, in which nickel occurs in amounts up to 500 ppm, perhaps is best explained by the similarities in the atomic properties of nickel and iron.

The absence of nickel from galena is understandable in view of the fact that the difference in covalent radius between nickel and lead is about 35 percent of the larger radius, too great for ready substitution of nickel for lead in galena.

Silver

Silver is very strongly concentrated in galena, a fact that has been known for a long time. However, there has been a dispute as to whether the silver that has been reported in analyses actually occurs in solid solution in the galena or is the result of contamination by a silver mineral. Palache, Berman, and Frondel (1946, p. 202) state that the silver that has been reported is presumably the result of contamination, whereas Goldschmidt (1954, p. 407) claims that galena can accept as much as 10,000 ppm silver in solid solution at higher temperatures, although unmixed metallic silver or silver sulfide usually is observed in such occurrences. The present studies clearly indicate that galena can contain more than 10,000 ppm silver without showing any signs under the microscope of the unmixing of another silver-rich mineral. In fact, textures involving galena and silver-bearing minerals that could be reasonably interpreted as the result of unmixing have not been observed in these investigations.

Because the atomic and ionic radii of silver (1.44 $\overset{o}{A}$ and 1.13 $\overset{o}{A}$, respectively) are considerably different from those of lead (1.74 $\overset{o}{A}$ and 1.32 $\overset{o}{A}$), Goldschmidt (1954, p. 408) doubts that the silver substitutes for lead in the galena structure. He suggests, instead, that the silver occurs in

the interstices that occur at the centers of the tetrahedral
groups of lead and of sulfur atoms, the dimensions of which
are about right to accom$\overset{m}{\underset{\wedge}{}}$odate the silver atom in tetrahedral
coordination. In essence, this is the process of interstitial
solid solution, so well known in metals but regarded as new
for minerals by Goldschmidt.

Among the other three minerals, sphalerite appears to
contain the least silver, whereas chalcopyrite and apparently
pyrite contain somewhat more. This order is not in full
agreement with that suggested by Goldschmidt (1954, p. 194),
which is, in order of increasing silver content: pyrite,
sphalerite, chalcopyrite, galena. Actually, Goldschmidt
placed pyrite first because, to his knowledge, pyrite had
never been proved to contain silver in solid solution. How-
ever, the results of the present investigations leave little
doubt that some pyrite, which under the mineragraphic micro-
scope is seen to be free of contamination by any other miner-
als, contains as much as 1000 ppm silver.

It might be argued that the magnifications obtainable
with the mineragraphic microscope are not sufficiently large
to exclude the possibility of extremely fine-grained mechanical
admixtures of silver-bearing minerals in pyrite. But, if this
view is held for the case in point, then it also must be held
for other examples, such as cadmium in sphalerite, for which
there is ample evidence (Kullerud, 1953; and others) that the
cadmium occurs in true solid solution in sphalerite. Further-
more, the probability is small that a mechanical admixture
would be so uniformly minute in grain size that none of the

grains would be visible microscopically, although a situation
such as this remains a possibility, judging from the occurrence
of cryptoperthite in feldspars.

Goldschmidt (1954, pp. 192-193) recognizes chalcopyrite
as a host mineral for silver, especially from the so-called
high temperature hydrothermal and magmatic deposits, but
apparently rejects sphalerite, judging from the following
statement (p. 193):

> "Earlier workers often alleged that zinc sulphide could
> be a host crystal for silver, but the spectrographic
> examination of very many lead-zinc ores, combined with
> a micro-metallographic investigation, demonstrates in
> nearly all cases that contamination by galena or other
> silver-bearing minerals is the cause of the alleged
> silver in sphalerite. Quite lately this has been
> demonstrated in a number of cases by I. Oftedal (1941)
> in the Oslo laboratory of the author."

The results of the present investigations do not support
the view that sphalerite is not a host for silver, for speci-
mens from which galena or other silver-bearing minerals are
absent, at least microscopically, contain as much as 300 ppm
or more of silver. But despite the fact demonstrated here
that silver occurs to an appreciable extent in uncontaminated
sphalerite, figure 12H clearly indicates that sphalerite is
a poorer host for silver than is chalcopyrite. Silver contents
of 1000 ppm in uncontaminated chalcopyrite are common.

The definite, although by no means extreme, preference
of silver for chalcopyrite over sphalerite is not readily
explained by differences in tetrahedral covalent radii, for
in the tetrahedral lattices of chalcopyrite and sphalerite,
silver (radius 1.53 $\overset{o}{A}$) should substitute about as readily
for zinc (1.31 $\overset{o}{A}$) as for copper (1.35 $\overset{o}{A}$) or iron (1.24 $\overset{o}{A}$).

However, in order to explain the preference for sphalerite of gallium, germanium, indium, and manganese, the greater ionic character of the M-S bonds associated with these metals can be called upon. Conversely, a metal that has less ionic character in its M-S bonds might equally well be expected to prefer chalcopyrite, especially if the bond is more metallic. Silver fulfills both of these latter requirements, and hence should be concentrated in chalcopyrite, as observed. Furthermore, it is probable that silver substitutes mainly for copper in chalcopyrite.

Tin

Tin is the only one of the 15 elements sought in the four minerals that shows a definite preference for chalcopyrite as a host (figure 11). It occurs in the chalcopyrite samples analyzed in these investigations in amounts as large as 8000 ppm, but the regional average is about 200 ppm tin. By analogy with the mineral stannite (Cu_2FeSnS_4), which is isostructural with chalcopyrite, it is evident that the tin in chalcopyrite is in the divalent state. Also by this analogy, it is suggested that the tin in chalcopyrite occurs in substitution for iron, and this leads to an interesting speculation concerning the possibility of a solid solution series between chalcopyrite and stannite. In this connection, Goldschmidt (1954, p. 394) points out that:

> "Many cases are known in which tin in small amounts enters sulphide minerals of other heavy metals, especially at higher temperature, and is again segregated at lower temperatures because of a decrease in solubility, usually as droplets of stannite."

Such relationships were not observed in the present investigations. In fact, stannite was not identified in any of the specimens represented by analyses in table 4. However, it is possible that not enough tin was present in the sulfide phase initially and hence did not unmix. If this is true, and there appears to be no other reasonable alternative, it may be concluded that even at the lower hydrothermal temperatures chalcopyrite can contain 5000 ppm or more tin in solid solution.

Pyrite from the more tin-rich regions contains as much as 1000 ppm tin, and the data available indicate that this mineral is as preferred a host for tin as is sphalerite. The substitution of appreciable amounts of tin for iron in pyrite perhaps is best explained by the fact that tin tends to form octahedrally directed bonds by utilizing the unstable d orbitals of the valence shell of electrons (Pauling, 1948, p. 184). In this coordination, tin has an effective radius of 1.45 $\overset{\circ}{A}$ and hence is not so greatly different from iron (1.23 $\overset{\circ}{A}$) that the substitution of tin for iron cannot readily take place.

On the other hand, in stannite, as well as in chalcopyrite and sphalerite, tin exhibits its even greater tendency to form tetrahedral sp^3 bonds, which result in an effective radius of 1.40 $\overset{\circ}{A}$. The slight enrichment of tin in chalcopyrite as compared with sphalerite (figure 12I) probably is due to the similarities in bond characteristics of tin and iron, and to the closely similar lattice constants of chalcopyrite and stannite. If the relationships between tin and

iron are important factors in the selectivity of tin, then it might be expected that iron-rich sphalerite, in general, would be richer in tin than iron-poor sphalerite.

According to Goldschmidt (1954, p. 395):

"I. Oftedal observed in a number of cases, when both sphalerite and galena were present in the same ore deposits, that tin at higher temperatures preferentially entered into the lead sulfide and at lower temperatures preferentially or exclusively into the zinc sulfide."

Although the present data on galena are incomplete, and there appears to be no reliable criterion for distinguishing high temperature from low temperature sphalerite and galena, the present investigations do not support Oftedal's interpretation. In fact, if Lindgren's classification of ore deposits is valid, and if the deposits that are represented by the present data have been properly classified, one might arrive at a conclusion opposite to that drawn by Oftedal.

A maximum of 300 ppm tin was found in the galena analyzed in these investigations, and Oftedal (1941) and Schroll (1952) report similar maxima for the tin content of galena from Norway and from southern Europe. The occurrence of considerable amounts of tin in galena may be explained by the similarities in both covalent and ionic radii of tin and lead, and by the fact that tin tends to form octahedral bonds*. Thus, tin is a prospective substituent for lead regardless of the final decision as to the exact nature of the bonding between lead and sulfur in galena. That tin is not present

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*Goldschmidt (1954, p. 406) has found that SnSb is isomorphous with PbS.

in greater amounts in galena perhaps reflects its preference for the tetrahedral structures.

Tellurium

Tellurium occurs in amounts as large as 1000 ppm in the galena of the Southwest, and a similar maximum is reported in Norwegian galena by Goldschmidt (1954). Warren and Thompson (1945) reported small amounts of tellurium in two sphalerite samples from British Columbia; and one sphalerite sample from Arizona that was analyzed in the present work contains 300 ppm tellurium. Pyrite and uncontaminated chalco-pyrite do not appear to contain tellurium in amounts greater than 100 ppm, the limit of spectrographic sensitivity. How-ever, Hawley (1952) reports small but undetermined amounts of tellurium in the pyrite of some Canadian gold ores.

A comparison of the Pb-S interatomic distance in galena (2.97 $\overset{\circ}{A}$) with the Pb-Te distance in the isomorphous altaite (3.21 $\overset{\circ}{A}$) reveals that the radius of tellurium in substitution for sulfur in galena is only about 13 percent larger than the radius of sulfur. On the other hand, tellurium in tetrahedral coordination, as in chalcopyrite, sphalerite, and pyrite, has a radius of 1.32 $\overset{\circ}{A}$, which is about 21 percent larger than the radius of sulfur (1.04 $\overset{\circ}{A}$). The reasons are apparent, therefore, for the preference that tellurium shows for galena.

Thallium

Chalcopyrite and pyrite were not analyzed for thallium in the present work, hence little can be said concerning the dis-tribution of this element in the sulfide ores of the Southwest.

The largest amount of thallium was found in galena (600 ppm), the only thallium-bearing galena analyzed. The most thallium-rich sphalerite, which contains 300 ppm, was obtained from the same polished section as the thallium-rich galena; hence, there is some suggestion that galena is a more favorable host than sphalerite for thallium. Apparently it was a similar observation that led Goldschmidt (1954, p. 338) to state:

> "In point of fact the author and his co-workers have never observed thallium as a constituent of natural iron disulphide. Where it has been found in such ores it is almost certainly connected with the presence of galena. In a recent monograph by I. Oftedal (1941) on spectrographic investigations of the minerals from Norwegian zinc ores, thallium was found exclusively in galena and in amounts up to 500 p.p.m. Tl. It was often accompanied by bismuth in the galena, and it is probable that one atom each of thallium and bismuth replace two atoms of lead.
>
> It is significant that the two related elements indium and thallium behave so differently when entering sulphide minerals. This is certainly due to differences in radii. The smaller indium invariably replaces zinc in sphalerite, while the larger thallium replaces lead in galena. It is not known whether the revelant radii in these minerals are ionic, metallic or tetrahedral covalent radii."

It is true that the few thallium-bearing Norwegian ores that Oftedal (1941) analyzed indicate that galena is the principal host for thallium, but even prior to Oftedal's work Stoiber (1940) demostrated that sphalerite from European zinc ores of "Mississippi Valley type" contains as much as 0.1 to 1.0 percent thallium. This was corroborated by Everard (1945), who found thallium in every one of 21 sphalerite samples from Belgian ores of the same type included by Stoiber. Futhermore, Schroll (1950; 1951), in a study of the lead-zinc ores from more than 40 deposits in southeastern Europe,

demonstrated that many of the sphalerite samples not only are thallium-bearing, in amounts as large as 1000 ppm, but that for a given deposit the sphalerite contains more thallium than the galena. Thus, it would appear that the conclusions concerning the exclusiveness of galena with respect to thallium are somewhat premature.

In connection with the statement quoted above, it might be mentioned that Schroll (1951) found no direct relationship between thallium and bismuth, as was first suggested by Oftedal (1941). Therefore, it is doubtful that thallium and bismuth occur in paired substitution for two lead atoms in galena in most cases; instead, they appear to behave entirely independently. Actually, unless one has preconceived ideas concerning the true nature of the Pb-S bond, it is not necessary to search for a trivalent element such as bismuth which could occur in paired substitution with univalent thallium, for both the atomic and covalent radii of thallium and lead differ by less than two percent. But if it is assumed that the bonding between lead and sulfur in galena is largely ionic, it then becomes necessary to call upon some mechanism such as paired substitution to account for the presence of thallium.

