# TRACE ELEMENTS IN SULFIDE MINERALS FROM THE CENTRAL MINING DISTRICT, NEW MEXICO AND THE BINGHAM MINING DISTRICT, UTAH

Thesis by

Arthur W. Rose

In Partial Fulfillment of the Requirements
for the Degree of
Doctor of Philosophy

California Institute of Technology
Pasadena, California
1958

## ACKNOWLEDGEMENTS

This study was originally suggested and outlined to the writer by Dr. James A. Noble, who has given encouragement, suggestions,and helpful criticism throughout all phases of the work. The writer is also greatly indebted to Dr. C. Wayne Burnham for many stimulating suggestions in planning the work and interpreting the data. Dr. Leon T. Silver encouraged the writer to undertake the studies of iron in sphalerite and of trace elements in igneous rock minerals, in addition to providing and arranging for use of mineral separation facilities and discussing the data. The writer has benefited greatly from discussions of iron in sphalerite with Daniel J. Milton and Bruce R. Doe.

The work was made possible by a fellowship from the Kennecott Copper Corporation held by the writer during the years 1955-56 and 1956-57. The fellowship paid for the field expenses and most of the analytical work. Officials of the Bear Creek Mining Company arranged the field work at Kennecott properties and also encouraged the work.

The method of x-ray fluorescence analysis for iron in sphalerite was developed largely by Mr. A. A. Chodos. Mr. Chodos has also given freely of his time in instructing the writer in the use of the emission spectrograph and x-ray fluorescence equipment. Miss Elisabeth Godijn carried out the analyses of chalcopyrite and pyrite from Bingham and of trace elements in igneous rock minerals. She also suggested the methods for wet chemical analyses. The many polished sections used in the study were made by Rudolf von Huene, who also instructed the writer in making the photomicrographs. Magnetic mineral separation equipment was kindly made available by the California Research Company of LaHabra, California.

Many individuals and companies have cooperated in the collection of specimens. Mr. G. J. Ballmer of the Kennecott Copper Corporation, and Mr. W. W. Baltosser and Mr. Fred Howell of Bear Creek Mining Company, arranged for the writer to have access to company property, facilities, and information in the Santa Rita area. Mr. C. C. Snell and Mr. J. I. Craig of the Empire Zinc Company arranged for collection of specimens from the Hanover mine. Officials and employees of the American Smelting and Refining Company, the Peru Mining Company, and the New Mexico Consolidated Mining Company also cooperated in the collection of specimens from their mines. Mr. W. R. Jones of the U. S. Geological Survey contributed much to the writer's understanding of the geology of the region.

In the Bingham mining district, the writer is particularly indebted to Mr. R. N. Hunt of the U. S. Smelting, Refining and Mining Company, and Mr. Allen James of Bear Creek Mining Company. Mr. Hunt arranged for collection of specimens from company property in the district, gave encouragement, many helpful suggestions, and comments on the work, and permitted release of the data on the company's property. Mr. James arranged for the collection of specimens from the Utah Copper pit and discussed the geology with the writer. In addition, the geological staff of the U. S. Smelting, Refining, and Mining Company freely gave assistance and advice in the collection of specimens. Numerous other geologists and company officials in both districts gave assistance to the field work in various ways.

Field assistance during the summer of 1956 was given by the writer's brother, Mr. Edward Rose. The writer is especially indebted to Mona Fitz-Simons for preliminary typing of the manuscript and for much of the drafting.

# ABSTRACT

A total of 143 samples of chalcopyrite, 230 samples of sphalerite, and a few samples of other hydrothermal minerals from the Central and Pinos Altos mining districts of New Mexico, and the Bingham mining district of Utah, have been analyzed spectrographically for trace element content. Most of the sphalerites have also been analyzed for iron content by an x-ray fluorescence method. For many elements, variations within single crystals and within mines show no correlation with variations of other elements in the sulfides, indicating that several factors, not temperature alone, are of importance in determining the trace element content of sulfides. Changes in the composition of the hydrothermal fluid with time and position are believed to be the most important causes of variations in the sulfides, but temperature and lack of equilibrium are also believed to be significant.

In the chalcopyrite and sphalerite from both districts the trace element contents are found to fall readily into two or more groups as defined by trace element content. The groups can generally be distinguished geographically and also show geologic and mineralogic differences, although enough similarities exist among groups in the Central mining district to conclude that temperature and other environmental factors are not the primary cause for the grouping, but that the differences probably existed in the hydrothermal fluids before they reached the site of deposition.

The trace element content of sphalerite from the Central mining district shows a poorly developed but distinct lateral zoning away from the Hanover-Fierro and Santa Rita stocks. This zoning in trace element content is accompanied by an increase in the Pb/Zn ratio and an increase in the average silver content of the ores. A similar zoning may exist in the trace element content of chalcopyrite from this district and in the trace element content of sphalerite from the Bingham mining district. In addition, a poorly developed vertical zoning in the trace element content of sphalerite appears to exist within one ore shoot at Bingham. Either a temperature gradient or concurrent progressive changes in the composition of the hydrothermal fluid and the site of deposition are suggested as possible causes for the zonal relations found.

Study of variability of trace element content of chalcopyrite and sphalerite within mining districts indicates that four or more properly selected samples are necessary to obtain a valid mining district average for use in regional studies such as that made by Burnham (1955).

The large variability of iron content of sphalerite within districts, mines, and even veins and single crystals is believed to result in part from variations in temperature, in part from lack of equilibrium between the sphalerite and the adjacent minerals and fluid during deposition, and in part from equilibrium with pyrite rather than pyrrhotite. It is suggested that the iron content of sphalerite is most correctly interpreted to give a minimum temperature of deposition of the sphalerite; that is, the temperature of deposition was at least as high as the value indicated by the iron content on the solvus of the FeS-ZnS system.

## CONTENTS

## ILLUSTRATIONS

PLATE

# INTRODUCTION

Investigations of trace elements in hydrothermal sulfide minerals have been carried out by a number of workers over the last twenty to thirty years. However, most of these studies were in the nature of reconnaissance investigations of the subject, utilizing relatively few sketchily-described specimens. Until the last few years, no really detailed studies of well-described and well-located specimens from single mines or mining districts were made. Discussions of the reasons for observed trace element distributions and for variations in trace element content of sulfides have been limited mainly to correlations with temperature of deposition, and to crystallochemical explanations of the observations. A complete summary and bibliography of work on the subject has recently been published by Fleischer (1955), and no attempt will be made to duplicate it here.

This study was inspired mainly by the work of Burnham (1955) concerning the regional significance of trace elements in sulfides. Burnham analyzed chalcopyrite and sphalerite from a large number of ore deposits in southwestern United States and northern Mexico and showed that the resulting trace element concentrations could be contoured to give several sinuous beltlike highs. These beltlike highs, which Burnham called metallogenic provinces, had similar positions for a number of trace elements and also passed through most of the larger mining districts in the western United States. Burnham's work raised a number of questions, and this study was undertaken in an attempt to answer some of these questions.

While covering a large area, Burnham analyzed only a few samples from any one mining district. Analyses of five to fifteen samples from a few districts convinced Burnham that variations of trace element content within districts were generally small compared to the variations between districts. Nevertheless, moderate to large differences did exist within districts, and these differences seemed worthy of investigation.

Work by the writer has had two main purposes. First, an attempt has been made to determine the amount of variability in trace element content within two large mining districts, the Central mining district in southwestern New Mexico, and the Bingham (or West Mountain) mining district in Utah. Consideration has been given not only to the amount of variability within the districts, but also to other factors which might be important in collecting a representative group of specimens from a mining district. The results of this part of the investigation are expected to be of value in determining the sampling procedure for any future regional studies of trace elements in sulfides.

Second, the geological setting of the samples has been studied in order to bring out any relationships between geological features and trace element content. It was hoped that this procedure would lead to a better understanding of the physical and chemical causes of the observed variations. To a limited extent this effort has been successful.

The writer initially planned to study trace elements in pyrite as well as in chalcopyrite and sphalerite, but after a few preliminary samples were analyzed, it seemed more desirable to concentrate on chalcopyrite and sphalerite rather than to add another mineral.

A third initial purpose involved the study of trace elements in the igneous rocks of the districts. The intent of this program, in addition to adding needed information on the distribution of chalcophile elements in rocks, was to find out if any correlation existed between trace elements in sulfides and the same elements in possible igneous source rocks.

A start on this problem has been made in the Central mining district, but could not be completed owing to lack of time. The few results are believed to be of some interest however.

Work on the project was initiated in the summer of 1955. During the summer of 1955 two and a half months were spent in the Central mining district. An additional two weeks were spent in the district in the summer of 1956. About four days were spent at the Hanover mine of the Empire Zinc Co. and a day or less each at the Groundhog, Pewabic, Kearney, and Grant County mines. Most of the zinc mines in the district have been closed in recent years owing to low zinc prices, and this situation has hindered the investigation somewhat. In 1955, the Groundhog mine was the only underground mine operating, and in 1956 only the Groundhog, Hanover, Kearney, and Bullfrog mines were operating. Conditions in Kennecott's Oswaldo mines were believed by the management to be dangerous and therefore samples from these mines could be obtained only from drill core. Samples from other abandoned or temporarily closed mines were collected largely from dumps and ore bins.

Six weeks during the summer of 1956 were spent at Bingham, about three weeks of this time being spent underground in the U. S. and Lark mines, and the remainder in the open pit. It was not possible to collect specimens from the Highland Boy, Utah Apex, and other abandoned mines on the west side of the district.

During the 1955-56 school year most of the specimens from the Central mining district were analyzed and studied. The work on trace elements in rocks was also carried out during this period. During 1956-57 the specimens from Bingham and a few specimens from the Central district were analyzed. Work on the iron content of sphalerite was carried out during the spring and fall of 1956.

# THE GEOLOGY OF THE CENTRAL MINING DISTRICT, NEW MEXICO

## Introduction

The geology of the Central mining district has been discussed in a number of reports and articles, among which are Paige (1916), Spencer and Paige (1935), Schmitt (1935b), Lasky (1936), Lasky and Hoagland (1948), and Hernon, Jones and Moore (1953). The geology presented here is taken largely from these reports. The paper by Hernon, Jones and Moore (1953) is the best summary. A geologic map of the Santa Rita quadrangle from this report is reproduced in figure 1. A more detailed map has recently been released (Hernon, et al, 1956).

The stratigraphic section is summarized in table 1. About 1000 feet of lower Paleozoic sedimentary rocks, dominantly dolomite and sandstone, are present. The Devonian Percha shale separates these dolomites and sandstones from about 1200 feet of upper Paleozoic limestone and shale. Mesozoic sediments are represented by the Beartooth quartzite and the Colorado formation, both Cretaceous, together aggregating at least 1100 feet. The original thickness of the Colorado formation is unknown because of several periods of post-Colorado erosion.