In view of the findings of Schroll (1950; 1951), the conclusion by Goldschmidt that the very different behavior of the related thallium and indium when entering sulfide minerals certainly is due to differences in radii has very little meaning. Actually, such a conclusion does not seem warranted on theoretical grounds alone, for the tetrahedral radius of thallium (1.47 $\overset{o}{A}$) is nearer that of zinc (1.31 $\overset{o}{A}$)

than is the radius of cadmium (1.48 $\overset{O}{A}$), and cadmium substitutes rather freely for zinc in sphalerite. Furthermore, the tetrahedral radius of indium (1.44 $\overset{O}{A}$) is almost insignificantly smaller than the radius of thallium.

Summary Statement

An attempt has been made in the foregoing discussions to demonstrate that the distribution of the trace elements among the four sulfides, pyrite, sphalerite, chalcopyrite, and galena is not determined by any single fundamental factor, but that each element behaves according to its properties and to the relationships of its properties to those of the constituent elements in the host minerals. This does not mean there is no system or order to the distribution, but it does mean that the observed distribution generally is the result of the interplay of several factors, all of which have not been considered in these discussions.

Trace Element Content of Sulfides Related to Type of Deposit

Attempts to associate certain minor and trace elements, or certain concentrations of elements, with particular types of ore deposits have been one of the chief concerns in nearly all the researches into the distribution of minor and trace elements in sulfide minerals since the very early work of De Launay and Urbain (1910). Except for this earliest work, in which more emphasis was placed on depth*, the general tendency has been to relate the minor and trace element content of certain sulfides, especially sphalerite, to the temperature type of deposit, mostly in terms of the Lindgren classification.

Thus Stoiber (1940) concluded that antimony and arsenic are concentrated only in sphalerite from low temperature deposits, and Hawley (1952) found the most arsenic in pyrite from low temperature gold deposits. The bismuth content of sphalerite, on the other hand, appears to increase with increasing temperature of formation, according to De Launay and Urbain (1910) and Goldschmidt (1954). Goldschmidt (1954) and Graton and Harcourt (1935) found that the cadmium content of sphalerite generally increases with decreasing temperature of formation, whereas Stoiber (1940) and Warren and Thompson (1945) found less cadmium in low temperature sphalerite ores than in mesothermal ores. However, all agree that sphalerite

---

*The depth concept of De Launay is not without its temperature significance. Furthermore, it carries with it an epoch, and consequently a province, connotation; i.e., ores deposited at a particular depth and hence in a particular temperature range are characteristic of certain epochs in certain regions.

from high temperature deposits generally contains the least cadmium. Goldschmidt (1954) concludes that pyrite and sphalerite from high temperature deposits generally contain the most cobalt, but he notes that Oftedal found the most cobalt in mesothermal pyrite.

There appears to be general agreement that the gallium content of sphalerite increases with decreasing temperature of formation (Graton and Harcourt, 1935; Stoiber, 1940; Warren and Thompson, 1945; Goldschmidt, 1954). There also is general agreement that germanium is concentrated in sphalerite from low temperature deposits (De Launay and Urbain, 1910; Graton and Harcourt, 1935; Abramov and Rusanov, 1938; Borovick and Prokopenko, 1938; Stoiber, 1940; Oftedal, 1941; Warren and Thompson, 1945; Fleischer and Harder, 1946; and Goldschmidt, 1954).

Indium is concentrated in sphalerite from high temperature deposits, according to Graton and Harcourt (1935), Abramov and Rusanov (1938), Borovick, Vlodavets, and Prokopenko (1938), Borovick and Prokopenko (1941), Prokopenko (1941), and Goldschmidt (1954); but according to Abramov and Rusanov (1938), Stoiber (1940), Oftedal (1941), and Warren and Thompson (1945), the greatest amount of indium occurs in sphalerite from intermediate temperature deposits. At least there is general agreement that sphalerite from low temperature deposits contains the least indium. However, Fleischer and Harder (1946) find no such correlation between the indium content of sphalerite and the type of deposit.

Warren and Thompson (1945) found the greatest amount of manganese in sphalerite from high temperature deposits and the least from low temperature deposits. Molybdenum is concentrated in sphalerite from medium temperature deposits, according to Stoiber (1940). Graton and Harcourt (1935) believe that silver is more abundant in sphalerite from medium to low temperature deposits, whereas De Launay and Urbain (1910) have arrived at the opposite conclusion. The tin content of sphalerite generally is highest in higher temperature ores, except in British Columbia where Warren and Thompson (1945) found the greatest amount of tin in sphalerite from medium temperature deposits.

The foregoing summary of the behavior of trace elements in sphalerite from different types of ore deposits, as observed by several workers, reveals that for some elements, notably germanium, there appears to be a correlation between the amount present and the type of ore deposit; for other elements, such as indium and silver, the correlation is poor; and for many others the data are insufficient to permit generalizations. Before definite conclusions are drawn, it should be recognized that the sampling of the so-called low temperature deposits is somewhat biased. Fully half the data that concern low temperature deposits represent only two regions, the Mississippi Valley region and the region of Europe that contains deposits of "Mississippi Valley type". Hence the data probably are unduly influenced by the sphalerite from two regions that, perhaps accidentally, have somewhat similar trace element contents, although there are

considerable differences as shown by Stoiber (1940) and Morris
and Brewer (1954).

It is possible, on the basis of evidence that still is
suggestive, that low temperature zinc sulfide deposits in sed-
imentary rocks, the constituents of which obviously have been
transported considerable distances ("Mississippi Valley type"),
could be richer in germanium than other types of deposits.
This is not so much because of low temperature, but because of
environment. That is, in passing through carbonaceous sedi-
ments, the solutions from which the sphalerite eventually was
deposited might have acquired the germanium that now is
concentrated in the sphalerite. This mechanism was considered
originally as a possible explanation for the appreciable
germanium content of the chalcopyrite that occurs, in associa-
tion with pitchblende, as a replacement of fossil wood in
certain of the Colorado plateau uranium deposits (see table 4,
districts 141 and 143).

If the "Mississippi Valley type" of deposit is excluded
from consideration, the present evidence does not support the
premise that sphalerite from epithermal deposits is richest
in germanium. Nor does it appear that the over-all trace
element content of either sphalerite or chalcopyrite is, in
general, closely related to the type of deposit in which the
mineral occurs. This could mean that the deposits studied
here are not properly classified, or that the trace element
content of sphalerite is not sensitive to temperature differ-
ences such as exist between epithermal and mesothermal
conditions, or that the classification has relatively little

temperature significance as far as the majority of Cordilleran
sulfide ore deposits are concerned. All these explanations
are considered meritorious and make the classifying, according
to temperature, of the ore deposits listed in tables 4 - 7
unwarranted. Furthermore, many deposits are placed in one or
the other (sometimes more than one) temperature category of
the Lindgren classification on the basis of their mineralogy,
and the mineralogy is determined to a very great extent by the
chemical composition. Hence, inasmuch as the trace elements
are controlled by the same processes that control the major
component elements of the ores, it is probable that the
chemical history, including the composition of the source
material, is at least as important as the so-called tempera-
ture type of deposit in determining the trace element content
of the sulfide minerals.

THE GEOGRAPHIC DISTRIBUTION OF TRACE ELEMENTS

General Statement

The existence of a distinct geographic distribution of trace elements in certain primary sulfide minerals was recognized very early by De Launay and Urbain (1910), but little emphasis was placed on the geographic or province aspect of the distribution until Stoiber (1940) pointed out that:

> "A closer similarity in composition of sphalerite from a single metallogenetic group of deposits than from deposits of a single temperature group suggests a further correlation between minor element content and the geology of sphalerite occurrence." (p. 513)

> "Sphalerite from the same metallogenetic group of deposits contains similar kinds and amounts of constituents but the composition of sphalerite from each region is distinctive." (p. 518)

This concept of a metallogenetic group that is characterized by a distinctive trace element content in sphalerite was enlarged upon by Warren and Thompson (1945, p. 334) who concluded that:

> "Metallogenetic provinces or zones are of primary importance in establishing the minor element content of sphalerite. Within a metallogenetic province or zone, the temperature and type of deposit in which the sphalerite occurs are important, but not determining factors.

> There appears to be a tendency for each mining camp in Western Canada to exhibit a characteristic assemblage of minor elements. This tendency is reflected in part by the minor elements which appear in sphalerite. There are several instances of one or more mines situated on the same, or intimately related lodes, exhibiting a striking similarity in their minor element content. However, in view of the fact that sufficient collaborative results are not yet available, no final conclusions relative to most of these minor areas may yet be made. Nevertheless, further work may profitably be carried on in this field: there is every indication that detailed studies will show that each important

orebody has a characteristic mineral assemblage
and, furthermore, a characteristic minor element
distribution in those minerals."

It is clear, then, that the concept of metallogenic
provinces that are defined by the trace or minor element
content of primary sulfide minerals has been fairly well
developed previously. It is also clear that more detailed
and comprehensive studies of the distribution of trace elements
in primary sulfides are needed in order to prove or disprove
the reality of such provinces, and to define some of these
provinces if they do exist. Thus, in the discussion that
follows, it is shown that a definite geographic distribution
of trace elements in certain primary sulfides (chalcopyrite
and sphalerite) exists. Moreover, some of the features of
the provinces thus defined in terms of the distribution of
certain individual trace elements are described.

Statistical Analysis of the Distribution of Trace Elements

In order to demonstrate the existence of a definite geo-
graphic distribution of trace elements in chalcopyrite and
sphalerite, it is necessary to determine whether the degree
of variation in the average concentration of a particular
element in one or the other of these minerals among the
mining districts is significantly greater than the degree
of variation among the individual samples from a single
mining district. Statistically, the hypothesis to be tested
is that the "between group variance" (the variance among all
the mining districts together) is not significantly different
from the "within group variance" (the variance within each of

the mining districts). If the results of the test cause this "null hypothesis" of equal variance to be rejected, it can be assumed, with a predetermined probability (level of significance), that there is a significant difference in the variances, and consequently that there is a definite geographic distribution of the particular element. In order to reduce the risk of rejecting an hypothesis that actually is true, a level of significance $\alpha = .005$ is selected. Thus, if the hypothesis of equal variance is rejected at this level of significance, there are less than five chances in one thousand that an error has been committed.

An assumption that underlies the simpler tests of the hypothesis of equal variance is that the deviations from the mean are normally distributed. This assumption was tested for the deviations from the arithmetic mean of the tin content of chalcopyrite and was found invalid, owing to a strong positive skewness (figure 13A). However, the deviations of the logarithms of the tin content from the geometric mean very closely approximate a normal distribution*, as shown in figure 13B. Therefore, the hypothesis of equal variance is tested on the assumption that the deviations of the logarithms of the concentrations from the geometric mean are normally distributed.

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*Ahrens (1954) found that the variations in the trace element content of igneous rocks closely approximate a lognormal distribution; and that trace element concentrations, in general, can be assumed to be distributed lognormally has been demonstrated very convincingly by Krige (1952 a,b) and by Sichel (1952) for gold assays in some African gold mines.

Figure 13. <u>A</u>, A frequency histogram of the percent deviations
from the arithmetic mean tin content of chalcopyrite with-
in each mining district. The strong positive skew indi-
cates that the deviations are not normally distributed
about the arithmetic mean. <u>B</u>, Frequency histograms of the
logarithmic deviations from the geometric mean tin content
of chalcopyrite within each mining district (heavy lines)
and among all the mining districts (light lines). In order
that the two histograms enclose equal areas, and hence be
directly comparable, the "between group" frequency scale
is made 124/59 (N_w/N_b) larger than the "within group"
frequency scale.
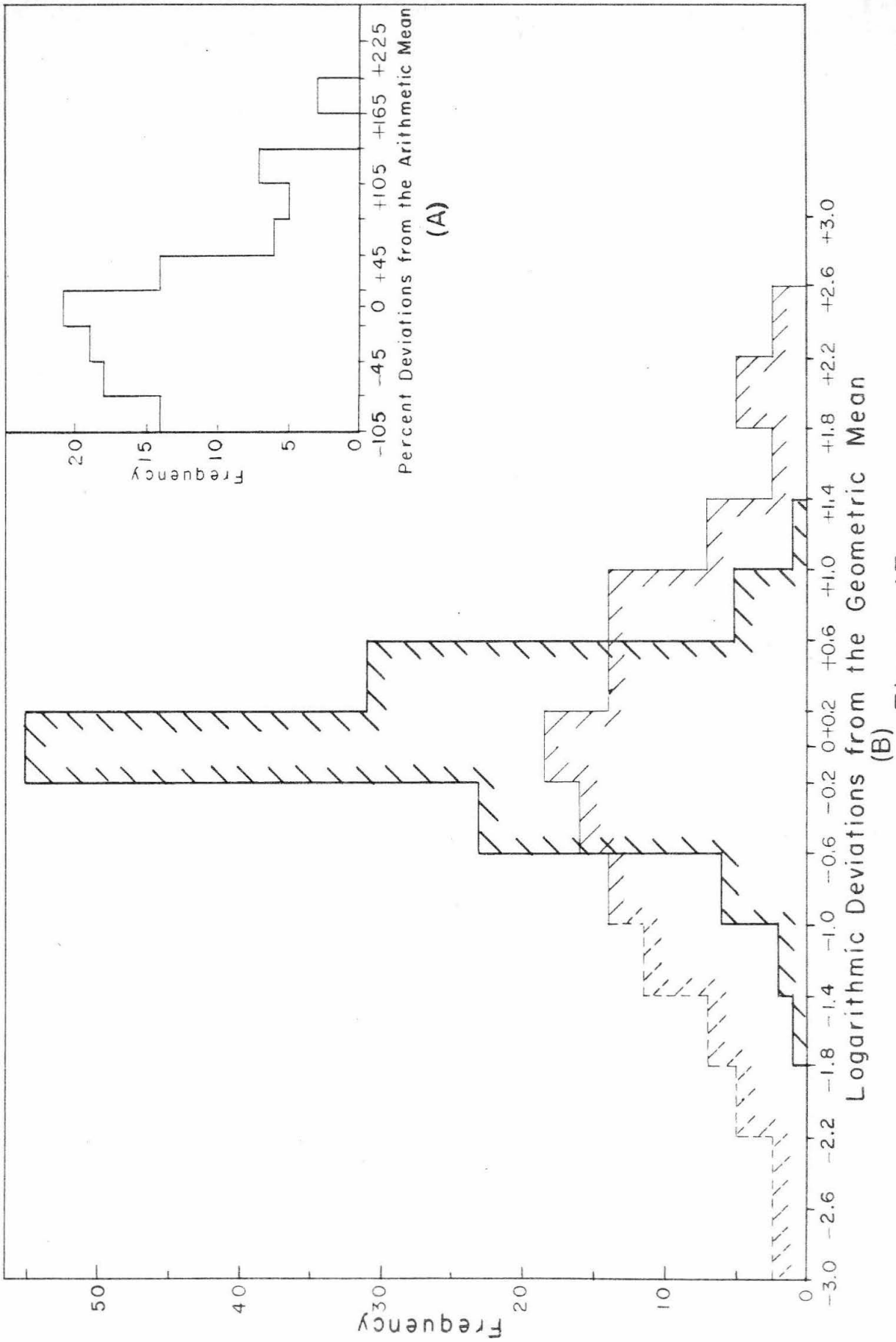
Figure 13