Following the deposition of the Colorado formation, the geologic history became more complicated. After some uplift, erosion, and broad folding, a number of sill-like bodies of quartz diorite magma were injected. Other minor bodies of dioritic rock were formed at about the same time. Two ages of quartz diorite porphyry have been distinguished by Lasky (1936), early and late. Quartz diorite porphyry occurs as three large sills in the Colorado formation, with a total thickness of over 2000 feet near the Groundhog Mine; as the "Marker Sill" in the Oswaldo formation throughout most of the district; and as a number of other small

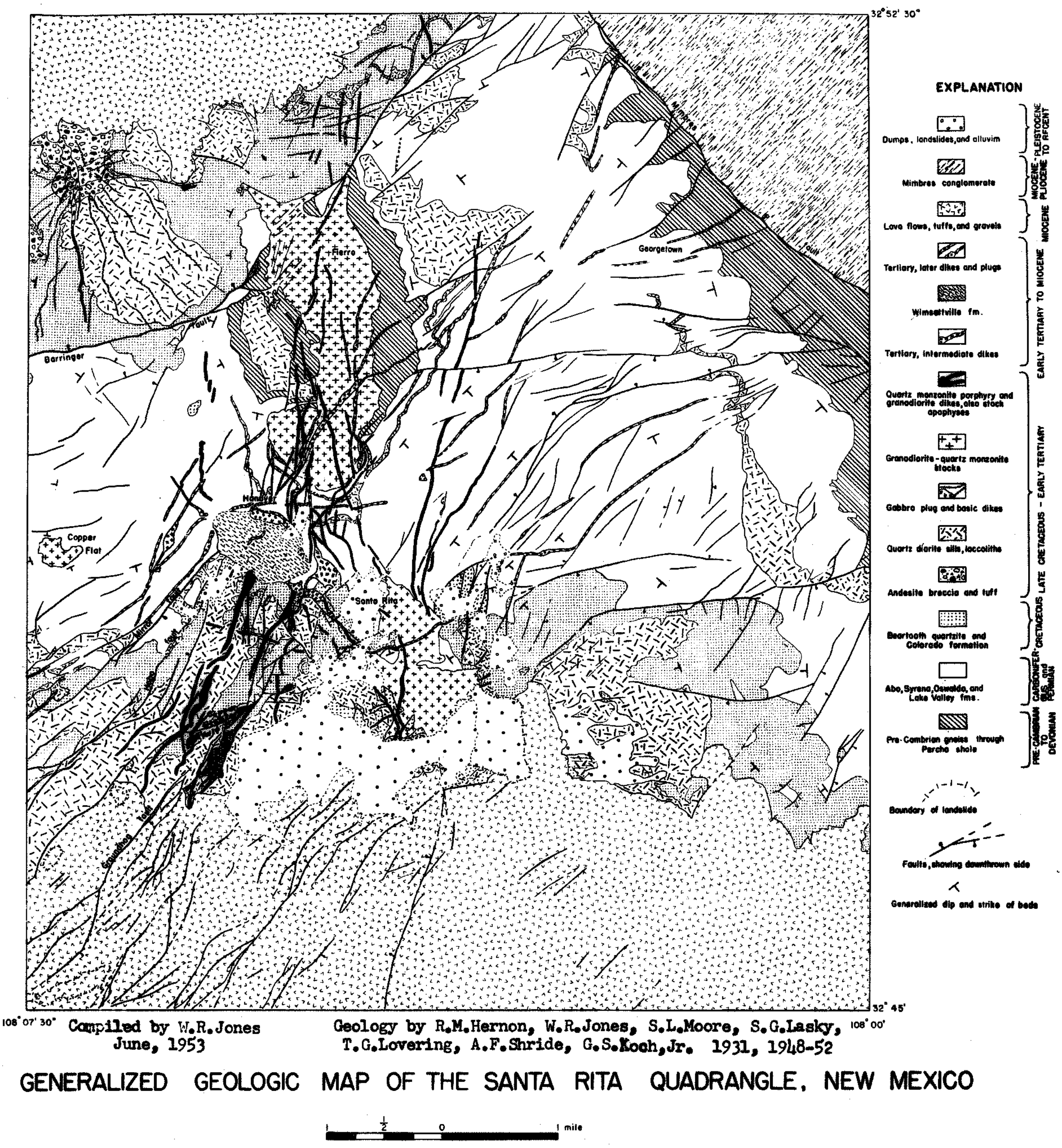


Figure 1. Geologic map of the Santa Rita quadrangle, New Mexico (from Hernon, Jones, and Moore, 1953).

Table 1

## GEOLOGIC FORMATIONS IN THE CENTRAL MINING DISTRICT, N. M.

After Hernon, Jones, and Moore (1953)

| System | Series | Formation | Character | Thickness |
|---|---|---|---|---|
| Quaternary | Recent and Pleistocene | Alluvium | Un-consolidated sand, gravel and clay on desert flats; stream filling. | |
| | | Unconformity | | |
| Tertiary | Miocene (?)-Pliocene | Mimbres conglomerate | Consolidated and deformed sand, gravel, silt and clay with interbedded basalt. | 1000 ± |
| | | Unconformity | | |
| " | Miocene (?) | Lava flows | Flows of basalt; local rhyolitic tuff | 850 |
| | | Unconformity | | |
| " | Miocene (?) | Rhyolite tuff | Rhyolite-quartz latite crystal tuff with local sand; pitchstone flow. | 0-700 |
| | | Unconformity | | |
| " | Miocene (?) | Lucky Bill formation | Gravel, sand, and pumiceous tuffs | 0-600 |
| " | Miocene (?) | Rubio Peak formation | Gravels, pumiceous tuffs and interbedded andesitic basalt | 0-600 |
| | | Unconformity | | |
| " | Lower Tertiary | Wimsattville formation | Gravel and Sand filling Wimsattville basin | 1000 ± |

Table I (Cont.)

| System | Series | Formation | Character | Thickness |
|---|---|---|---|---|
| | | Unconformity | | |
| Cretaceous | Upper Cretaceous | Colorado formation | Black shale in lower 200', sandstone and shale in upper part. | 1000+ |
| " | Upper (?) Cretaceous | Beartooth quartzite | Quartzite with minor sandstone and local limy and shaly beds. | 66-140 |
| | | Unconformity | | |
| Permian | | Abo formation | Red shale with thin beds of limestone and limestone conglomerate | 0-200 |
| Pennsylvanian | | Syrena formation | Upper part, limestone with thin shaly partings; lower part mainly grey and green shale | 400 |
| " | | Oswaldo formation | Chiefly limestone with thin shale partings in upper part; lower part, massive blue limestone, basal 20' shale | 400 |
| | | Unconformity | | |
| Mississippian | | Lake Valley formation | Upper part, white crystalline limestone (Hanover or Crinoidal limestone); lower part gray limestone to shaly limestone. | 300-400 |
| Devonian | | Percha shale | Black fissile shale overlain by gray shale with limestone nodules | 230-315 |

Table I (Cont.)

| System | Series | Formation | Character | Thickness |
|---|---|---|---|---|
| | | Unconformity | | |
| Silurian | | Fusselman limestone | Cherty dolomite | 500± (including Fusselman |
| Ordovician | | Montoya limestone | Dolomite and cherty dolomitic limestone; sandstone at base | |
| | | El Paso limestone | Dolomite and limestone, sandy in lower part | 500± |
| Cambrian | | Bliss sandstone | Glauconitic and hematitic sandstone and sandy limestone | 145 |
| | | Unconformity | | |
| Pre-Cambrian | | | Granite, gneiss,schist and ultrabasics. | |

bodies. These intrusions thickened and stiffened the sedimentary section, and probably are responsible for causing much of the subsequent deformation to occur by faulting rather than by folding as occurred in the preceding episodes. Both types of quartz diorite show slight to severe alteration wherever exposed. Lasky (1936) and Kerr et al (1950) conclude that part of this alteration is either deuteric or pre-ore hydrothermal. This early stage of alteration resulted in the development of chlorite, epidote, albite, calcite, and quartz in varying amounts.

The next event in the geologic record is the eruption of breccia and tuff to form the Cretaceous (?) andesite breccia unit of Hernon, Jones and Moore (1953), most widespread to the west and north of the mining district. This was closely related to the intrusion of a radial swarm of andesite and diorite dikes around an orthoclase gabbro plug in the northwest corner of the Santa Rita quadrangle.

The emplacement of granodiorite porphyry stocks at Santa Rita, Hanover-Fierro and Copper Flats is the next event recorded in the district. The Santa Rita stock and the northern two thirds of the Hanover-Fierro mass apparently have nearly vertical contacts (Ordonez et al, 1955, Kniffen, 1930) but the Copper Flats stock and the southern portion of the Hanover-Fierro stock contract with depth and are not stocks in the strict sense. They have concentric anticlines and synclines around their margins (Schmitt, 1939, Lasky and Hoagland, 1948) and have apparently pushed aside their walls. The granodiorite porphyry masses at Santa Rita and Hanover-Fierro are quite similar in composition, mineralogy, and texture, and may be connected at moderate depth. The intrusion of these masses was accompanied by some faulting and fissuring.

Following the emplacement of the granodiorite stocks, details of the magmatic and hydrothermal history differ significantly from place to place, and these details will be presented in discussions of individual mines. The next district-wide event, merging with the intrusion of the granodiorite, was the intrusion of a group of granodiorite porphyry dikes, a term which includes apophyses of the stocks as well as dikes of similar appearance cutting the stocks. Cutting the granodiorite porphyry dikes are a group of quartz monzonite porphyry dikes differing from the granodiorite porphyry dikes largely in texture.

The metasomatic phenomena resulting in the ore deposits and most of the widespread wall rock alteration occurred after the intrusion of the granodiorite stocks and apparently ceased not long after the intrusion of the quartz monzonite porphyry dikes. This period of intrusion and mineralization was accompanied by widespread faulting, fissuring, and brecciation.

According to Hernon, Jones and Moore (1953) and Hernon et al (1956) a group of quartz monzonitic dikes, called by them "intermediate age Tertiary dikes" followed the quartz monzonite porphyry dikes and the ore deposition, but preceded the formation of the Wimsattville basin, a roughly circular area of breccia, tuff and gravel just south of Hanover. However, underground exposures at Hanover and elsewhere indicate that the formation of the Wimsattville basin, which is probably a caldera or volcanic vent, may have been pre-ore in part, and that only the near-surface filling of the basin may have occurred at this late stage.

Dikes of latite and quartz latite cut all the previously mentioned units and are believed to correlate with the thick sequence of Miocene (?) volcanics which lies unconformably on top of the andesite breccia. These volcanics include rocks from rhyolite tuff to olivine basalt, but are dominantly andesite, latite and quartz latite. Basin and Range type faulting, minor vulcanism, and deposition of alluvium have taken place since then.

Structurally, the Central mining district lies in a region of gently dipping sediments with local changes in attitude caused by folding and tilting near the areas of igneous activity and zones of faulting. The Basin and Range type of faulting has also left some blocks elevated relative to adjoining blocks. Within the mining district faulting on a large and small scale has been an important mode of deformation.

The first of several episodes of important faulting followed the intrusion of the quartz diorite sills (Lasky, 1936). The faults of this period have a dominantly northeast trend, although elements with a north to northwest trend and an almost east trend probably were also developed at this time. Later faulting, apparently occurring almost continuously during the period of intrusion of the granodiorite and quartz monzonite porphyry and deposition of the ore, consisted largely of further movement along faults already established. The dikes of the area have commonly been intruded along faults, and later fault movement as well as ore deposition has commonly taken place along these zones of faults and dikes.