The analysis of the data in table 4 for the tin content
of chalcopyrite is summarized in table 8*. A comparison of

Table 8

Analysis of Variance of Tin in Chalcopyrite

Source of Variation	Sum of Squares	Degrees of Freedom	s^2	F
Between Groups (Among all mining districts)	37.67	54	0.711	
				3.84 $\neq\neq$
Within Groups (Within each mining district)	22.94	124	0.185	

$F_{0.995}(54,124) = 1.79$ (Dixon and Massey, 1951, p. 313)

the computed variance ratio (F) with the critical variance

ratio at the .005 level of significance clearly indicates

that the hypothesis of equal variance must be rejected. Hence,

it is concluded that the variations in the tin content of

chalcopyrite among the mining districts are significantly

greater than the variations within each mining district. This

same conclusion is readily surmised from a comparison of the

frequency histograms shown in figure 13B. The frequency

histogram shown in heavy lines represents the distribution of

the logarithms of the tin concentrations about the means for

each of the mining districts, and the frequency histogram

shown in light lines represents the distribution of the district

geometric means about the grand mean for all the mining dis-

tricts in the sample. The two histograms enclose equal areas

and are therefore comparable.

*The general form of this table was adopted from Krumbein and
Miller (1953).

A similar analysis of variance of the cadmium content of sphalerite yields the results summarized in table 9 and figure 14. Again it is clear that the hypothesis of equal variance must be rejected. Cadmium is of particular interest

Table 9

Analysis of Variance of Cadmium in Sphalerite

Source of Variation	Sum of Squares	Degrees of Freedom	s^2	F
Between Groups (Among all mining districts)	2.79	63	0.044	
				3.79 $\neq$
Within Groups (Within each mining district)	2.08	177	0.012	

$F_{0.995}(63,177)$ = 1.53 (Dixon and Massey, 1951, p. 313)

because of the relatively small range in its content in sphalerite throughout the Cordilleran region, the total variation being little more than tenfold. This is reflected in the small between-group variance (s^2 = 0.044) as compared with tin (s^2 = 0.711). Also of interest is the very small within-group variance, which emphasizes the remarkably uniform cadmium content of sphalerite within most mining districts.

The tin content of chalcopyrite and the cadmium content of sphalerite have been selected for statistical analysis because an inspection of tables 4 and 5 indicated that these elements perhaps show the strongest tendency toward a definite geographic distribution. Consequently, they cannot be considered as representative of the elements, the distribution of which is shown in the maps of plates 1 - 12. In order to obtain a more accurate appraisal of the general validity of

Figure 14. Frequency histograms of the logarithmic devia-
tions from the geometric mean cadmium content of
sphalerite within each mining district (heavy lines)
and among all the mining districts (light lines). In
order that the two histograms enclose equal areas, and
hence to be directly comparable, the "between group"
frequency scale is made 177/63 (N_W/N_b) larger than the
"within group" frequency scale.
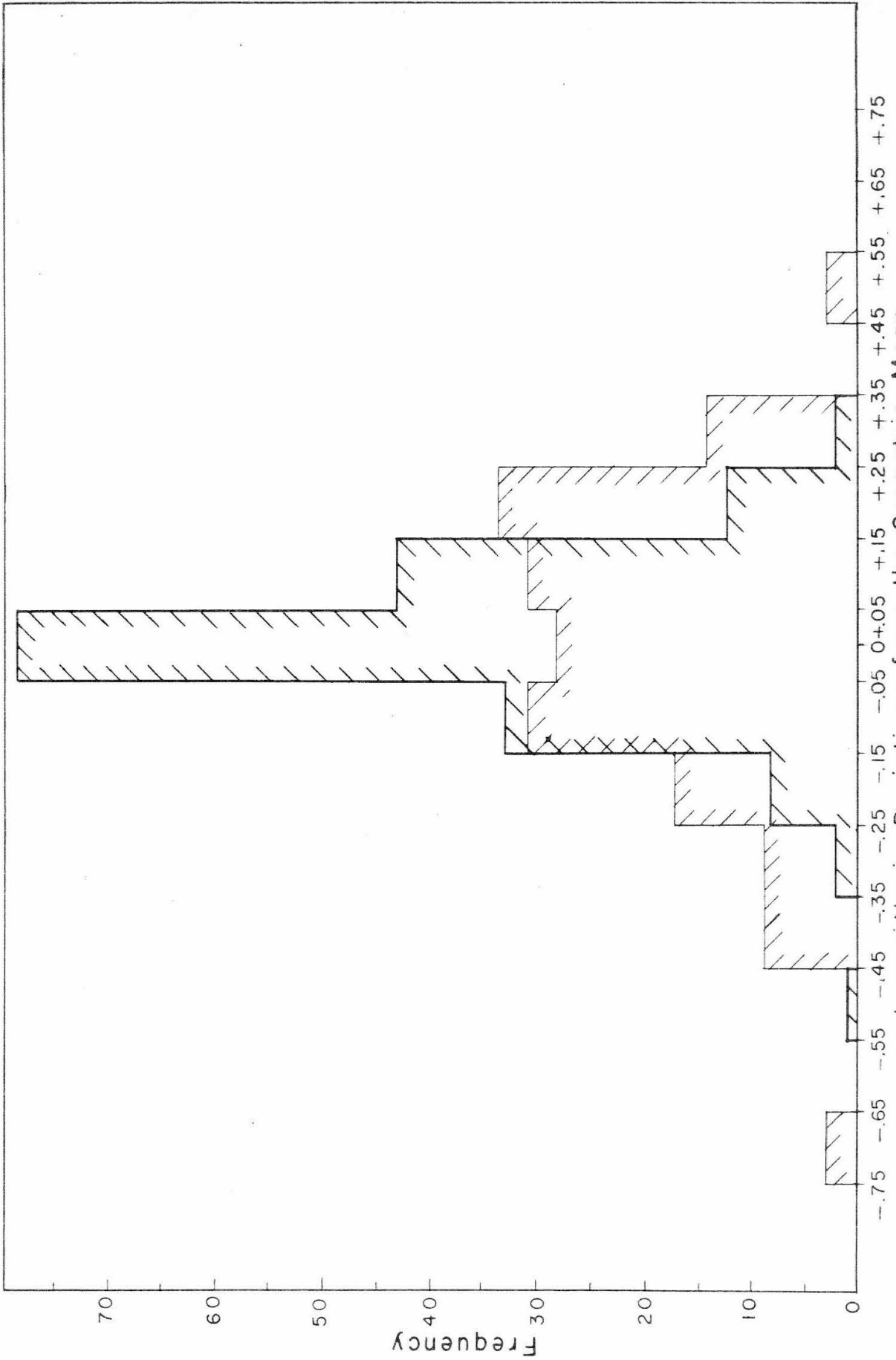
Figure 14

Logarithmic Deviations from the Geometric Mean

the features shown on these maps, another statistical analysis
was made of the cobalt content of sphalerite, which is consid-
ered typical of the elements represented in plates 1 - 12.
The results of this analysis are summarized in table 10 and
shown graphically in figure 15.   Once again it is clear that

Table 10

Analysis of Variance of Cobalt in Sphalerite

Source of Variation	Sum of Squares	Degrees of Freedom	s^2	F
Between groups (Among all mining districts)	39.99	61	0.667	
				3.09 //
Within groups (Within each mining district)	27.58	129	0.216	

$F_{0.995}(61,129)$ = 1.75 (Dixon and Massey, 1951, p. 313)

the hypothesis of equal variance must be rejected, and that
there is a significant difference in the variances.

It should be emphasized that all available data have been
utilized in the statistical analyses that have been summarized
in the foregoing; i.e., every mining district that is repre-
sented in tables 4 and 5 by more than one spectrochemical
analysis is included in the statistical analyses.   Although
this procedure furnishes the most accurate statistical infor-
mation concerning the data utilized in the construction of
plates 1 - 12, it does not permit a precise evaluation of the
variances that actually exist within each of the mining dis-
tricts.   The reasons are that much material was utilized in
the present studies about which nothing is known firsthand

Figure 15. Frequency histograms of the logarithmic devia-
     tions from the geometric mean cobalt content of sphal-
     erite within each mining district (heavy lines) and
     among all the mining districts (light lines). In
     order that the two histograms enclose equal areas, and
     hence be directly comparable, the "between group" fre-
     quency scale is made 129/62 (N_W/N_b) larger than the
     "within group" frequency scale.

Figure 15

Logarithmic Deviations from the Geometric Mean
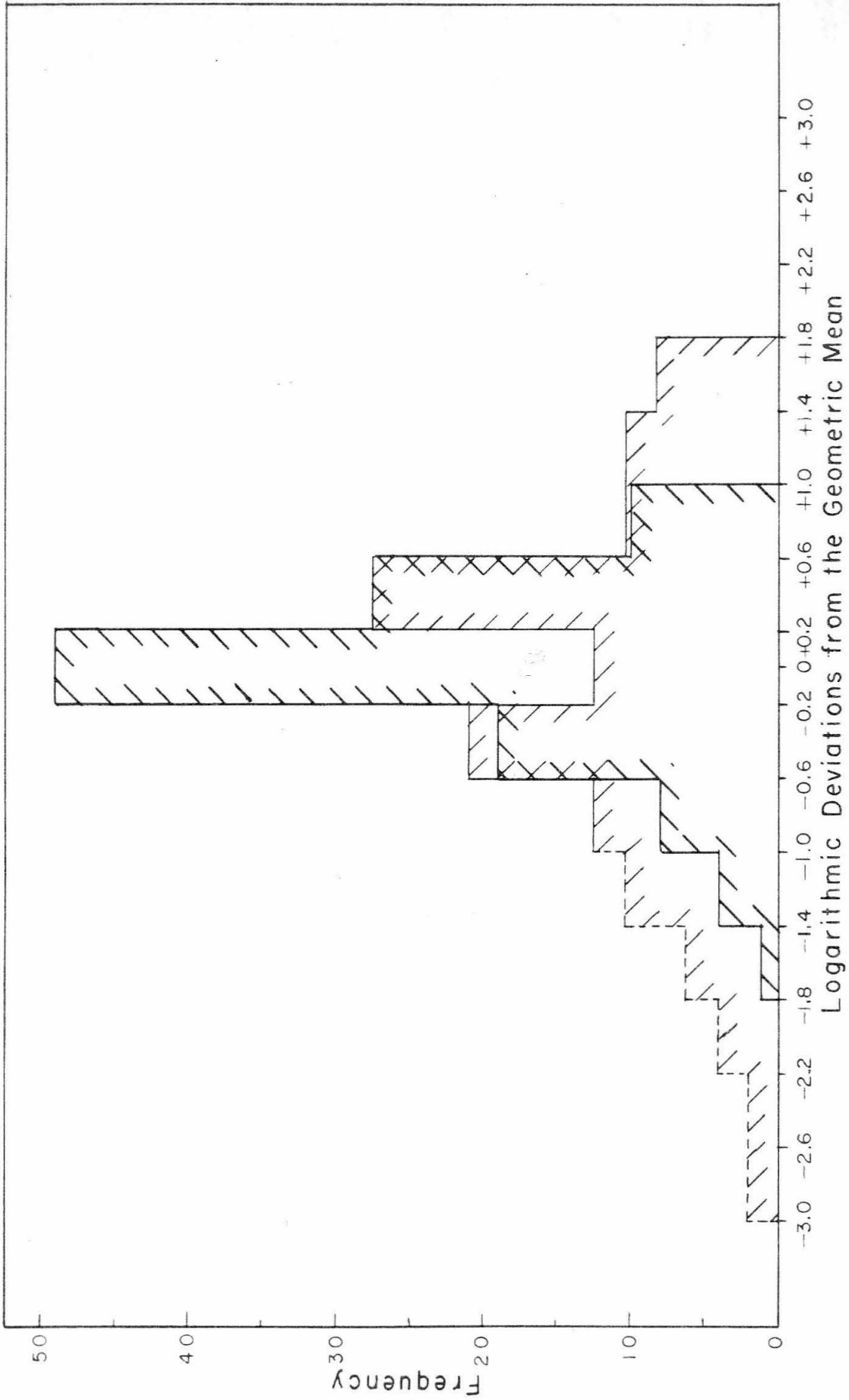
and hence some of which is likely to be incorrectly labeled; and the data are grouped into arbitrary geographic units, the mining districts, the sizes of which are greatly different in different regions.

An estimate of the effect these two factors might have on the within-group variance can be obtained by a comparison of the within-group variance of a group of samples, the sources of which are known, with the within-group variance of all the data. Thus, an analysis of variance was made of the tin content of chalcopyrite that was collected by the writer or was obtained firsthand from the collector. This analysis is summarized in table 11, and a comparison with table 8 reveals that the within-group variance of the reliable

Table 11

Analysis of Variance of Tin in Selected Samples of Chalcopyrite

Source of Variation	Sum of Squares	Degree of Freedom	s^2	F
Between Groups (Among all mining districts)	16.52	18	0.918	
				12.1 //
Within Groups (Within each mining district)	3.39	45	0.076	

$F_{0.995}(18,45$ = 2.62 (Dixon and Massey, 1951, p. 313)

data is less than half the within-group variance of all the data. It is also evident from the variance ratio (F) in table 11 that if the sampling is completely reliable and the geographic unit is the mine or relatively small group of mines, the significance of the differences in the "district" averages would be even greater than tables 8 - 10 indicate. It is

concluded, therefore, that there is no statistical reason to doubt the existence of a well defined geographic distribution of trace elements in chalcopyrite and sphalerite.

The Geographic Distribution of Trace Elements in Chalcopyrite

The existence of a definite geographic distribution of trace elements in chalcopyrite and sphalerite having been demonstrated with a fairly high degree of probability, there remains the description of the salient features of the provinces defined by this distribution. Therefore, in the discussion that follows, the geographic distribution of each of the trace elements in chalcopyrite will be described in alphabetical order, with special emphasis placed on those elements that are represented in plates 1 - 6.

Antimony

It has not been possible to determine precisely the geographic distribution of antimony in chalcopyrite for three reasons: (1) chalcopyrite does not readily accept appreciable amounts of antimony into its crystal structure; (2) the spectrographic sensitivity of antimony is relatively poor, about 30 ppm, precluding a knowledge of the distribution of smaller quantities; and (3) antimony-bearing minerals, particularly tetrahedrite, commonly are associated with chalcopyrite and therefore are potential contaminants in many places.

The high concentrations of antimony in galena from some areas, as shown in table 7, make this mineral a potential indicator of the geographic distribution of antimony.

However, in the absence of sufficient data on the trace element content of galena, a general idea of the geographic distribution of antimony may be obtained from a knowledge of the distribution of silver (plates 4 and 11). This is possible because, as noted previously, antimony nearly always is associated with greater than average amounts of silver (cf. tables 4, 5, and 7), although the converse is not true; i.e., silver-rich ores are not always antimony-rich.

Arsenic

The geographic distribution of arsenic in chalcopyrite is even more difficult to determine than the distribution of antimony, because of the poorer spectrographic sensitivity of arsenic (about 100 ppm). However, the chances of contamination are not as great because tennantite and enargite are considerably less abundant than tetrahedrite, and arsenopyrite does not generally form intergrowths with chalcopyrite.

In general, arsenic is not common enough in spectrographically detectable amounts to permit the determination of its geographic distribution. Furthermore, unlike antimony, arsenic does not appear to be associated with silver or any other of the elements sought. This difference in behavior between arsenic and antimony with respect to silver is further exemplified by the rarity of argentian tennantite as compared with argentian tetrahedrite (freibergite).

Bismuth

The geographic distribution of bismuth is not well defined owing to the erratic behavior of the bismuth content

of chalcopyrite within many of the mining districts. There-
fore, no attempt has been made to evaluate its distribution
quantitatively. However, in a very general way, it may be
noted that bismuth is a more common constituent of chalcopyrite
from deposits in southern Arizona and adjacent parts of Sonora,
and along the belt that extends northwestward through the
central part of Arizona to the Nevada border (plate 6).
Throughout the remainder of the Southwest, bismuth appears to
be distributed sporadically along the belts of high combined
trace element content that are shown in plate 6.

It is possible that the erratic behavior of bismuth in
chalcopyrite is a consequence of its very strong preference
for galena. That is, the amount of bismuth that is incorpo-
rated in the chalcopyrite lattice during crystallization from
bismuth-bearing hydrothermal solutions might well depend upon
the amount of lead present, as well as upon the concentration
of bismuth. The higher than average concentrations of bismuth
in some of the chalcopyrite analyses in table 4 may be the
result of contamination by galena, but nearly all the very
high bismuth contents occur in samples that were associated
in the polished sections with bismuth-bearing minerals such
as bismuthinite.

Cadmium

No reliable data are available concerning the geographic
distribution of cadmium in chalcopyrite. The likelihood of
contamination by admixed sphalerite, which contains essential-
ly all the cadmium in the average base metal ores, is too

great to warrant any geographic interpretation of the cadmium analyses in table 4.

Cobalt

The geographic distribution of cobalt in chalcopyrite is shown in plate 1. In the construction of this and the other maps in plates 1 - 12, wherever an alternative existed in the direction of trend of the belts, the distribution of tin in chalcopyrite (plate 5) was used as a guide. The main reason for doing this is that tin exhibits a better defined and more consistent geographic distribution than any of the other elements investigated.

An interesting feature of the distribution of cobalt is the association of fairly large amounts of it with the pitch-blende-bearing ores in southeastern Utah (districts 141* and 143). This association of cobalt with uranium, which apparently is worldwide, leads to interesting speculation concerning the cobalt-rich belt that extends from north central Mexico north-northwestward, probably to very near the New Mexico border. However, it should be pointed out that although nearly all pitchblende or uraninite-bearing ores are cobalt-iferous, not all cobalt ores are uraniferous.

Another feature of the distribution of cobalt in chalco-pyrite is the weakness of the Central belt through Arizona and the Eastern belt in New Mexico and parts of Colorado. The fork in the Western belt in Nevada is problematical, for it

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*The cobalt content reported for district 141 might be in error owing to possible contamination by cobaltite, which is present in the polished section.

is based on very scanty data.

It is possible that cobalt is subject to enrichment and impoverishment factors similar to those that might affect bismuth. That is, the presence of abundant pyrite, which is much the better host for cobalt, could cause the chalcopyrite to become impoverished in this element. However, Gavelin and Gabrielson (1947) have found no such effect in the pyrite and chalcopyrite from the same specimen. Thus, if the pyrite contains a higher than average amount of cobalt, the chalco-pyrite generally contains a higher than average amount also.

Germanium

Germanium is a rare trace element in the chalcopyrite of the Southwest. The only really noteworthy occurrences are in the chalcopyrite from the Colorado plateau uranium deposits (districts 141 and 143), and from the copper ores of Butte, Montana (district 172).

The occurrence of appreciable amounts of germanium in the chalcopyrite that, together with pitchblende, replaces fossil wood, suggests the possibility that the germanium might not have been originally associated with the sulfides, but was merely acquired by the chalcopyrite through the replacement of slightly germaniferous fossil wood. This explanation is just an alternative to the hypothesis of a primary origin for the germanium, and it certainly cannot be the explanation for the presence of germanium in the chalcopyrite from Butte, Montana.

Indium

The geographic distribution of indium in chalcopyrite is shown in plate 2. Important features of this distribution are the discontinuous nature of the belts, the northeast trend in Colorado along the "Colorado mineral belt", and the east-west trend in Mexico.

More important than the northeast trending belt in Colorado, however, is the area of very low indium content that lies across the belt in the San Juan region. The ore deposits in this area of anomalously low indium content are in the Tertiary San Juan volcanics, whereas the deposits in the more indium-rich areas on either side are in older, mostly sedimentary rocks. This phenomenon is discussed further on, in connection with tin, which has a similar distribution.

An apparent association of indium with tin has been noted by several workers (Borovick and Prokopenko, 1939; Brewer and Baker, 1936; Fleischer and Harder, 1946). A comparison of plates 2 and 5 indicates that there are very few deposits of chalcopyrite that are indium-rich and tin-poor, but that there are many deposits that are tin-rich and indium-poor. This suggests another unilateral association similar to those of antimony with silver and uranium with cobalt, but not vice-versa.

Manganese

No attempt has been made to evaluate quantitatively the geographic distribution of manganese in chalcopyrite for two reasons: (1) much of the manganese could readily have come

from the wall rocks of the deposits; and (2) the behavior of manganese in chalcopyrite generally is erratic. Both these difficulties doubtless stem from the fact that manganese is somewhat more oxyphile than the other elements here under consideration. Consequently, the number of factors that influence the concentrations of manganese, both in the solutions and in the solid phases, are greatly increased.

Molybdenum

The molybdenum content of chalcopyrite, like manganese, is very erratic in behavior within many mining districts. Consequently, it has not been possible to present even a semiquantitative picture of its geographic distribution. It can be seen from table 4, however, that the molybdenum content of chalcopyrite is greater along the Central belt in Arizona (plate 6) than in any other region, except the one that includes the two Colorado plateau uranium deposits (districts 141 and 143).

It is of interest to note that chalcopyrite from the molybdenite-rich Climax mine in Colorado and Childs-Aldwinkle mine in Arizona is not particularly molybdenum-rich (about 10 ppm), whereas chalcopyrite from other, molybdenite-poor deposits may contain several hundred parts per million molybdenum. No logical explanation for this phenomenon has been forthcoming. Perhaps it is connected with some unusual paragenetic factors.

Nickel

The geographic distribution of nickel in chalcopyrite, as shown in plate 3, has several features in common with the distribution of cobalt, as might be expected from the chemical similarities of the two metals, but there are some important differences. The two Colorado plateau uranium deposits (districts 141 and 143) are nickeliferous as well as cobaltiferous. The Friday mine at Julian, California (district 52), is relatively richer in nickel than in cobalt. This may be an expression of the fact that this deposit is one of the few presumedly magmatic segregation sulfide deposits in the Southwest. However, the continuation of a nickel-rich belt northwestward through district 51, a contact metamorphic deposit, indicates that the high nickel content of the chalcopyrite from the Julian district is largely a regional feature, and that perhaps a local enrichment is superimposed upon it.

The fork in the Western belt in northwestern Nevada is problematical, as is a similar feature in the distribution of cobalt. However, a specimen of chalcopyrite (N-122, district D, table 4) from the Stone mine, Pershing County, Nevada, the exact location of which is unknown, is nickeliferous and probably came from this west fork about midway between the junction with the Western belt and district 93.

The northeast trend in the extreme southeastern part of Nevada also is problematical, mainly because it is not consistent with the trends of the other trace elements. The deposit in district 131 that furnished the indications for

this trend has been classed as a magmatic segregation deposit by Lindgren and Davy (1924). Hence it would appear that the nickel content of chalcopyrite from some deposits of extreme type such as this perhaps should not be compared with the nickel content of hydrothermal ores that are associated with the intermediate and more silicic intrusive rocks.

Silver

The relatively common occurrence and the great range in concentration of silver in chalcopyrite combine to produce a well defined geographic distribution, as shown in plate 4. However, because of the danger of contamination by silver-bearing minerals, no attempt has been made to distinguish on the map the geographic distribution of silver contents in excess of 100 ppm. The area in central Nevada between districts 99, 110, 125, and 130 on one side, and districts 103, 113, and 129 on the other, for lack of information, is covered on the map with the 30-100 ppm pattern.

A feature of plate 4 that is of particular interest is the fairly direct relationship between the silver content of chalcopyrite and the regional productivity of silver (cf. plate 13). There might be mentioned in this connection the Comstock district (112) in western Nevada, several deposits in central and south-central Nevada, the Colorado mineral belt, and many deposits in Chihuahua, Durango, Zacatecas, San Luis Potosi, etc.