Within the district, the most important effect of this faulting on the relative position of the sedimentary formations has been to form a horst-like structure of northeast trend (Spencer and Paige, 1935). This structure is bounded on the northwest by a single large normal fault, the Barringer fault, and on the southeast by a group of faults centering on the Groundhog fault, and including many of the ore-bearing structures. The zones of most intense rock alteration and ore deposition are found along these two zones of faulting, and within and around the Santa Rita, Hanover-Fierro and Copper Flats granodiorite porphyry stocks.

The mineralogy of the wallrock alteration differs widely from place to place in the district. In the pure Mississippian and Pennsylvanian limestones near Hanover and to the south and southeast, replacement by garnet, pyroxene and magnetite is most common. Shaly sediments and igneous rocks in the same area have been replaced by epidote, tremolite-actinolite, and chlorite. The dolomitic lower Paleozoic rocks near Fierro have been replaced by wollastonite, serpentine, magnetite and tremolite. Igneous rocks in the Santa Rita area and at the north end of the Hanover-Fierro stock have altered to clay minerals, sericite and quartz. It is probable that some of the differences in alteration minerals are the result of differing character of the altering fluids and differing conditions of temperature and pressure at the time of alteration, but many local differences are clearly related to the composition of the original rock.

Ore deposits in the district can be classified as follows (modified after Hernon, Jones and Moore, 1953):

1. Magnetite deposits near the contact of the Hanover-Fierro, Santa Rita, and Copper Flats stocks.

2. Replacement deposits of zinc with variable amounts of lead and copper:

    a. Nearly lead-free replacement zinc deposits around the south lobe of the Hanover-Fierro stock, north and northwest of the Santa Rita stock, along the Barringer fault close to the north end of the Hanover-Fierro stock, and around the Copper Flat stock.

    b. Replacement deposits of zinc with lesser amounts of lead and copper in a broad belt extending southwest from Hanover and along the northeast extremity of the Barringer fault.

3. Vein deposits of zinc, lead, and copper in the southwest quarter of the quadrangle.

4. Secondarily enriched, disseminated copper deposits in and around the Santa Rita stock and in the sheared and brecciated rocks along the Barringer fault.

5. Replacement bodies of silver in the Fusselman limestone at Georgetown.

6. Small scattered replacement bodies of manganese in the late Paleozoic rocks close to the Barringer fault.

7. Gold in veins and in placer deposits near the village of Vanadium.

## Hanover and Pewabic Mines

The Hanover mine (also known as the Empire Zinc mine) of the Empire Zinc Company, and the Pewabic mine of the Peru Mining Company are located near the southern margin of the Hanover-Fierro stock and have produced an important fraction of the zinc mined so far in the district. Schmitt (1935, 1939), and Lasky and Hoagland (1948), have described the geology. Sphalerite with little chalcopyrite and very little galena is associated with silicate, oxide and iron sulfide minerals which have replaced the Mississippian and Pennsylvanian limestones. In the sediments along some parts of the contact with the granodiorite stock, a crude mineralogical zoning away from the stock can be distinguished. A magnetite zone is present nearest the stock, with zones of garnet and pyroxene, sulfides, marble, and limestone at increasing distances from the contact. In detail however, the distribution of minerals is determined to a large degree by structural features, and many exceptions to the zonal pattern occur. In particular, the ore directly south of the stock is localized along north to northeast trending faults and dikes.

Much of the ore has replaced the coarse-grained pure Mississippian Hanover limestone, and many ore bodies are largest just below the overlying Pennsylvanian Parting shale. Some ore has been mined from the Lower Blue limestone below the Hanover limestone, and, especially at the Pewabic Mine, from the Middle Blue limestone above the Parting shale. These upper Paleozoic formations have been folded along portions of the contact with the stock into an overturned syncline nearest the contact and an anticline farther away. At the Pewabic Mine a block folded in this manner is cut off at the base by a thrust fault, below which the sediments are presumably less distorted.

Schmitt (1935a, Pg. 36-38) has distinguished the following structural situations of ore bodies at Hanover:

> 1. Most of the ore occurs as podlike, thick lenslike or other 'three-dimensional' shoots extending from top to bottom of the Hanover limestone and lying adjacent to the outer contact of a silicate zone largely of andradite, which follows the intrusive contact. In further detail these orebodies were localized by high-angle faults which either coincide with the garnet-limestone contact or cut it at a large angle.
>
> 2. Next in importance are vertical 'two-dimensional' or tabular ore-bodies, virtually veins, which follow the contacts of high-angle dike-faults that radiate from the main intrusive contact. The ore extends from top to bottom of the Hanover limestone with little change in width, except in places an increase just under the Pennsylvanian shale bed, and shows a tendency to weaken or disappear near the bottom of the favorable horizon. One of these 'veins' has a strike extension of more than 1000 ft., and in this case the ore, although connected, can be further subdivided into shoots for which the localizing factors are not obvious. ***
>
> 3. Third in importance are horizontal or gently dipping ($0^o$ to $10^o$) 'two-dimensional' or blanket orebodies, which follow the contact of the Hanover limestone with the overlying shale and are associated with gently flexed anticlines or synclines.
>
> 4. One 3500 cu. ft. orebody has the shape of an inverted cone, the base of which abuts the bottom of the 18 ft. Pennsylvania shale bed. It is associated with the intersection of a fault dike and a sharp change in the dip of the sedimentary wall rock.

> 5. Another orebody about 350 ft. long and 30 ft. in diameter is 'one-dimensional' or chimneylike, is enclosed by the Hanover limestone, and dips 30° toward the main intrusive. The causes for this form and localization are not apparent, but there is reason to believe that the chief factor was the intersection of a flat thrust, which dips toward the intrusive, with a high angle normal fault.

Figure 2, after Kerr et al, 1950 shows the shape of some ore bodies in the Hanover Mine.

Of the ore bodies at the Pewabic Mine, Schmitt (1939, pg. 808) says:

> The typical ore body of the mine may be described as a pod-like to cigar-shaped mass about 40 feet in diameter, 600 feet long bearing northeast along strong northeast fractures, enclosed by the Middle Blue or Hanover limestone or both, and cross-cutting these horizons with a flat pitch generally not far above the basal thrust fault. In other words, it follows the intersection of the thrust fault and related flat shear with vertical fracture zones. On either side of the pod-like 'backbone', manto-like fins often spread out along cross fractures.

The relationship of the ore to the granodiorite porphyry dikes shows that the period of zinc deposition followed the intrusion of the granodiorite porphyry dikes, and therefore also the solidification of the exposed portion of the granodiorite porphyry stock. The relationship of the ore to the quartz monzonite porphyry dikes is not certain. According to Hernon, Jones and Moore (1953), most of the sphalerite was probably deposited before the intrusion of the quartz monzonite porphyry dikes. The deposition of magnetite, garnet, and epidote may have preceded in part the intrusion of the granodiorite porphyry dikes, and was largely complete before the intrusion of the quartz monzonite porphyry dikes, according to the same authors.

Schmitt (1939) has published the diagram shown in figure 3b, summarizing the sequence of deposition of minerals at the Pewabic mine based on many macroscopic and microscopic observations. Concerning the Hanover mine, Lasky and Hoagland (1948, pg. 107) say:

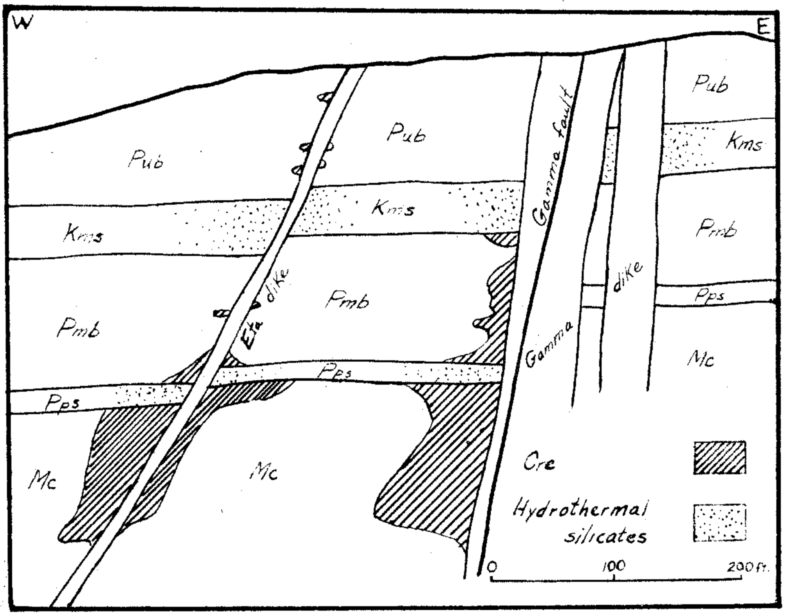


Figure 2. Generalized diagram of ore occurrences along the Gamma and Eta dikes, Empire Zinc mine.

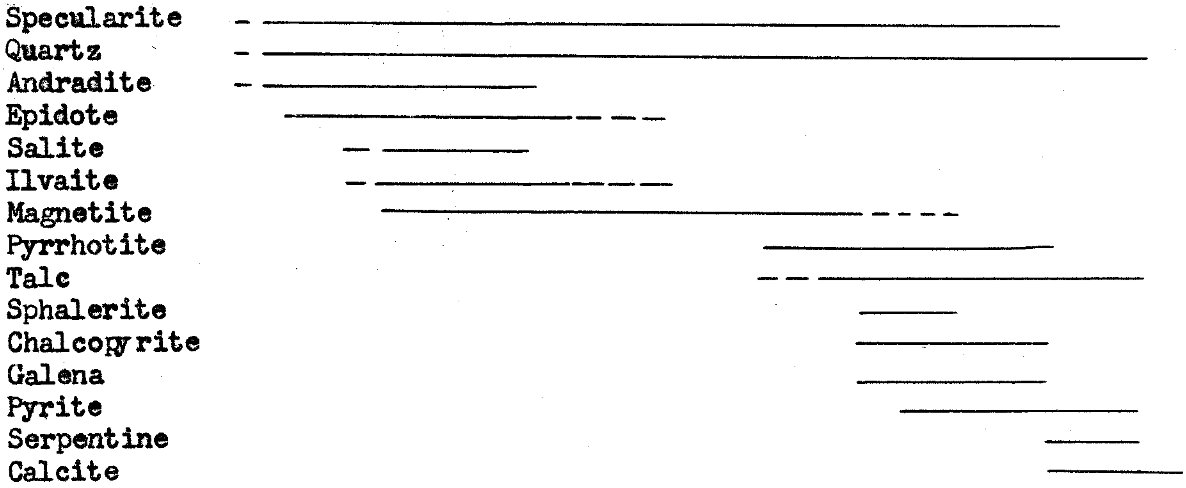
| | |
|---|---|
| Pub | Upper blue limestone |
| Kms | Marker sill |
| Pmb | Middle blue limestone |
| Pps | Parting shale |
| Mc | Crimoidal limestone |

(after Kerr et al, 1950)

## FIGURE 3

(a) PARAGENESIS AT THE HANOVER & PEWABIC MINES (This work)

(b) PARAGENESIS AT THE PEWABIC MINE AFTER SCHMITT (1939)



> * * * ilvaite seems to have followed the salite instead of having been contemporaneous with it; specularite seems to have recurred sporadically over an extended period instead of having been continuously deposited, and pyrite seems to have appeared before the sphalerite as well as after the earliest galena.