The difference in the silver content of chalcopyrite from the two Colorado plateau uranium deposits (districts 141 and

143) is of interest in connection with a possible relationship between the distribution of silver and of uranium. Thus, although the present evidence is only suggestive, it is possible that the silver-rich belt on which district 143 is presumed to lie joins the Eastern belt in southwestern New Mexico. Such an interpretation is compatible with the present knowledge of the associations and distribution of cobalt and of the distribution of uranium deposits*.

Tin

The existence of a very pronounced regional distribution of tin in chalcopyrite was recognized very early in the present studies, and hence more emphasis has been placed on the distribution of tin than on most of the other elements. In fact, the realization that tin, perhaps more than any other metal, is concentrated into certain regions of the earth's crust has led to the use of its distribution, as shown in plate 5, as a model in the construction of several of the maps in which the distribution is not so well defined. Conversely, the distribution of some other elements, notably silver, has been used to work out some of the details of the tin distribution. For example, without knowledge of the silver distribution, it would have been about as reasonable to continue the Western belt for tin southward west of district 52.

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*Recently specimens of very rich pitchblende ore, presumably from Chihuahua, have been acquired by some American mineral collectors.

One of the more remarkable features of the tin distri-
bution in plate 5 is the continuity of the Central belt. This
is in contrast to the Eastern belt, which is very strongly
expressed along most of the Colorado mineral belt, but which
apparently does not continue through southern New Mexico.
However, the tin deposits of the Taylor Creek district, New
Mexico, about 60 miles north of district 83, may be signifi-
cant in connection with the southward extension of the tin-
rich belt from Colorado.

In the San Juan region of southwestern Colorado, the
Eastern tin belt is practically severed by a tin-poor area.
A similar feature occurs in the heart of the Western belt in
north-central Nevada (district 98). Although the cause for
this phenomenon is not known, the fact that all the deposits
that exhibit this anomaly occur in thick piles of tuffaceous
volcanic rocks perhaps is significant. It is possible that
the higher oxidizing environment of these rocks promotes the
early separation of tin from the sulfide-bearing solutions
and the fixation of it in cassiterite. This tentative
explanation gains plausibility from the similar behavior of
indium, an element that, because of chemical similarities to
tin, would be expected to react to the postulated conditions
in a similar manner.

Tin exhibits a well defined geographic distribution not
only as a trace element in chalcopyrite and sphalerite, but
as economically important deposits as well. This distribution
of tin has been known for many years, and the problems
connected with it have been summarized recently by Goldschmidt

(1954, pp. 92-93) as follows:

"A difficult problem in the geochemistry of tin is the question, whether or not tin is distributed evenly in corresponding rocks of different regions of the globe. The data available seem to indicate that there are important regional variations. It was observed long ago, and probably even known to prehistoric man, that an obviously regional concentration existed, but the average amount of tin in ordinary magmatic rocks seems also to show regional variations." "The scarcity of tin deposits in the enormous region stretching from the northern Urals to near the North American west coast is certainly not due to the absence of such magmatic rocks as are commonly followed by tin deposits in 'tin regions'.

Tin is not the only metal which is subjected to such regional concentrations and deficiencies. Tungsten in this respect is very closely associated with tin in the same type of deposits. Molybdenum also is subject to regional variations, but these seem to be independent of those of tin and tungsten or even reciprocal to them, as in Norway, where tin and tungsten are practically absent while workable molybdenum deposits are found associated with granites of very different geological ages from early Precambrian to Permian.

The absence of workable tin deposits in large regions of the earth, which are also characterized by the scarcity of even small amounts of tin minerals, seems also to be followed by a scarcity of tin as a 'trace element' as indicated by spectroscopic observations on magmatic rocks.

The problem then arises, Is this unquestionable difference in the abundance of tin (and tungsten or molybdenum) in various regions of the globe due to regional differences in the efficiency of the processes that concentrate tin in such rocks as granites?"

The positiveness of Goldschmidt's statements concerning the regional distribution of tin, tungsten, and molybdenum are of considerable interest, as well as somewhat puzzling, for practically nowhere else in the discussion of the geochemistry of the elements is there a suggestion that similar relationships might exist with respect to the other elements. In fact, in most of the discussions in the literature

concerning the crustal abundance of the elements, the assumption is implicit that earth materials from relatively small regions of the globe are representative of the whole.

The reciprocal relation of molybdenum to tin and tungsten that Goldschmidt suggests is not supported by the present studies, at least not on the trace element level. A majority of the molybdenum-bearing chalcopyrite deposits, as well as the more important molybdenite deposits, occur within or very close to the tin belts as they are defined in plate 5. In fact, tin has been a byproduct in the recovery of molybdenum at the Climax mine in Colorado (district 62).

Combined Metal Content of Chalcopyrite

A comparison of the maps in plates 1 - 5 reveals a close relationship between the positions and trends of the belts of greater than average trace element content. This relationship is significant, for it implies a fairly high degree of correlation in occurrence among the metals, at least among the five metals represented. In order that these distributional relationships might be more readily visualized, the district average cobalt, indium, nickel, silver, and tin contents of chalcopyrite have been combined as the logarithms of their products, and the distribution of the quantities thus obtained are shown in plate 6. The reason for combining the individual metal contents in this manner is to reduce the effect of unusually high concentrations of a particular metal that otherwise would dominate the combined metal content.

Before proceeding to a detailed discussion of plate 6, it should be emphasized that the belts shown represent an aggregate effect. If the maps of any two of the constituent elements are superimposed, it will be seen that in many places the axes of the individual belts do not coincide, whereas in other places, such as in central Arizona, most of the belts very nearly coincide. This means that although the degree of correlation in occurrence between the five metals is fairly high, it is by no means perfect. If another group of metals had been combined in similar fashion, the axes of the aggregate belts doubtless would not exactly coincide with those shown in plate 6, although they would be essentially parallel in trend. However, the significant fact demonstrated in plate 6 is that the belts of the five metals individually overlap to such an extent that their aggregate effect results in a very well defined geographic distribution of the combined metal content of chalcopyrite.

Although the distribution of trace elements in chalco-pyrite is unknown in the region of central Mexico south of the southern end of the patterned area in plate 6, the distribution of metalliferous deposits suggests that the continuation of the belt shown would be mainly in a south-southeasterly direction. Also from the distribution of metalliferous deposits, there is a very vague suggestion that the Western belt eventually joins this main belt, perhaps in the region of the state of Queretaro. North of this hypothetical junction, the main belt trends northwestward through San Luis Potosi and thence west-ward into Zacatecas. In Zacatecas the main belt branches;

one branch belt continues westward and the other turns north-
westward. In the vicinity of the junction, each of the five
metals makes a significant contribution to the combined metal
content. In the northeastern branch, cobalt, nickel, and
silver are the main contributors, and indium and tin are
relatively unimportant. On the other hand, indium, silver and
tin are most important in the southwestern branch, and cobalt
and nickel are practically lacking.

The northeastern branch, characterized by cobalt, nickel,
and silver, continues north-northwestward as the Eastern belt
into southwestern New Mexico, thence north-northeastward and
northward through New Mexico into southwestern Colorado. In
southwestern Colorado, the Eastern belt changes course again
to the northeast, along the Colorado mineral belt. However,
the combined metal content of the chalcopyrite of the Eastern
belt in Colorado is no longer characterized by cobalt, nickel,
and silver, but by indium, silver, and tin; the same assem-
blage as the one that characterizes the southwestern branch
in Zacatecas.

This southwestern branch, which becomes the Central belt
in the United States, courses first westward through Durango,
thence northwestward through Sinaloa and northward through
Sonora into southeastern Arizona. Thence, through a weak
connection, the Central belt continues northwestward through
central Arizona and westward into Nevada and California,
whence it veers back northeastward and continues into north-
western Utah. The character of this belt remains much the
same from Zacatecas to south-central Nevada. From Nevada

northeastward, the indium content decreases and is compensated
by an increase in nickel and, to a less extent, cobalt. The
tin, as well as the silver, persists, however, and becomes the
characteristic feature of the Central belt.

The extension of the Western belt southward from southern
Arizona is conjectural. Presumably it is the belt that joins
the main belt in Queretaro, and it very likely is silver-rich.
The combined metal content of chalcopyrite in the Western belt
in southern Arizona consists largely of cobalt, silver, and
tin. Nickel also becomes important in southern California.
In central California, the Western belt branches, but the main
branch, to which the name Western belt is still applied, con-
tinues northeastward through Nevada. The western branch,
characterized by silver and tin, courses northward into
northern California.

The Geographic Distribution of Trace Elements in Sphalerite

The geographic distribution of trace elements generally
is not as well defined in sphalerite as in chalcopyrite, hence,
sphalerite is not as suitable a geographic indicator as is
chalcopyrite. The principal reason for the mediocrity of
sphalerite in this respect is that tin, the mainstay of the
trace element distribution in chalcopyrite, is somewhat
erratic in behavior in sphalerite. Moreover, cadmium, which
in sphalerite should be the counterpart of tin from the stand-
point of uniformity of content within each district, is not
very suitable as a geographic indicator because the total
range in its concentrations is only about tenfold, not great

enough to produce a well defined geographic distribution in many large regions. In view of these disadvantages, less emphasis is placed on sphalerite as an indicator of the geographic distribution of trace elements than is placed on chalcopyrite.

Antimony, Arsenic, and Bismuth

The behavior of antimony, arsenic, and bismuth in sphalerite is very much the same as in chalcopyrite. Therefore, the discussions of the geographic distribution of these elements in chalcopyrite are equally applicable to sphalerite.

Cadmium

An attempt was made to represent the geographic distribution of cadmium in sphalerite on a map, but it was abandoned because a great deal of uncertainty arose as to the significance of the small differences in cadmium content among mining districts throughout large areas. This uncertainty is a consequence of the small total range in the cadmium content of sphalerite throughout the Southwest. However, in some regions where the range in cadmium content of sphalerite is from about 1000 to 10,000 ppm, such as in southern Arizona and southwestern New Mexico, the distribution is well defined and is consistent with the trends in the distribution of the other trace elements. On the other hand, in Nevada and in most of northern Mexico, the total range in cadmium content is so small that no definite distribution can be discerned. This generally uniform behavior of cadmium in sphalerite is interpreted as an indication that whatever the processes may be that concentrate

and/or disperse the elements in the earth's crust, they cannot
effectively separate nor can they distinguish cadmium from the
chemically very similar zinc.

Cobalt

The geographic distribution of cobalt in sphalerite, as
shown in plate 7, resembles in several respects the distribu-
tion of cobalt in chalcopyrite, although there are some im-
portant differences. With respect to similarities, the East-
ern belt in Mexico is particularly noteworthy. There are also
similarities in the Western belt in southern Arizona, central
Nevada, and presumably in California. In general, however,
the differences are more noteworthy than the similarities.
The near lack of cobalt in chalcopyrite from the Central belt
in Arizona is in contrast to the well developed belt in the
cobalt content of sphalerite. Similarly, in New Mexico and
Colorado, chalcopyrite gives little indication of the exist-
ence of an Eastern belt, whereas sphalerite exhibits two
cobalt belts in New Mexico and a pronounced though somewhat
irregular distribution in Colorado. There is an indication
of a northeast as well as a northwest trend in the cobalt
content of sphalerite in Colorado, but the data are not
absolutely conclusive.

Gallium

The gallium content of sphalerite has a fairly well
defined geographic distribution, as shown in plate 8, but
there are some complicating local irregularities. Some of
these irregularities conceivably might be due to contamination

by gallium-bearing aluminous wall rocks, but the magnitude of such an effect probably would be small. The relatively high concentrations of gallium in sphalerite from the Central belt in Utah and the Western belt in Nevada are especially noteworthy. There is again a strong indication of a northwest trending belt in Colorado, whereas there is little indication of a northeast trend parallel to the Colorado mineral belt.

Germanium

The most striking features of the geographic distribution of germanium in sphalerite shown in plate 9 are the relatively high concentrations in the Central and Western belts in Nevada and the general scarcity elsewhere in the Southwest. This is in contrast to the general abundance of germanium in sphalerite throughout much of the Mississippi Valley region. The sphalerite deposits in the Western belt in central and northeastern Nevada are of particular interest as potential commercial sources of germanium. The determining factor in this respect, of course, would be the amount of sphalerite in the deposits.

Indium

A unique feature of the geographic distribution of indium in sphalerite (plate 10) is the fork in the Central belt in southern Nevada. The cause for this anomalous feature is not apparent. It stands in strong contrast to the distribution of indium in chalcopyrite, for chalcopyrite from this region is practically free of indium.

There is again a strong indication of a north-northwest trend in the Eastern belt in Colorado, although the northeast

trend of the Colorado mineral belt also is expressed. The
Eastern belt in New Mexico is evident in the indium content
of sphalerite, whereas indium is absent from the chalcopyrite
of this region.

In chalcopyrite there appears to be a definite association
of indium with tin; i.e., indium-rich chalcopyrite also gener-
ally is tin-rich. No such relationship exists between indium
and tin in sphalerite from the Southwest, for there are many
indium-bearing sphalerite samples that are not tin-bearing.

Manganese and Molybdenum

Although the average manganese content of sphalerite is
several times that of chalcopyrite, the characteristics of its
behavior in the geographic sense are very similar in the two
minerals. Hence the generalizations concerning the geographic
distribution of manganese in chalcopyrite are equally appli-
cable to sphalerite. Similarly, the behavior of molybdenum
in sphalerite is essentially the same as in chalcopyrite,
except for a slightly lower average concentration in sphalerite.

Nickel

Generally the nickel content of sphalerite is not great
enough to reveal a well defined geographic distribution by
itself. However, an examination of table 5 indicates that
most of the slightly nickeliferous sphalerite occurs within the
belts defined by the nickel content of chalcopyrite (plate 3).
Hence, if the sphalerite from a district is nickeliferous, the
chalcopyrite from that district also is likely to be nickel-
iferous. This is in agreement with the findings of Gavelin

and Gabrielson (1947), that nickel, cobalt, and manganese generally do not bear reciprocal relationships among the sulfide minerals from the same hand specimen. Furthermore, this is true not only for nickel, cobalt, and manganese, but for silver, tin, and other elements as well.

Silver

The geographic distribution of silver in sphalerite (plate 11) is very similar to the distribution of silver in chalcopyrite (plate 4), although generally it is more irregular. These irregularities result in a distribution pattern in Colorado that, in addition to being unusual, suggests that the silver-rich belt that coincides with the northeastern part of the Colorado mineral belt branches southwestward into two belts. The southeastern branch presumably extends southward as the Eastern belt into New Mexico. The northwestern branch continues southwestward along the Colorado mineral belt, perhaps into northeastern Arizona where it presumably turns back southeastward and joins the Eastern belt again in southwestern New Mexico.

The genetic significance of the great width of the Western belt in Nevada is not clear, but its economic significance is well attested by the amount of silver that has been produced from this region. Also, the distributional relationships of silver in sphalerite in western Chihuahua, northeastern Sonora, and southeastern Arizona are not clear, and the interpretations indicated in plate 11 should be regarded as tentative.

Thallium

Thallium occurs in sphalerite from only four of the mining districts sampled in this study (districts 68, 104, 106, and 140), and therefore little can be said concerning its geographic distribution. However, all the thallium-bearing sphalerite analyzed also is germanium-bearing, and inasmuch as germanium is not a common trace constituent of sphalerite in the Southwest, the association suggests that perhaps the geographic distribution of thallium is closely related to that of germanium.

Tin

The erratic behavior of the tin content of sphalerite within several of the mining districts, and even within a single crystal, already has been discussed, and is cited here as the main reason why no attempt has been made to represent cartographically the geographic distribution of tin in sphalerite. Despite the erratic behavior, however, most of the sphalerite samples that contain appreciable amounts of tin are from the tin-rich belts shown in plate 5. Moreover, the indications of a geographic distribution of tin in sphalerite are strong enough to enable Warren and Thompson (1945, figure 1) to outline a tin belt in British Columbia.

Combined Metal Content of Sphalerite

The geographic distribution of the combined metal content of sphalerite is shown in plate 12. The component elements are cobalt, gallium, germanium, indium, and silver, and these are combined to form the log product concentration in the

manner described for the corresponding combined metal content of chalcopyrite. In view of the many irregularities in the distribution of the component metals, it is somewhat surprising that as consistent a distribution as shown in plate 12 was obtained.

The essential features of the distribution of the combined metal content of sphalerite are very similar to those of the corresponding distribution for chalcopyrite. That is, there are three main belts, the Eastern, Central, and Western belts, and a subsidiary west branch of the Western belt in California. However, because the geographic coverage of sphalerite samples is not as great as for chalcopyrite samples, the features and inter-relationships of each of the belts are not as well known.

Cobalt and silver are the main contributors to the Eastern belt in north-central Mexico and in New Mexico, although in the latter place indium becomes increasingly important. All the elements except germanium are important in the Eastern belt in Colorado, where, in contrast to chalcopyrite, the main trend appears to be northwesterly. Again all but germanium are important contributors to the Central belt from south of the International boundary to the Nevada border. From southern Nevada northeastward, germanium is an important contributor and cobalt becomes unimportant. In the portion of the Western belt that is known, only indium is relatively unimportant.

A Comparison of the Combined Metal Contents of
Chalcopyrite and Sphalerite

A comparison of the geographic distribution of the combined metal contents of chalcopyrite and sphalerite reveals striking general similarities. Throughout the Southwest, exclusive of Colorado, the belts defined by the combined metal contents in the two minerals either are essentially coincident or closely parallel. The significance of this empirical relationship seems to be that the seven metals represented in the two maps, and probably the sulfophile metals in general, are very closely related in the sulfide ore deposits of the Southwest.

Although the trends of the Central and Western belts in Nevada are essentially parallel for both minerals, the axes of the belts for chalcopyrite lie about 50 miles northwest of the corresponding axes for sphalerite. In Colorado, on the other hand, there appears to be an intersection of the Eastern belts for the two minerals. The Eastern belt for chalcopyrite is very nearly parallel to the northeast trending Colorado mineral belt, whereas the Eastern belt for sphalerite appears to cross the Colorado mineral belt with a northwesterly trend, although a weak northeast trend along the mineral belt also is evident.

The principal reason why the belts do not everywhere coincide is that the positions of the belts for each of the component metals are not exactly the same, and of the seven metals that are represented on the two maps only three are common to both. The belts of the remaining four elements,

two in each mineral, are sufficiently different in their positions, then, to cause a shift in the positions of the belts for the combined metal contents. However, had the four elements, or a certain combination of pairs, been chemically similar, the evidence suggests that the belts of combined metal contents in the two minerals would have been nearly coincident. For example, the belts for the two chemically similar elements, gallium and germanium (plates 8 and 9) are essentially coincident, whereas the belts for chemically dissimilar elements, such as nickel and tin (plates 3 and 5) are far from coincident.

It is possible that a relationship such as this is largely responsible for the irregular distribution of indium in sphalerite (plate 10), for in some respects indium is similar to gallium and in others it is similar to tin. Thus, in regions where the belts of tin and gallium do not coincide, as in southern Nevada, the distribution of indium might tend to resemble that of tin in one area and to resemble that of gallium in another.

METALLOGRAPHIC PROVINCES

The foregoing discussion has been concerned with the geographic distribution of trace elements in two primary sulfide minerals, chalcopyrite and sphalerite. Considered from a more general point of view, the metals that have been investigated also are trace elements in the ore deposits and in the earth's crust, and as such are no different in most essential respects from the other metals, such as copper, gold, lead, tungsten, and zinc, which also are trace elements in the earth's crust. Hence, it might be expected that whatever processes have operated to produce a geographic distribution of one chemically heterogeneous group of sulfophile elements, very probably have produced a similar geographic distribution of another group of sulfophile elements. That such a relationship exists between the two groups of metals is demonstrated by silver, which is a member of both.

Thus silver as a trace element in chalcopyrite and sphalerite has been shown to possess a well defined geographic distribution; and a comparison of plates 4 and 11 with plate 13*, which shows the distribution of ore deposits in which silver is an important constituent of the ores, reveals that all the important silver producing districts lie within the belts defined in plates 4 and 11. Therefore, the distribution of silver as an economically important constituent of the ores is consistent with the distribution of silver as a trace constituent of two sulfide minerals. Furthermore, inasmuch

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*Plates 13 - 17 were adapted from maps made by Dr. J. A. Noble in 1954.

as the distribution of silver is consistent with the distribution of all the other trace elements investigated, there is good reason to expect that the general distribution of the sulfophile elements also would be consistent with the distribution of these trace elements.

A further comparison of plate 13 with plates 4 and 11, and with plates 6 and 12, reveals that the silver deposits are not uniformly distributed along the belts defined by the trace element distribution, but tend to be concentrated in greatly attenuated elliptical areas, the long axes of which coincide with the axes of the belts. This phenomenon is analogous to the variations observed in the concentrations of a particular trace element along the axes of the belts, or to the resulting changes in the relative importance of that element along the belts of the combined metal contents. However, the higher concentrations of silver as a trace element in chalcopyrite and sphalerite generally extend for greater distances along the belts than do the corresponding silver-rich deposits. Therefore, there might be a distinction between the metallographic province in the trace element sense and the metallographic province in the economic or production sense, although the trace element province includes the economic or production province.

Unfortunately, copper, gold, lead, tungsten, and zinc cannot be treated in a manner similar to silver, because no data are available for them as trace elements in the sulfide minerals of the Southwest. However, by analogy with such chemically diverse elements as cobalt, gallium, germanium,

indium, nickel, and tin, all of which bear a consistent distributional relationship to silver, there is good reason to expect that the distribution of deposits of copper, gold, lead, tungsten, and zinc also would be consistent with the distribution of silver deposits.

Thus, all of the major copper deposits, as well as a majority of the minor ones, can be seen in plate 14 to lie within belts that are consistent in trend and position with the belts defined by the trace element distribution, especially the combined metal content of chalcopyrite (plate 6). Furthermore, copper metallographic provinces can be defined within these belts. For example, two and possibly three copper metallographic provinces occur within the Central belt; one that is centered in Arizona, but which extends southward into Sonora; another that extends from eastern Nevada into north-central Utah; and, by extrapolation, possibly a third that includes Butte, Montana. There are two clearly recognizable copper metallographic provinces in the Western belt and its western subsidiary branch. One province includes the western branch in California and adjacent parts of the main Western belt in Nevada. This province might extend northeastward across Nevada to the Idaho boundary, although it is weakly developed throughout most of its length in Nevada. The other lies in southern Arizona and adjacent parts of Sonora. The Eastern belt contains only one prominent copper province. This extends northwestward through southwestern New Mexico into eastern Arizona, where it disappears beneath the volcanic rocks of the Colorado plateau. In addition, a very weakly

developed copper province appears to be centered in central
Colorado and to extend northward into Wyoming. Although this
province is relatively insignificant from the standpoint of
copper production, it is of especial importance here because
it does not appear to reflect the northeast trend of the
Colorado mineral belt.

The distribution of gold deposits (plate 15) is even
better defined than the distribution of copper deposits, de-
spite the complications introduced by unusual economic factors.
In general, the distribution of gold deposits most closely
resembles the distribution of silver as a trace element in
chalcopyrite and sphalerite (plates 4 and 11), and consequently
reflects the distribution of silver deposits as well (plate
13). However, the gold metallographic provinces do not neces-
sarily coincide with the silver metallographic provinces. For
example, the most prominent gold province extends along the
Western belt from southern California to northern Nevada, and
northwestward along the western subsidiary branch in northern
California as far as southern Oregon. Perhaps the second most
prominent gold province is the one that lies in the Eastern
belt in central and southwestern Colorado. Gold, unlike
copper, strongly reflects the Colorado mineral belt; but like
copper, it also reflects a north-south trend through Colorado.
Gold also differs from copper in the relative weakness of the
gold metallographic provinces in the Central belt. A weakly
developed gold province lies in northwestern Utah and perhaps
extends into southeastern Nevada, but probably it does not
join the Arizona gold province. It is possible that a third

very weakly developed gold province in the Central belt is centered in the vicinity of Butte, Montana, if extrapolation of the central belt northward from Utah is warranted. The regional relationships of the gold deposits of the Black Hills, South Dakota, are not yet clearly understood.

The distribution of lead deposits in the western United States (plate 16) most closely resembles the distribution of the combined metal content of sphalerite (plate 12). The economically most important lead metallographic province in the Cordilleran region extends from northern Idaho northward into British Columbia. The belt in which this province lies is largely conjectural, but from the work of Warren and Thompson (1945), together with extrapolations from the present work, it is suggested that the three main belts that are distinguished in the Southwest join in Idaho and Montana to form a single major belt that trends generally northwestward through the region included in this lead province.

In the southwestern United States, lead metallographic provinces occur in all three of the main belts, but the province in the Western belt that extends from eastern California into northeastern Nevada is relatively unimportant economically. In the Central belt there are two lead provinces. One extends from northwestern Arizona northwestward into Nevada and thence northeastward into northern Utah, and the other extends from southeastern Arizona southward for an unknown distance into Sonora. The lead deposits in the Eastern belt in New Mexico probably belong to the same province as the lead deposits in Colorado. Moreover, this lead

metallographic province doubtless extends southward through Chihuahua into Durango and probably somewhat farther.

Inasmuch as there are only about 25 zinc deposits in the western United States, as shown in plate 17, it is difficult to define zinc metallographic provinces with much assurance, although it is clear that nearly all the zinc deposits lie within the three main belts, particularly those defined by the combined metal content of sphalerite (plate 12). It is possible that there are only three important zinc metallographic provinces in the western United States. One such province appears to extend from the vicinity of Butte, Montana, north-westward into northernmost Idaho and southern British Columbia; a second extends along the Central belt from north-central Utah to southern Arizona and perhaps into Sonora; and a third lies in the Eastern belt and apparently extends from Colorado southward through New Mexico into Chihuahua. A noteworthy feature of plate 17 is the relatively rare occurrence of zinc deposits in the Western belt. In this respect, the distribution of zinc deposits resembles that of lead deposits, but is in contrast to the distribution of tungsten deposits, which is next to be described.