The writer's observations on about 75 polished sections and hand specimens from the area, plus limited field observations agree in general with the conclusions of Schmitt (1939) and Lasky and Hoagland (1948) concerning the sequence of deposition. However, many of the relationships observed in the polished sections were developed by replacement, and although the textures suggest relative ages they could usually be interpreted in more than one way. Relatively little evidence of veining or deposition in open spaces was found, particularly with regard to the sulfide minerals. Although it was hoped that several different generations of sphalerite or chalcopyrite could be distinguished, only limited success was attained in this respect. Because the polished sections were chosen to expose areas of sphalerite or chalcopyrite from which samples could be taken, they may not fully represent the occurrence of some minerals. Some comments on occurrence and paragenetic relationships of the observed minerals follow.

Magnetite is present in 10 of the polished sections, in some cases as euhedral grains and in others as rounded grains. It is usually associated with hematite. Two examples of magnetite pseudomorphs after platy hematite were seen. (figure 4). The relationships of magnetite to sphalerite are not always clear. In two sections broad "veins" of small magnetite grains occur in sphalerite but might represent antecedent veins (figure 5). The rounded shape of some magnetite grains probably results from partial replacement by sphalerite. In one section sphalerite veins magnetite pseudomorphous after hematite. Magnetite is most abundant near the contact with the granodiorite stock.

The garnet is close to andradite in composition as indicated by color, optical properties and chemical analyses by Schmitt (1939). It is present in many of the specimens, most commonly as euhedral grains which have subsequently been partially replaced and veined by sphalerite, quartz, hedenbergite and other minerals (figure 6). Many crystals show a slight color zoning in hand specimen and similar zoning of reflectivity in polished sections.

Chemical analyses by Schmitt (1939) indicate that the pyroxene in the deposit has a composition in the hedenbergite to ferro-salite range (50-100% $CaFeSiO_3$ molecule). This mineral is generally called hedenbergite in the district. It occurs as radiating prisms up to several inches in length and as finer-grained aggregates of varying color. The latter type of occurrence is common with the ore specimens collected. In most sections the hedenbergite is observed to be intergrown with quartz, carbonates and other minerals. Many sections show sphalerite apparently replacing hedenbergite around the margins, although several examples of unreplaced euhedral prisms of hedenbergite in sphalerite were observed (figure 7). Allen (1953, 1957) has recently discussed other silicate minerals from Hanover.

Epidote is generally restricted to the shaly sediments and the igneous rocks and was present in only a few ore specimens.

Small amounts of quartz are present in most specimens. The age relations are difficult to establish, but several periods of deposition seem to be represented. Veinlets of quartz cut broken garnet crystals but do not continue into the surrounding sphalerite. Euhedral quartz crystals appear to have formed both before and after sphalerite. Veinlets of quartz, commonly associated with calcite, cut all the hypogene minerals in many sections and probably fill fractures developed during one of the post-ore episodes of igneous activity.

According to Schmitt, ilvaite, a silicate of ferrous and ferric iron, is a common gangue mineral at the Pewabic mine, and is never found far from sphalerite. It was observed in only a few specimens in this study, and is believed to be less common in the Hanover mine than in the Pewabic mine. Veinlets of sphalerite cutting ilvaite were observed in one specimen.

Calcite is abundant in the form of the marble host rock of the deposits, and also occurs as scattered remnants within the zone of metasomatic silicates and oxides. Small amounts of calcite occur with some of the ore, and in a few specimens, calcite is the major gangue mineral. These latter occurrences typically have a vuggy texture. In a number of similar vuggy specimens ankerite is present ($n_o$ about 1.71). Siderite was observed as small grains on the surfaces of large single crystals of sphalerite projecting into the open spaces, with large crystals of calcite, dolomite and quartz covering the siderite (see later description). Late veinlets of calcite with quartz are common, as previously discussed. Except for the late veinlets and the coatings in open spaces the age relations of carbonates could not be determined with certainty.

Pink prismatic rhodonite occurs in two specimens (CEN-221 and 222) but the age relations are not clear. The manganese-calcium pyroxene johannsenite has been described from the Hanover mine by Schaller (1938).

About half of the polished sections disclose small quantities of platy hematite. At least three periods of deposition are represented. Some hematite is replaced by sphalerite (figure 24). Much hematite occurs as veinlets in sphalerite, usually with quartz (figures 8, 11). Although some of the latter examples could be antecedent veinlets, most hematite-quartz veinlets are relatively continuous and are believed to be later than sphalerite. Hematite plates are replaced by chalcopyrite and galena. Hematite plates occur in pyrite and appear to be replaced by it (figure 9). Some fine-grained hematite in hedenbergite, magnetite, and other iron minerals was probably developed by post-ore igneous activity or supergene phenomena.

Chlorite was found in one specimen (CEN-204) associated with galena, abundant pyrite, and quartz.

Pyrite is present in almost every specimen collected, although in many instances it could be detected only in polished section. Some pyrite occurs as tiny veins cutting sphalerite (figure 12). These pyrite veinlets are later than chalcopyrite and galena because the latter sulfides show no tendency to be localized by the fractures controlling the pyrite, and in a few cases they are veined by it. Cubes of early pyrite are replaced along surfaces and cracks by sphalerite, chalcopyrite and galena (figure 14, 15). Much pyrite could not be placed definitely in relation to other minerals. It occurs as anhedral grains in sphalerite and probably includes material deposited both earlier and later than sphalerite. In a few polished sections, anhedral to euhedral pyrite grains are arranged in lines suggesting control by cleavage or fractures in the sphalerite, and hence deposition later than the sphalerite (figure 13). In other polished sections, pyrite of anhedral shape is associated with partly replaced cubes, and may represent early pyrite which has lost its cubic form by replacement.

Pyrrhotite is more common in ore from the Pewabic mine than at the Hanover mine. Most sphalerite associated with pyrrhotite has a relatively high iron content (see later discussion). In the polished sections studied, it occurs as small ragged grains and blebs in sphalerite. On the basis of relationships to be discussed in the following paragraph, its age is inferred to be slightly earlier than sphalerite.

Marcasite is abundant in some polished sections of ore from the Pewabic mine, and was found in a few sections from the Hanover mine. The marcasite found at the Hanover mine is intergrown with pyrite, the two minerals occurring together as aggregates scattered through the sphalerite and as veinlets cutting the sphalerite. Marcasite is thus regarded as a relatively late mineral. The marcasite at the Pewabic mine occurs as aggregates up to several millimeters in size in many cases with rectangular outlines, with the texture shown in figure 16, 29, or 31. For reasons to be treated more fully in the discussion of the Cleveland mine, this lamellar or colloform marcasite is believed to result from replacement of pyrrhotite. Sphalerite appears to replace these aggregates of marcasite grains, and since these are inferred to be replacements of pyrrhotite, then pyrrhotite is probably earlier than sphalerite. Although the sphalerite cuts across the rectangular outlines of the aggregates, the replacement is not controlled by the interlayering of marcasite with gangue constituents, suggesting that marcasite may be later than sphalerite.

Sphalerite ranges in color from yellow-brown to dark chocolate brown, depending mainly on its iron content. In all but a few cases, the color of the sphalerite appeared to be uniform within the hand specimens. The grain size ranges from a few tenths of a millimeter up to several centimeters, averaging about a millimeter. Much of it, especially the coarser grained material, is twinned. In about three quarters of the polished sections, blebs and lamellae of chalcopyrite are present in the sphalerite, as shown in a number of the photomicrographs. The distribution of chalcopyrite blebs in the sphalerite is usually not uniform (figures 17, 18, 19 and others).

The blebs may be abundant in a few crystals in a section and almost lacking in the remainder, or they may occur along lines or in patterns suggesting control by cleavage or growth zones. Blebs may be most abundant near the margins of grains (figure 22) or most abundant in the centers of grains (figure 17). The size as well as the abundance of the blebs may show a relationship to grain boundaries or other features.

In addition to occurring as blebs in sphalerite, chalcopyrite also occurs as relatively rare irregular grains of a few tenths of a millimeter and up, and as small grains in gangue minerals and pyrite. The writer believes that much of the chalcopyrite replaces sphalerite, but this conclusion is based only on a few definite veinlets of chalcopyrite cutting sphalerite (figures 20, 21) plus the following arguments:

1. The very uneven distribution of chalcopyrite blebs in some sphalerite is difficult to explain by exsolution or simultaneous deposition, particularly cases in which only a few sphalerite grains in a large area of sphalerite contain chalcopyrite blebs (figure 19). Most other compositional features of the sphalerite, such as its color and trace element content, suggest that the sphalerite was homogeneous within single polished sections.

2. In some specimens, the proportion of chalcopyrite blebs present reaches about 20% of the intergrowth. This seems a relatively large amount of chalcopyrite to have been in solid solution in the sphalerite.

3. Chalcopyrite appears to replace sphalerite along the rims of sphalerite grains in contact with gangue minerals (figure 22).

However, it seems possible that some of the chalcopyrite has exsolved from the sphalerite, particularly the cases showing a relatively uniform distribution of blebs with a decrease in abundance along grain boundaries

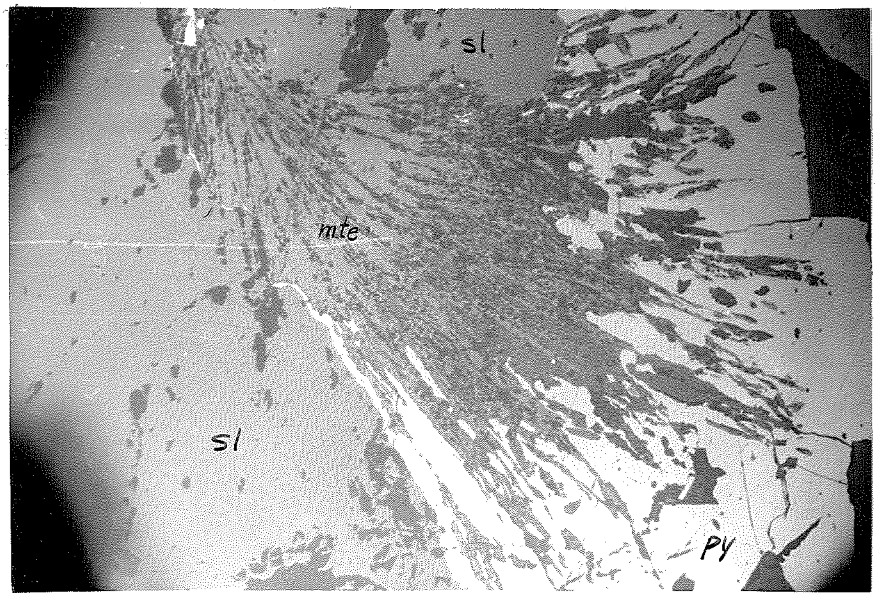


Figure 4. Photomicrograph, CEN-174. Magnetite pseudomorph of hematite, with pyrite and sphalerite (x 100).