The distribution of tungsten deposits in the western United States is shown in plate 18, the data for which were obtained largely from Kerr (1946, figures 2 - 4, and plate 1). Kerr (pp. 3 - 10 and figure 1) recognizes three "tungsten arcs" in the western United States that are defined by the distribution of tungsten deposits and known occurrences of tungsten minerals. A comparison of plate 18 and Kerr's

figure 1 with plates 6 and 12 indicates that the three "tungsten arcs" correspond very closely with the three belts defined in this study.

Doubtless the most prominent tungsten metallographic province in the western United States lies in the Western belt (Kerr's "western arc"), and extends from southern California into northern Nevada. Second in importance are the much smaller provinces in the Central belt (Kerr's "central arc"). One of these smaller tungsten provinces lies in southern Arizona and certainly extends into Sonora. A second very small province, which actually may be a northwest extension of the southern Arizona province, lies in western Arizona and adjacent parts of California. A third province in the Central belt extends northeastward through southeastern Nevada. A single tungsten-rich district in Colorado, the Boulder tungsten district, justifies the recognition of a weak tungsten province in the Eastern belt (Kerr's "eastern arc") that extends northeast-southwest along the Colorado mineral belt. In general, the distribution of tungsten deposits most closely resembles the distribution of the combined metal content of chalcopyrite.

From a consideration of the foregoing features, it is concluded that there is a definite and consistent relationship between the distribution of some of the metals, as important constituents of ore deposits, and the distribution of the same or similar metals as trace elements in the sulfide minerals, chalcopyrite and sphalerite. Furthermore, and more specifically, this relationship consists in the repeated occurrence

of three main belts in the Southwest that, although not every-
where coincident for each of the metals, are nevertheless
generally closely parallel in trend. However, within each of
these three main belts, the distribution of metalliferous
deposits is not uniform, and this non-uniformity has given
rise to what are here called metallographic provinces. The
metallographic provinces thus defined are to be distinguished,
on the other hand, from the metallogenic provinces, the nature
of which will be discussed in the following section.

METALLOGENIC PROVINCES

The term metallogenic province was defined in the introduction as a region of the earth that is characterized by a greater than average concentration of a particular metal or assemblage of metals, and in which the metalliferous deposits possess certain genetic relationships. This definition differs from that for a metallographic province only in the additional stipulation of a genetic relationship, but unless this relationship can be found, metallogenic provinces are indefinable.

It was shown in the preceding section that in the Southwest the metallographic provinces occur within belts that are consistent in trend and position with belts defined by greater than average concentrations of trace elements in chalcopyrite and sphalerite. This close relationship indicates that the concentration into belts of commercial quantities of metals such as copper, gold, silver, etc., on the one hand, and of trace elements such as cobalt, silver, tin, etc., on the other, are essentially the same phenomenon. Therefore, if metallogenic provinces of trace elements are definable, then metallogenic provinces in the general sense also are definable.

The existence of a genetic relationship among the ore deposits within each of the belts is evident from the very nature of the belts themselves. Thus, throughout the known length of the Central belt, the chalcopyrite is characterized by a greater than average tin content, whereas on either side of this belt the chalcopyrite is very deficient in tin. This phenomenon cannot logically be attributed to the wall rocks

or to a particular type of associated intrusive rock, for the same types of wall rocks and intrusive rocks occur both within and outside the belts. Nor can this phenomenon be attributed to any process or combination of processes that is peculiar to one metallogenic epoch, for at least four metallogenic epochs, from Precambrian to late Tertiary, are represented in the ore deposits within the Central belt.

In view of these facts, and of the fact that the belts extend over very great distances, the most logical conclusion would appear to be that the belts are of deep seated origin, perhaps in the sub-crust and/or outer parts of the mantle. This view has been concisely summarized by Spurr (1923, p. 444), as follows:

> "The phenomenon on which I have just touched, of metallographic provinces characterizing certain zones, belts, limited areas, or even spots on the earth, and that independently in large measure of the distribution of granites, diorites, or diabases, rhyolites, andesites, or basalts (although closely associated in general with belts of igneous activity and crustal disturbance), can hardly be explained except by postulating a highly individualized distribution of the metals in that portion of the earth beneath or at the base of those rocks which are exposed to our view by erosion, or beneath what we conveniently though perhaps inaccurately term the crust."

If it is assumed that the cause or causes for the belt-like distribution of metals is deep-seated in origin, then two alternatives occur. On the one hand, it might be postulated that through the controlling influence of some deep-seated feature that has existed throughout geologic time, a certain process or set of processes has operated within and throughout the belts during each metallogenic epoch to produce the observed distribution of the metals; whereas outside the belts

this process or set of processes has not operated because the controlling deep-seated feature does not exist there. Such an hypothesis is not readily acceptable because of the total obscurity concerning the nature of the "deep-seated controlling feature".

On the other hand, perhaps it is possible that the deep-seated cause for the beltlike distribution of the metals is a beltlike compositional heterogeneity in the source materials of the ores that has existed since early in the history of the earth. Accordingly, the ores derived from these source materials would reflect their nature regardless of the metallogenic epoch in which a particular deposit was formed. Of course, in order to explain the origin of the heterogeneity, it is necessary to postulate that at some stage in the early history of the earth certain processes operated within beltlike regions to concentrate a metal or assemblage of metals, and did not operate, at least not to as great an extent, outside the beltlike regions. The important advantage of this hypothesis is that it does not necessitate the recurrence within a belt of the same process or set of processes at several widely separated intervals of geologic time; nor is the "deep-seated controlling feature" any longer an enigma.

Although the hypothesis of beltlike compositional heterogeneities in the source materials is favored here, it is not essential for the establishment of metallogenic provinces, for whether the causes are compositional heterogeneities or processes controlled by a deep-seated feature of unknown nature, the ore deposits within a particular belt are genetically

related through the process that caused the beltlike distribution.

Thus, the southwestern United States and northern Mexico contain at least three main metallogenic provinces, each of which corresponds to one of the three main belts defined by the distribution of trace elements in the sulfides. In addition, there are some more or less minor metallogenic provinces, such as the west branch of the Western belt in California. Also, the mercury metallographic province that extends from San Luis Obispo County, California, northward into Oregon very likely is a metallogenic province, as well, although no data are available to substantiate this. Similarly, there is a suggestion of another mercury metallographic (and metallogenic?) province that extends from the Big Bend region of Texas southward as far as the state of San Luis Potosi.

Each of the three metallogenic provinces (belts) can be distinguished, as a whole, by the predominant metals produced from it. Thus, the Western belt can be referred to as the Gold-silver-copper province, the Central belt as the Copper-silver-gold province, and the Eastern belt as the Silver-gold-copper province. A distinction such as this suggests a crude zonal arrangement of the metals. For example, the Central metallogenic belt is distinctive for its high copper content, whereas the two gold-rich provinces lie on either side in the Western and Eastern metallogenic provinces. However, lead and zinc appear to be less abundant in the Western belt, whereas tungsten is more abundant in the Western belt than in the other two belts.

It is not known to what extent the relationships just described are real or the result of over-generalization; the evidence indicates that they are real. However, it is probable that features such as the zonal arrangement are fortuitous and merely reflect over-all similarities on the one hand, and differences on the other, of the processes of concentration in the source materials in each of the metallogenic provinces.

Thus, it seems that the metallogenic provinces are long, serpentinous, beltlike features in the earth's crust that, here and there along their trends, contain abnormally high concentrations of certain metals or groups of metals, the metallographic provinces. Furthermore, each of the main metallogenic provinces is a composite of several metallogenic provinces, each of which is characterized by a single metal or a group of chemically(?) similar metals. Consequently, within each main metallogenic province or belt there are deposits that perhaps are not genetically related, but all deposits that are genetically related lie within the province. For example, the Central metallogenic province is a beltlike province perhaps as wide as the Central belts in plates 6 and 12 combined, but the Central tin metallogenic province is a beltlike province approximately as defined in plate 5.

THE METALLOGENIC PROVINCES IN RELATION

TO OTHER GEOLOGIC FEATURES

In speaking of the "Great Silver Channel", which he visualized as a very narrow, long, straight silver metallographic province, Spurr (1923, p. 463) says:

> "Along this line in North and South America occur most of the celebrated silver mines in the world, like the Comstock, Tonopah, Santa Eulalia, Guanajuato, Pachuca, Cerro de Pasco, and Potosi. This wonderful straight line slashes clean across mountain ranges and other geologic structures, and continues its course independent of them. This is shown in Nevada, where it cuts at an angle of nearly 45° across the trend of the north-south-trending desert ranges. In Mexico, it shows an utter disregard of the main geologic features and mountain chains -- starting in northern Sonora west of the main range, or Sierra Madre, it cuts diagonally across this on to the central Mexican Plateau, with its short desert ranges; and in the south of Mexico, its unswerving course carries it back across the Sierra Madre again, for this range curves much like the west coast line."

In addition to the "Great Silver Channel", Spurr recognized several other shorter channels, some of which are nearly at right angles to the "Great Silver Channel". These features led him (p. 483) to postulate:

> "The data which I have above outlined are, of course, sketchy, but do indicate the existence in North America of two sets of intersecting straight belts or channels of silver (with other metals), running respectively northeast and northwest. These channels correspond rudely in trend to the skeletal geometrical framework of the continent; and the major channel, which is of world proportions, parallels rudely the eastern side of the Pacific."

> "Here, then, is a discovery of prime scientific and commercial importance. This channel system is marked by a continuity or rather a chain system (like beads on a wire) of consanguineous magma occurrences and also consanguineous ore occurrences. In part -- in large part -- both magma and ore chains have no evident relation to the major belts of folding and faulting of the rocks, and therefore appear to belong to a zone below the zone of surface wrinkling and breaking."

A comparison of Spurr's data (figure 74, p. 459, and figure 75, p. 460) with plates 1 - 12 of the present paper, especially plates 6 and 12, reveals that the deposits that Spurr visualized as constituting a single metallographic belt or "channel" actually occur in three different metallogenic provinces that are by no means straight lines. Furthermore, instead of two sets of belts, one trending northwest and the other northeast, there appears to be only one set that has variable trends.

The purpose of pointing out these discrepancies is not so much to emphasize the disagreement, but to indicate that Spurr's conclusion of the independence of the metallographic belts from other major geologic features may not be valid, if the metallogenic belts actually have the forms shown in plates 6 and 12 instead of the oversimplified straight lines that Spurr has drawn. In fact, a comparison of these latter maps with the Tectonic Map of the United States, which is reproduced in part as plate 19, reveals some remarkably close relationships between the metallogenic belts and the tectonic trends.

Thus, northward from north-central Mexico, where a strong east-west tectonic trend is reflected in an east-west trend in the metallogenic belts, the Central and Eastern metallogenic belts trend very nearly parallel to the tectonic trends. The trends of the Western belt, however, do not appear to bear as close a relationship to the tectonic trends as do the Central and Eastern belts. For example, there appears to be a considerable divergence in the two trend axes in southwestern Arizona. Furthermore, although there is a general parallelism

of trends in southern California, northward the trends again
diverge, so that the Western belt appears to bear a cross-
cutting relationship to the axis of elongation of the Sierra
Nevada batholith. However, in view of the branching nature
of the Western belt in this part of California, the divergence
in trends might be more apparent than real. Northeastward
through Nevada there is a weak but discernible tectonic belt
that is closely parallel in trend to the Western metallogenic
belt.

Another feature of the Western metallogenic belt in the
United States which serves to distinguish it from the Central
and Eastern belts is its association with exposed batholithic
intrusives. In the north it assuredly passes through the
heart of the Idaho batholith. Southwestward through Nevada
it is associated with granitic intrusives that probably are
related to the Sierra Nevada batholith (Ferguson, 1944). The
association with Sierra Nevada type intrusives persists south-
ward through California; and in southern California the Western
metallogenic belt trends diagonally across the northern
exposed part of the Southern California batholith. This
relationship may be more significant in view of the statement
by Larsen, et al. (1954) that the three batholiths just men-
tioned are essentially of the same age (approximately 105
million years).

There is an indication, then, that the main extension of
the Sierra Nevada batholith might be northeastward through
Nevada, perhaps to a junction with the Idaho batholith, and
that the northwest trend into northern California is merely

a branch, analogous to the branch in the Western metallogenic
belt. An interpretation such as this would provide not only
a more consistent tectonic picture and relationship to the
metallogenic provinces, but would be compatible with the
position of the boundary between the so-called "Paleozoic-
Mesozoic-Cenozoic" orogenic belt and the "Cretaceous-Cenozoic"
orogenic belt very near the eastern margin of the Western
metallogenic belt, as proposed by Eardley (1951, plate 1).
However, in view of the age relations that recently have been
indicated, the distinction between "Mesozoic" (Nevadian?) and
"Cretaceous" might not be significant.

Billingsley and Locke (1941) also have discussed apparent
relationships between the distribution of some of the more
important mining districts of the western United States and
various structural features. Their figure 13 (pp. 52-53),
which presents these relationships in the "continental frame-
work", is reproduced in part as plate 20. In general, there
is fairly good agreement between the trends and positions of
several of the "orogenic belts" shown by Billingsley and Locke
and the metallogenic belts defined here. This is particularly
true of the belts in New Mexico, southern Arizona, central
Nevada, and Utah. However, the present work, as well as the
information available on the Tectonic Map (plate 19), which
was published subsequent to Billingsley and Locke's work, does
not indicate the existence of the "Walker line" which the
latter authors visualize as extending northwestward through
southwestern Nevada. Instead, the so-called "Walker line" in
Arizona actually appears to bend around the western margin of

the Colorado plateau and to continue north-northeastward through Utah as Billingsley and Locke's "Early Tertiary" orogenic belt.

The uncertainty connected with the existence of the "Walker line" in Nevada leads to further uncertainties concerning the significance of "...superimposed orogenic movements or of intersecting lines of successive motion, or of persistent deep seated breaks..." (1941, p. 58) in determining the loci of the "clusters" of "ore deposits of upper magnitudes", for there are no "upper magnitude" ore deposits near the intersection of the Tertiary orogenic belt and the "Walker line" in southern Nevada or northwestern Arizona. Furthermore, it is doubtful that many mining districts could be found in the North American Cordillera that would not possess one or more of the three determining features required by Billingsley and Locke.

Despite these objections, however, many of the orogenic belts established by Billingsley and Locke doubtless are real and are of considerable importance in connection with the metallogenic belts. In fact, some of the trend lines, taken in conjunction with the more prominent of those shown on the Tectonic Map (plate 19), lead to interesting speculation on the extensions of the metallogenic belts defined in the present study. For example, the west branch of the Western belt in California might be extended northward into Oregon and thence northeastward across Oregon to a junction with the main belt in Idaho. Furthermore, the Western belt appears to join the Central belt in central Idaho to form the "Main belt". This

relationship also is suggested from a consideration of the distribution of the ore deposits alone.

Billingsley and Locke (1941) distinguish three orogenic epochs in the western United States since the Precambrian. The earliest of these epochs, the "final Paleozoic", characterizes the orogenic belt in Oregon (the west branch of the Western belt ?). The orogenic belt that corresponds to the Western metallogenic belt is presumed to be early Cretaceous, and the youngest orogenic belt, which corresponds to the Central belt, is supposed to be early Tertiary. Although these age distinctions may be valid for the orogenic belts, they have little or no significance with respect to the metallogenic provinces, for there are as many as four different epochs of mineralization represented within any one of the orogenic belts.

In view of the evidence that is presented in plates 19 and 20, and in plates 1 - 12, it is concluded that a generally close relationship exists between the trends of the major tectonic features and the trends of the metallogenic provinces (belts), as they are here defined. However, there does not appear to be any relationship between the ages of the orogenic belts and the ages of the ore deposits that occur within them. For example, three or four different periods of mineralization are represented in the ore deposits in the Tertiary orogenic belt of central Arizona. Also, in the "early Cretaceous" orogenic belt in central Nevada (the Western metallogenic belt) there are both early and late Tertiary deposits. These relationships suggest that although the ore deposits and the regional tectonic or orogenic features are closely related in

origin, as shown by the close parallelism of the tectonic or orogenic belts and the metallogenic belts, neither is the cause or the effect of the other, but both the gross tectonic features and the metallogenic provinces are the effect of some more fundamental cause. Further, this more fundamental cause probably is not the postulated deep-seated compositional heterogeneities alone, but a combination of compositional heterogeneities and closely associated physical discontinuities, both of which may have arisen during the same events of early earth history.

THE IMPORTANCE OF METALLOGENIC PROVINCES IN EXPLORATION

The concepts of metallogenic provinces and metallographic provinces are of the utmost importance in the exploration for new ore deposits and mining districts provided these provinces can be defined with some assurance. Once defined, the metallogenic provinces provide valuable information concerning the most probable regions of the earth in which to search for important ore deposits, whereas a knowledge of the metallographic provinces is of value in determining the parts of the metallogenic provinces that are most likely to contain important deposits of a particular metal or assemblage of metals.

As an illustration of these principles, let it be assumed that the search is for a large silver-rich deposit in the southwestern United States. An examination of plates 4 and 11 indicates the metallogenic provinces in which there are higher than average concentrations of silver, and plate 13 indicates in which parts of these metallogenic provinces silver reaches its highest concentrations. These latter areas, the silver metallographic provinces, then, hold the most promise for the discovery of an important silver deposit.

Another important application of the results of the present investigations is in the enlargement of existing metallographic provinces. For example, the central Arizona copper province is likely to be enlarged, not to the northeast or to the southwest, but along the Central metallogenic belt to the northwest or to the south, especially to the south. This conclusion also has statistical support, for 19 of the 21 major copper producing districts of the Southwest lie along

the belts defined by the combined metal content of chalco-
pyrite (plate 6), even though the metallogenic provinces thus
defined are regarded as only close approximations to the true
copper metallogenic provinces.

However, the greatest significance of the results of the
present investigations perhaps is not so much in the direct
application to individual problems of exploration, as it is
in the establishment of a foundation for the attack on these
individual problems and the pointing of a way to their solu-
tions. In other words, the present investigations are re-
garded as a necessary first step toward an understanding of
the factors involved in the distribution and behavior of the
more sulfophile elements in the earth's crust.

A logical second step toward this understanding would be
an investigation of the relationships, if any exist, between
the distribution of certain trace elements in the primary
sulfide minerals and their distribution in the igneous rocks
and minerals of the same region. This should be accompanied
by a more comprehensive investigation of other primary sulfide
minerals, including pyrite and galena, in addition to chalco-
pyrite and sphalerite.

A third aspect of this general problem that is more
directly applicable to the problems of exploration is a
detailed investigation of the relationships among the trace
element contents of the sulfides, the fresh wall rocks, and
the altered wall rocks in some well developed major mining
districts, as well as in some minor districts. It is known
from the present investigations, for example, that small but

detectable differences in the trace element content of sphal-
erite exist between ore bodies or groups of ore bodies in
certain large districts, such as the Park City district, Utah;
and detailed studies of these variations in the ore minerals,
the altered wall rocks, and the unaltered rocks may provide
means not only of locating centers of mineralization, but
perhaps ultimately of assessing the importance of newly dis-
covered areas of alteration.

CONCLUSIONS

The main objectives of these investigations have been to determine whether metallogenic provinces, as they are here defined, exist, and to describe some of the essential features of these provinces in the event their existence can be shown. The present approach to these problems is based on the hypothesis that one of the more obvious ways in which ore deposits might be related is through common or related sources, and that the nature of the source might be reflected in the primary ores that are derived from it. Hence, a detailed investigation was made of the trace element composition of two primary sulfide minerals, chalcopyrite and sphalerite, with the purpose of discovering any regional differences that might exist in their trace element content.

The investigation of the causes for an erratic behavior of certain trace elements in the sphalerite from several mining districts led to an examination of the variations in trace element content within single crystals of sphalerite and chalcopyrite. The uniform cadmium content of a large single crystal of sphalerite (HAN-20) tentatively is attributed to the association of cadmium with zinc in the fluids prior to deposition of the crystal. The variations in the cobalt, manganese, and silver contents of this crystal tentatively are attributed to variations in the composition of the fluids; and the erratic behavior of tin perhaps is related to the occurrence of numerous cavities and inclusions in the large crystal. Both of the chalcopyrite crystals studied (NY-4 and MEX-35) contain indium and silver, and throughout both crystals the amounts of

the two elements remain nearly constant. The behavior of tin in one of the crystals (MEX-35) is somewhat erratic, perhaps owing to the contamination of the two tin-bearing samples by surface tarnish.

It is suggested that the trace element content of different parts of a large single crystal perhaps is more variable than the trace element content of an equivalent mass of finer grained replacement type chalcopyrite or sphalerite, owing to the more varied conditions of crystallization of large crystals in open spaces. A tentative conclusion drawn from the single crystal studies is that the general level in trace element content of a sulfide mineral is dependent largely upon the composition of the fluids from which the mineral crystallized, and that generally the physical conditions of temperature and pressure and the nature of the wall rocks have minor but perhaps measurable effects.

There does not appear to be any one fundamental principle that will reasonably explain the observed distribution of trace elements among the four minerals, pyrite, sphalerite, chalcopyrite, and galena, particularly between chalcopyrite and sphalerite. The distribution of some of the elements appears to be best explained on the basis of relationships among the relevant atomic, covalent, and ionic radii. For the distribution of other elements, an association of the chemically similar elements in the fluids prior to deposition, as well as progressive changes in the composition of the fluids during deposition, appears to be a more satisfactory explanation. For still other elements, notably cobalt, gallium, germanium,

indium, and manganese, the distribution between sphalerite and chalcopyrite can be explained on the basis of presumed differences in the degree of ionic versus covalent and metallic character of the metal-sulfur bonds in the two minerals. It is concluded that the factors that govern the distribution of trace elements among the sulfides are very complex, and that the observed distribution generally is the result of the interaction of perhaps several of these factors.

An incomplete review of the literature indicates that there is not general agreement concerning the relationship between the trace element content of sulfides, especially sphalerite, and the temperature type of deposit. The general lack of agreement probably is a consequence of the fact that the metallogenic province in which the mineral occurs is the principal factor in determining the general trace element content. Furthermore, it is very difficult to determine precisely the temperature category in which a particular ore deposit belongs.

Although it is apparent merely from an inspection of the data (tables 4 and 5) that a definite geographic distribution of some trace elements in chalcopyrite and sphalerite exists, the data have been analyzed statistically for the purpose of testing this deduction. It is concluded from the statistical analysis that there is no good reason to doubt the existence of a definite geographic distribution of some of the trace elements in chalcopyrite and sphalerite.

The most important feature of the geographic distribution of the trace elements in these two minerals is the occurrence

of three main belts of greater than average trace element content, here called the Eastern, Central, and Western belts. These belts generally are consistent in trend for all the metals investigated, and are either coincident or closely parallel in position. The three belts appear to branch from a main belt or "trunk" in central Mexico, to exist more or less independently in northern Mexico and the southwestern United States, and to join again in the northwestern United States, in Idaho and Montana.

The significance of these belts becomes more apparent when it is realized that all the important silver deposits, and most of the unimportant ones, lie within the belts defined by the distribution of silver as a trace element in chalco- pyrite and sphalerite. Furthermore, the deposits of other metals, such as copper, gold, lead, zinc, and tungsten, also are distributed in belts that are consistent in trend and position with the belts defined by the trace element content of chalcopyrite and sphalerite. The belts defined by the trace element content of the sulfides contain the metallo- graphic provinces in the trace element sense, and here and there along them are abnormally high concentrations of a particular metal or group of metals that constitute the metallographic provinces in the production or economic sense.

The origin of the beltlike features is not known. They doubtless are very old features that have persisted throughout known geologic time. The facts that they are independent of time, that they are independent of the type of wall or intru- sive rocks, and that they extend over vast distances indicate

that the beltlike distribution of the metals is of deep-seated origin, perhaps in the sub-crust or outer parts of the mantle. Furthermore, the persistence of one metal throughout nearly the entire length of a belt, such as the persistence of tin in the Central belt, indicates that the deposits within the belt are genetically related, perhaps through a compositionally heterogeneous source region, the configuration of which also is beltlike. It is suggested, then, that the belts defined by the geographic distribution of the metals are the metallogenic provinces; and that they probably owe their origin to deep-seated compositional heterogeneities in the source regions of the ores and merely reflect these heterogeneities.

Contrary to the beliefs of Spurr (1923), the metallogenic provinces or belts actually are fairly closely related, especially in trend, to the major tectonic features, as shown by a comparison of plates 1 - 12 with the Tectonic Map of the United States (plate 19). There is also a fairly close relationship between these metallogenic belts and the "orogenic belts" defined by Billingsley and Locke (1941) and shown in plate 20. There is, in general, no specific relationship between any of the metallogenic belts and a particular type of rock, either igneous, metamorphic, or sedimentary, although the Western metallogenic province in the United States is more closely associated with batholithic rocks than are the other provinces.

The direct applicability of this knowledge of metallogenic provinces to problems of exploration consists mainly in the elimination from intensive prospecting of large regions

that are shown here to be relatively barren. In addition, the
metallogenic provinces defined here indicate in which direc-
tion existing metallographic provinces are likely to be
enlarged.

However, the chief value of the results of the present
work is in the establishment of a foundation upon which
further work of a similar nature can be based. Thus it is
proposed that the igneous rocks and minerals of the same
region should be studied in similar fashion to ascertain if
a relationship exists between the trace element content of
these rocks and the sulfide ores. Further, once the regional
distribution of trace elements in the minerals, rocks, and
ores is known, a firm basis is provided for comparative
studies of the individual mining districts.

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