In this and all subsequent photomicrographs the following abbreviations are used:

| | |
|---|---|
| sphalerite | sl |
| pyrite | py |
| chalcopyrite | cp |
| pyrrhotite | po |
| galena | gn |
| marcasite | mc |
| magnetite | mte |
| hematite | hem |
| quartz | qtz |
| calcite | cal |
| garnet | gar |
| hedenbergite | hed |

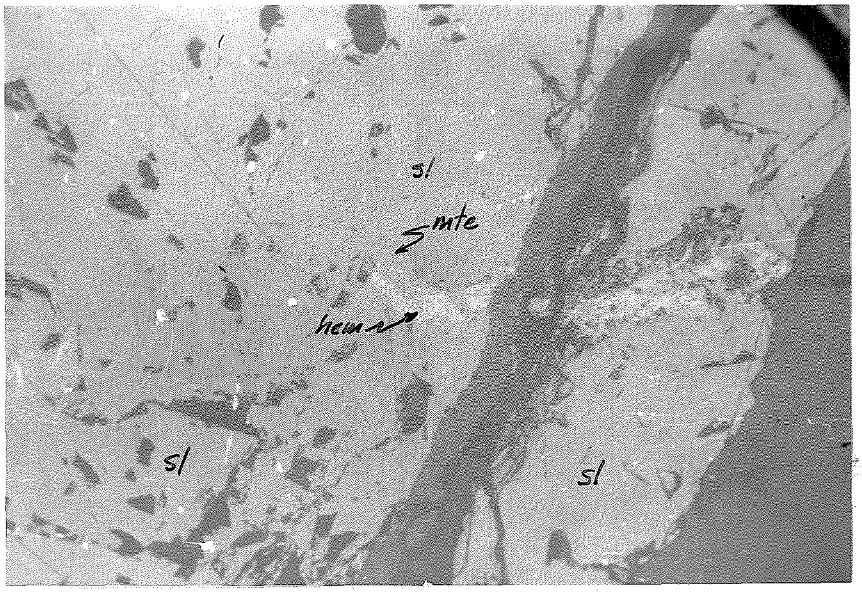


Figure 5. Photomicrograph. Hematite-magnetite vein in sphalerite, cut by gangue; also blebs of chalcopyrite and grains of pyrite in the sphalerite. (x 100).

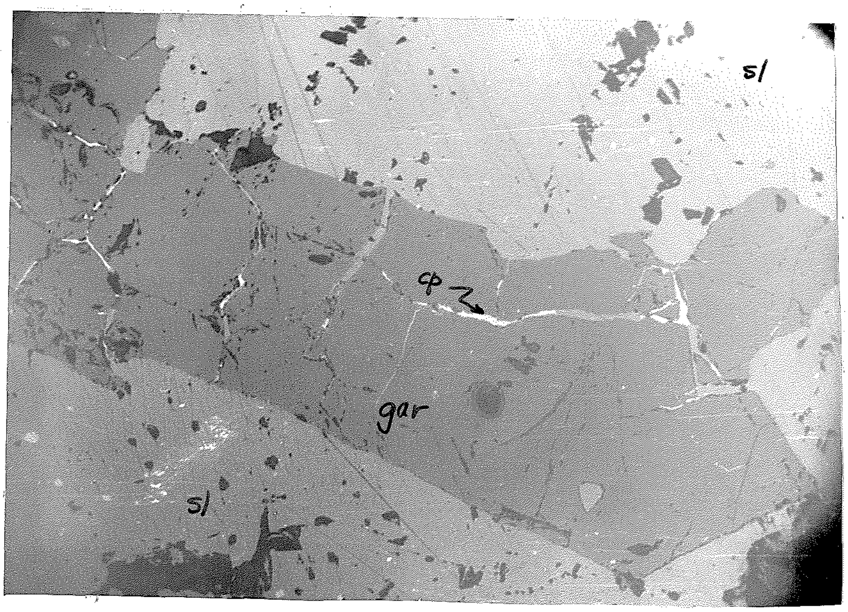


Figure 6. Photomicrograph of CEN-229. Sphalerite and chalcopyrite vein and replace garnet (x 100).

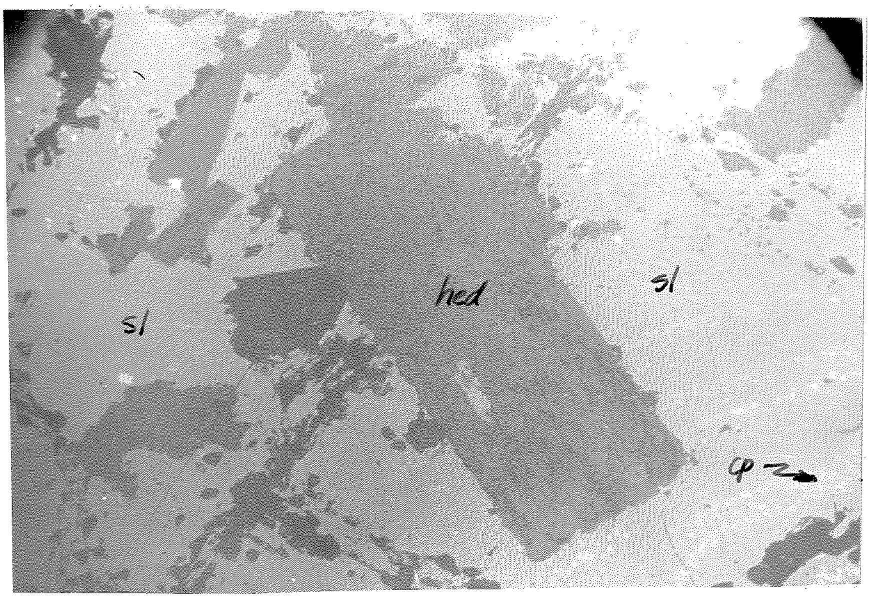


Figure 7. Photomicrograph of CEN-218. Hedenbergite prism in sphalerite with chalcopyrite blebs (x 100).

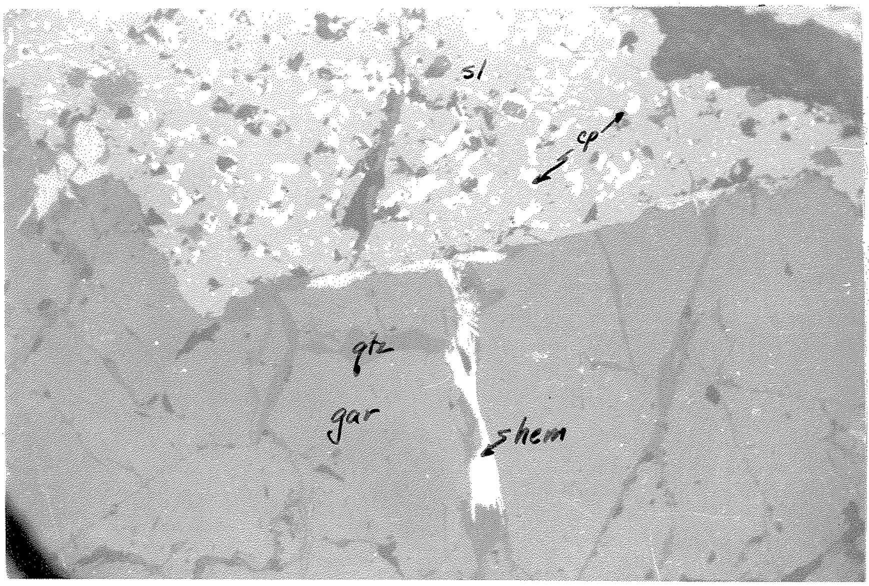


Figure 8. Photomicrograph of CEN-217. Veinlet of hematite cutting garnet and bordering sphalerite containing abundant chalcopyrite blebs (x 100).

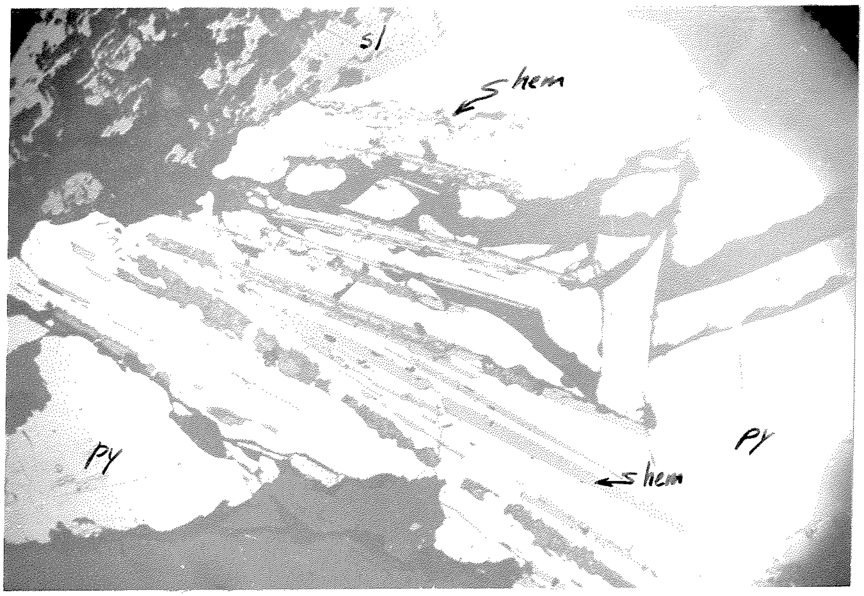


Figure 9. Photomicrograph of CEN-217. Plates of hematite partially replaced by pyrite (x 100).

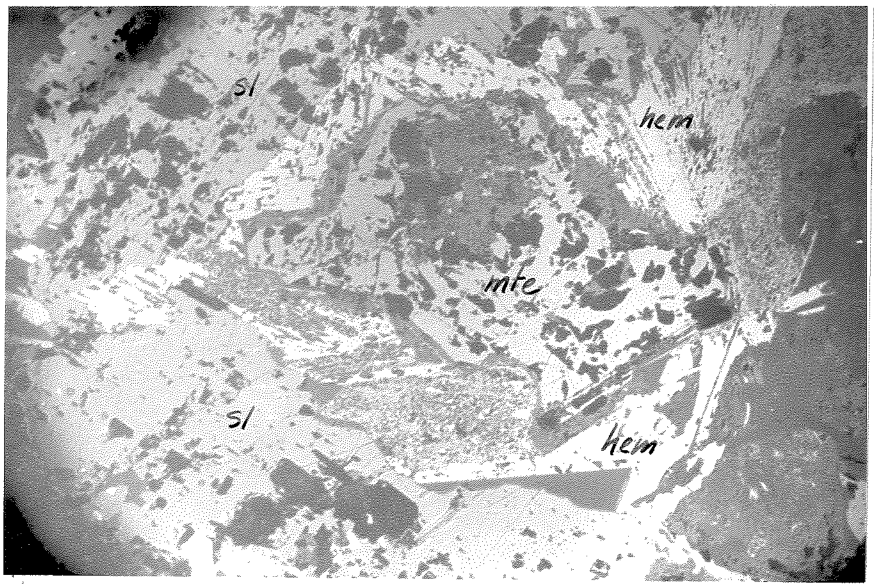


Figure 10. Photomicrograph of CEN-217. Hematite rimming magnetite and enclosed by sphalerite (x 100).

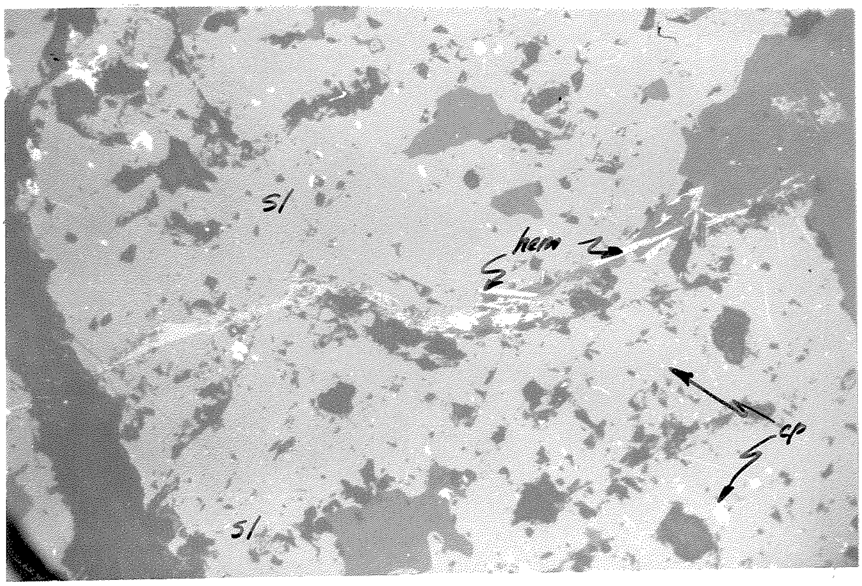


Figure 11. Photomicrograph of CEN-217. Vein of hematite and quartz cutting sphalerite (x 100).

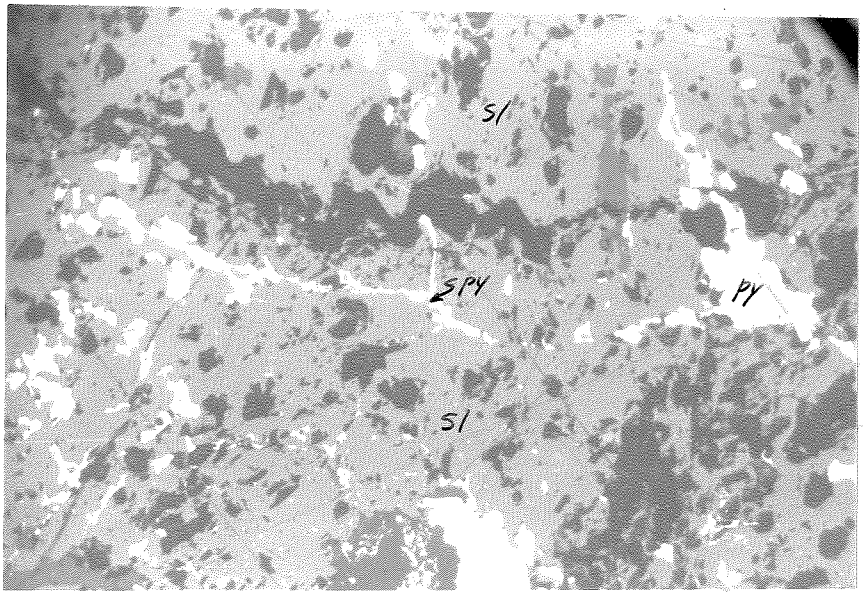


Figure 12. Photomicrograph of CEN-217. Pyrite veining and replacing sphalerite (x 100).

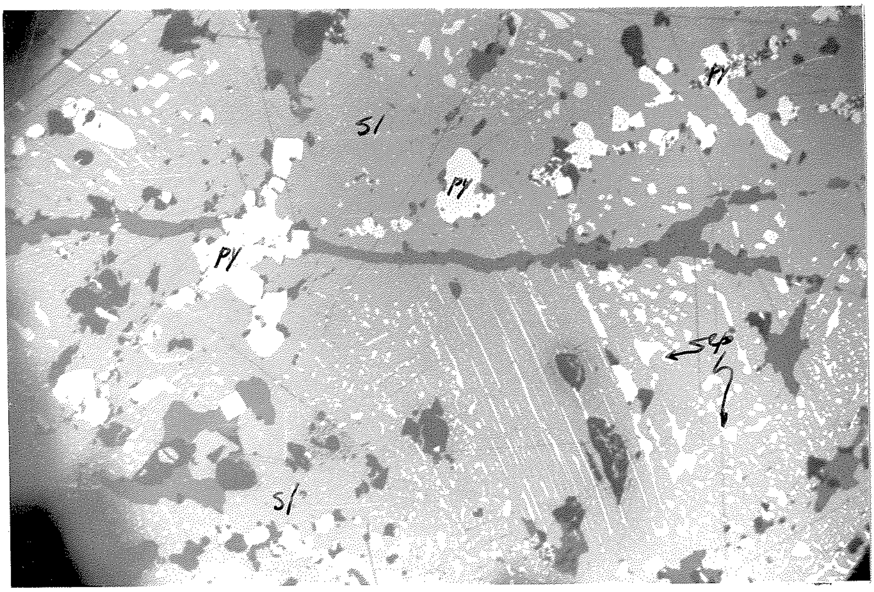


Figure 13. Photomicrograph of CEN-193. Aligned grains of pyrite and lamellae and blebs of chalcopyrite in sphalerite (x 100).

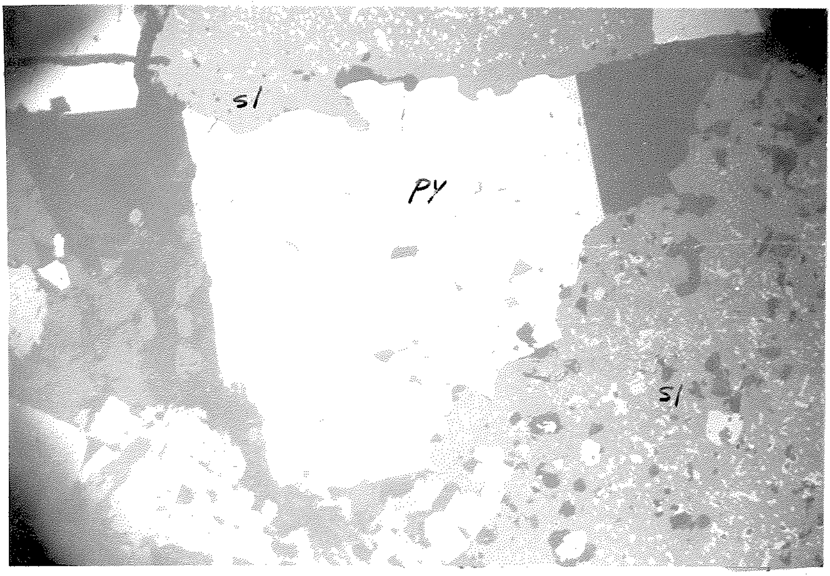


Figure 14. Photomicrograph of CEN-228. Cube of pyrite partially replaced by sphalerite containing abundant chalcopyrite blebs (x 100).

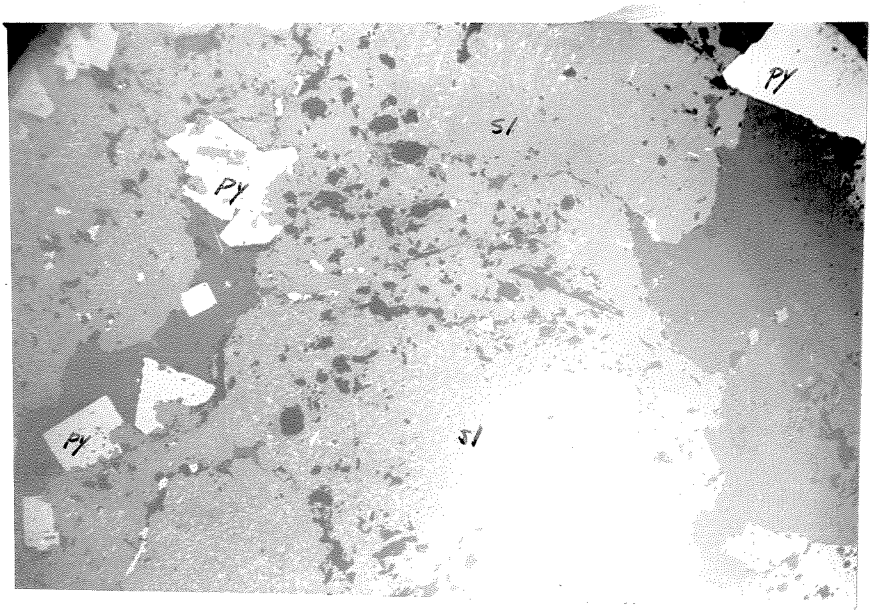


Figure 15. Photomicrograph of CEN-228. Pyrite replaced by sphalerite containing abundant chalcopyrite blebs (x 100).

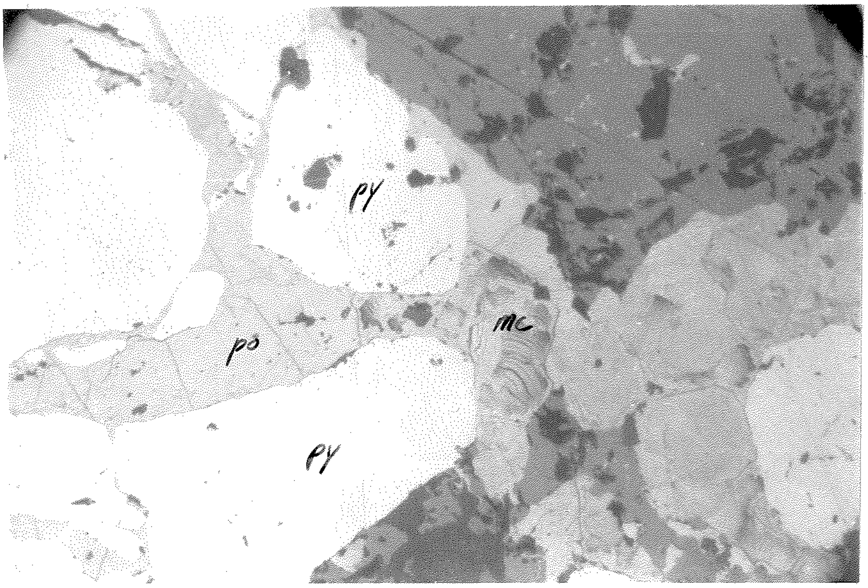


Figure 16. Photomicrograph of CEN-525. Pyrite replaced by pyrrhotite which has altered to marcasite, all enclosed by sphalerite (x 100).

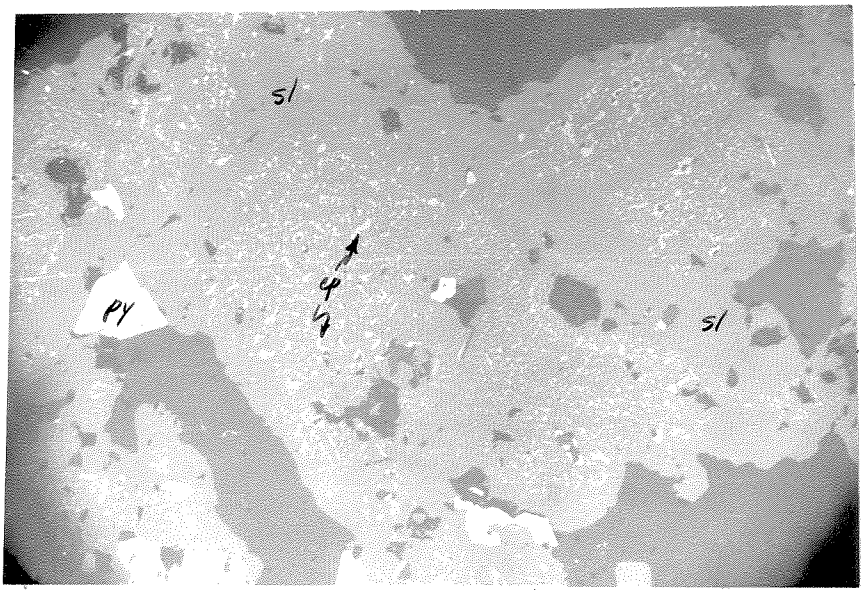


Figure 17. Photomicrograph of CEN-228. Chalcopyrite blebs in sphalerite, with rims of sphalerite grains free of blebs (x 100).

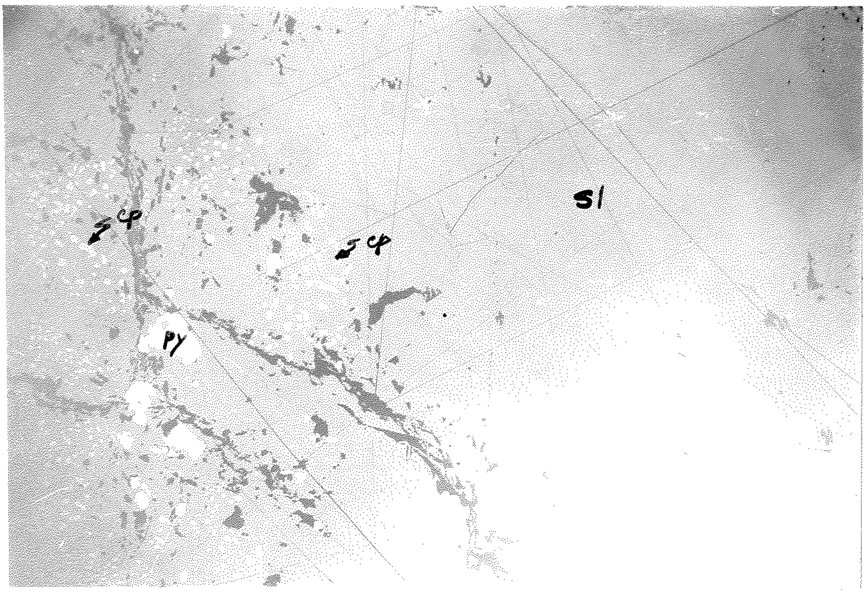


Figure 18. Uneven distribution of chalcopyrite blebs in sphalerite, with a few grains of pyrite (x 100).

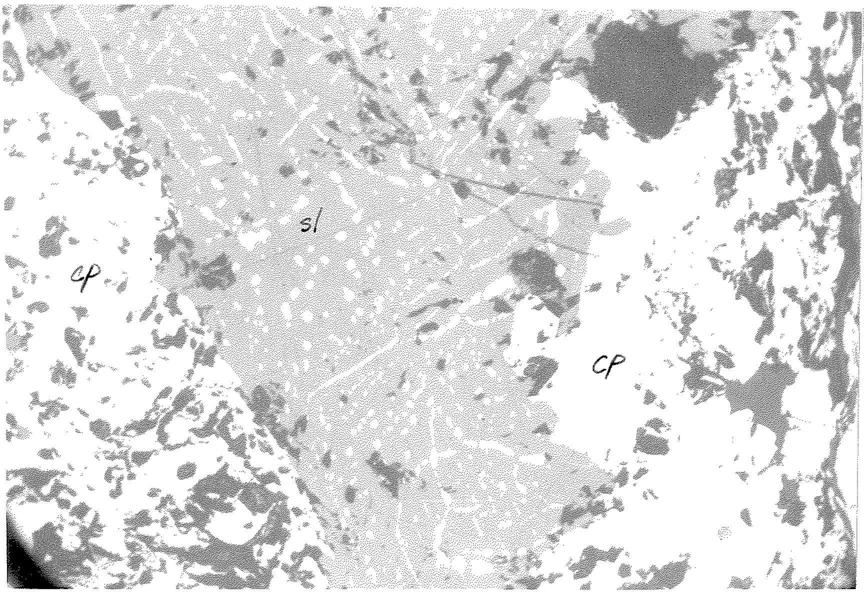


Figure 19. Photomicrograph of CEN-578. Chalcopyrite as grains and as blebs and lamellae in sphalerite (x 100).

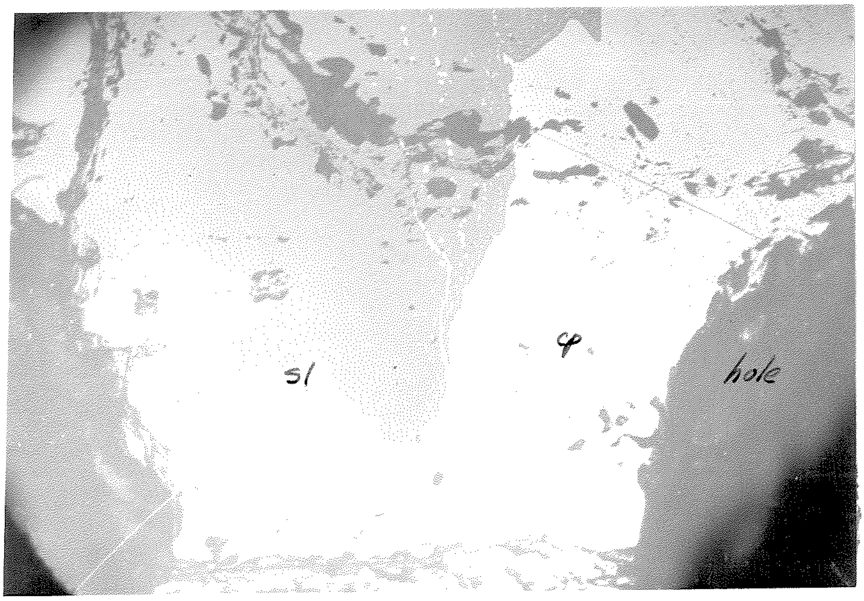


Figure 20. Photomicrograph of CEN-218. Chalcopyrite vein cutting sphalerite, with chalcopyrite blebs restricted to the margins of the sphalerite grain (x 100).

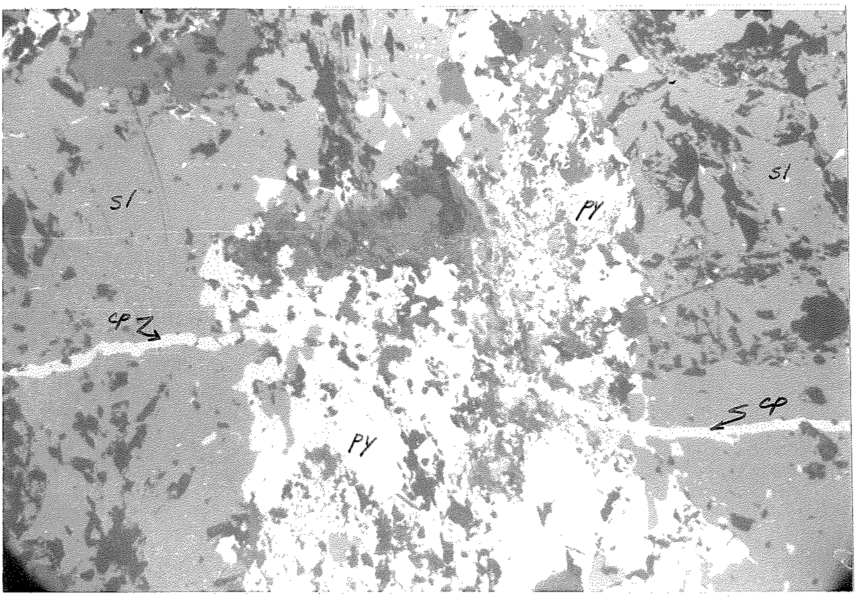


Figure 21. Photomicrograph of CEN-577. Chalcopyrite veining sphalerite and pyrite (x 100).

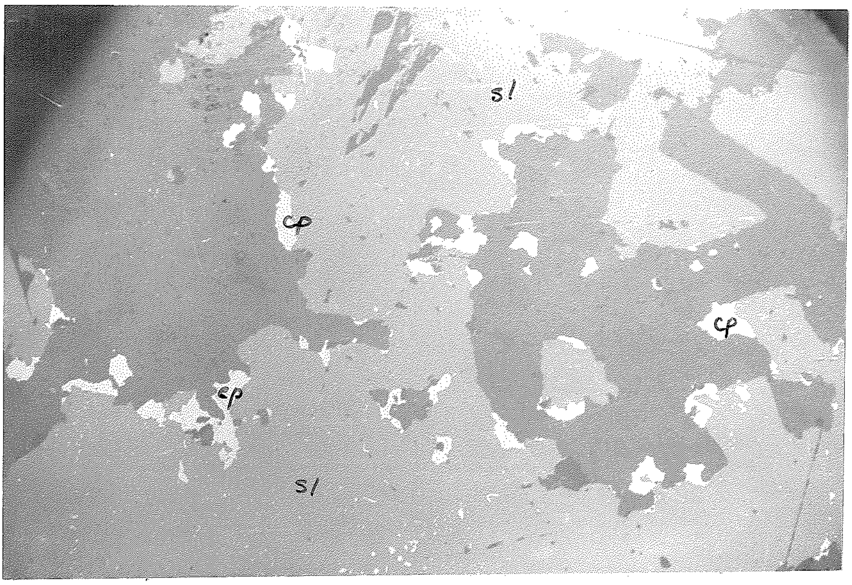


Figure 22. Photomicrograph of CEN-218. Chalcopyrite replacing sphalerite on the margins of grains (x 100).

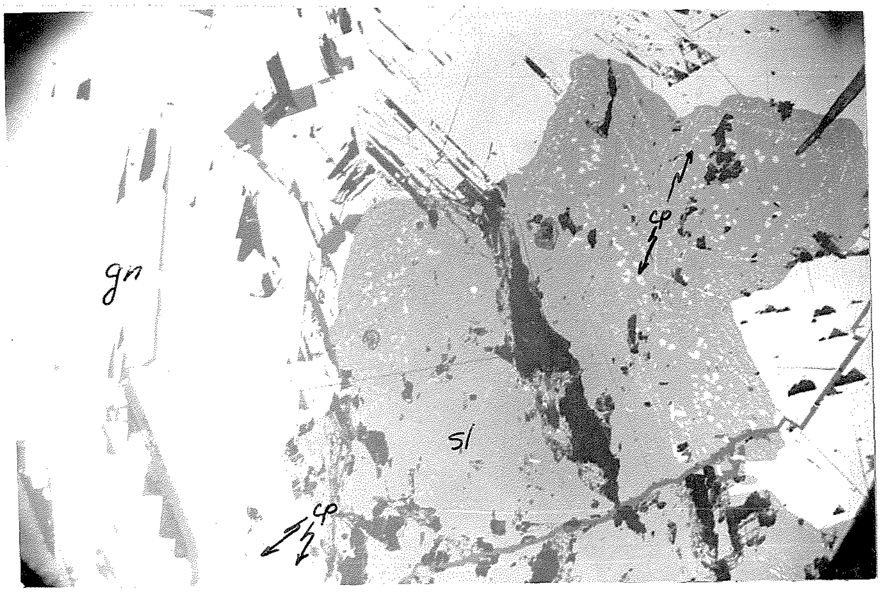


Figure 23. Photomicrograph of CEN-210. Chalcopyrite blebs in sphalerite concentrated near the contamts of galena and sphalerite (x 100).

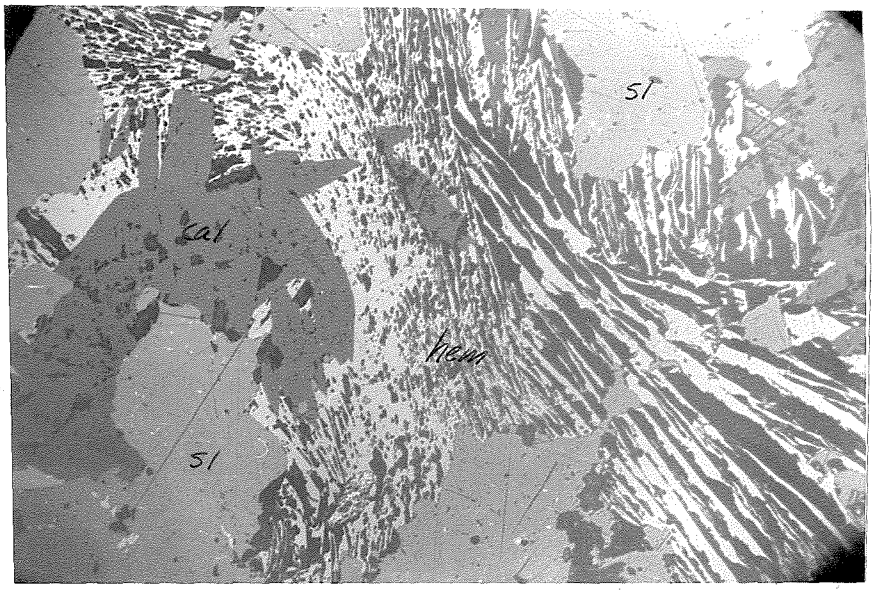


Figure 24. Photomicrograph of CEN-221. Hematite plates replaced by sphalerite (x 100).

or along zones cutting across the sphalerite. This sort of distribution is consistent with exsolution of the chalcopyrite near grain boundaries and fractures where the chalcopyrite could leave the sphalerite host in the time available. No evidence of chalcopyrite earlier than sphalerite was noted.

Galena occurs in small quantities in about half of the specimens, and is commoner in the specimens from the area south of the stock than in the area west of the stock and the Pewabic mine. When present in small quantities the galena occurs as sparse rounded blebs in the sphalerite, but when present in larger quantities it appears to replace sphalerite along grain boundaries and along contacts of sphalerite with gangue. One example of galena veining chalcopyrite was seen. In two specimens chalcopyrite bordered relatively large areas of galena, suggesting that chalcopyrite followed galena.

Small quantities of a mineral believed to be cosalite were noted in one section. A few blebs of a pinkish mineral were found in two sections but could not be identified. Covellite and bornite were noted in some sections.

Figure 3 shows the generalized sequence of deposition deduced by the writer. Deviations from this pattern probably occurred in any one small area, but the sequence is believed to represent the total process fairly well.

## Chino Mine

The largest mining operation in the district is the Chino mine of the Kennecott Copper Corporation at Santa Rita. From the open pit of this porphyry copper deposit have been mined large tonnages of copper ore. Current production now averages less than one percent copper. Molybdenite is also recovered from the ore.

The ore occupies a severely shattered and altered granodiorite porphyry stock and extends into adjacent sediments and quartz diorite sills. The dominant ore mineral is chalcocite, largely supergene in origin. Small amounts of other supergene minerals are present, especially in the oxidized zone. Chalcopyrite and bornite can be found with some searching in the northern end of the deposit. Chalcopyrite has been found in polished sections from other parts of the mine.

In recent years, mining has been confined to the South Pit, now about a mile in diameter and over 400 feet deep. Earlier mining operations excavated the smaller North Pit. The two pits are separated by the "Island". The ore-bearing sedimentary rocks and quartz diorite sills of the South Pit area show an argillic and sericitic alteration similar to that in the granodiorite porphyry, but north of the North Pit the sediments contain chalcopyrite associated with epidote, magnetite, and other tactite minerals. Pyrite is abundant in all the ore.

Study of the wallrock alteration by Kerr et al (1950) led to the recognition of four stages of alteration in the granodiorite porphyry stock. Stage 1 is represented by almost unaltered rock containing books of shiny black biotite and phenocrysts of fresh plagioclase. In stage 2 the biotite is chloritized and the feldspar partly argillized. The presence of hydromica pseudomorphs of biotite characterizes stage 3. In stage 4, sericite and quartz dominate, and only rare indications of phenocrysts can be found. Stage 1 is found only in part of the North Pit, and stage 2 is most common in the northern half of the deposit. Much of the South

Pit is in stage 3 or 4. Kerr et al (1950) found that ore-grade material was most common in stage 3.

Leroy (1954) published additional work correlating ore with alteration. He found three types of veinlets in the more altered porphyry; barren quartz, quartz-alunite (molybdenite), and quartz-sericite-pyrite. The barren quartz group is cut by the other two varieties. Leroy believed that the quartz-sericite-pyrite type consistently cut the quartz-alunite type. The writer has seen a number of examples of quartz-alunite veinlets cutting quartz-sericite-pyrite veinlets and believes additional work would indicate a more complicated relationship. Leroy found that some pyrite of the quartz-sericite-pyrite veins contains minute chalcopyrite inclusions. The writer has also observed such inclusions in about half of the polished sections of pyrite studied from the South Pit.

Several other possible primary sources of the copper were discussed by Leroy. Veins of pyrite partially replaced by steely chalcocite were considered to be hypogene. Polished section study by Leroy also disclosed the presence of disseminated chalcopyrite in one area and chalcopyrite-bornite intergrowths in a few other areas. Both the latter types of occurrence were associated with sericite.

The writer collected a number of chalcopyrite specimens from the northwest corner of the "Island". (CEN-30, 31, 32, 42, 45, possibly 589). This chalcopyrite occurs as fillings of open fissures in stage 2 granodiorite porphyry. Pyrite is present in most of the specimens, specularite in several, and marcasite in one. Chalcopyrite appears to have been deposited after the pyrite, but otherwise the age relations are not clear. The feldspar in the adjacent rock is argillized and some biotite is chloritized but other biotite appears fresh. In several specimens, the groundmass of the granodiorite contains notable quantities of biotite. No increase in the intensity of alteration near the veins was noted. There is surprisingly little alteration in the area containing the chalcopyrite, compared to the South Pit area.

Chalcopyrite-bearing specimens of drill core from east of the North Pit have also been examined (CEN 65 -84). In this area the Syrena and Oswaldo formations have been shattered, intricately intruded by quartz diorite and granodiorite, and metasomatized. Magnetite, pyrite, epidote, actinolite, chlorite, and clays are prominent alteration minerals. Chalcopyrite occurs both in veinlets and disseminated through the tactite, commonly filling in between grains of magnetite and pyrite. A similar specimen of chalcopyrite with pyrite and magnetite was collected from the northwest side of the North Pit. An occurrence of chalcopyrite in veinlets associated with dark chlorite (CEN-580) was found in the northwest corner of the South Pit. The enclosing wallrock here is a gray hornfels, originally part of the Abo or upper Syrena formation.

One specimen bearing a small chalcopyrite veinlet was collected from a quartz monzonite porphyry dike on the south wall of the South Pit. A polished section disclosed the presence of sphalerite and galena in addition to chalcopyrite and pyrite. Megascopic and thin section inspection shows a strong chloritization near the veinlet decreasing in intensity but not disappearing at greater distances from the vein. Plagioclase is completely sericitized. Magnetite is present in the less altered part of the rock but disappears near the vein. This occurrence may be similar to the chalcopyrite mentioned by Hernon et al (1953) in quartz monzonite porphyry dikes at Chino. To the writer's knowledge it is the first reported occurrence of sphalerite or galena in the pit area.

Leroy, who has made the most detailed study of the origin of chalcocite, the dominant ore mineral, says (1954, p. 762): "Evidence strongly suggests a supergene origin for most chalcocite and consequently for the ore as a whole." After considering several possibilities he concludes: "Disseminated bornite-chalcopyrite forms the principal source of copper for the development of supergene chalcocite". If this is so, essentially all the chalcopyrite originally present has been removed in the oxidation and enrichment process, a factor which must be considered in interpreting the results of the trace element analyses. Also, not all the several types of chalcopyrite mentioned on the preceding pages have been found in amounts large enough for trace element analysis, possibly resulting in a biased sample of the deposit as a whole.

The presence of chalcopyrite veinlets in the quartz monzonite dikes shows that at least some of the chalcopyrite was deposited after the solidification of these dikes. However, the chloritic alteration and the presence of galena and sphalerite are not typical of the other chalcopyrite occurrences, so this chalcopyrite may be of different age than the main copper mineralization.

Kerr et al (1950) found a correlation between clay mineral content of the quartz monzonite dikes and the stage of alteration in the adjacent granodiorite, thus suggesting that the dikes are pre-alteration.

It seems probable that the main copper deposition was closely related in time to argillization, sericitization and silicification. If the quartz monzonite dike can be considered pre-alteration, then the dike is also pre-copper mineralization. At Hanover, zinc mineralization is believed to have largely preceded intrusion of the quartz monzonite dikes, and thus is earlier than the copper mineralization at Chino.

Unfortunately, the evidence is not entirely clear, and it seems possible to the writer that both copper and zinc deposition overlapped the period of intrusion of the quartz monzonite dikes.

Several periods of pyrite deposition are represented by the abundant pyrite at Chino. Numerous examples of one pyrite vein cutting another can be seen, and several sequences of three pyrite veins have been seen by the writer. Much of the pyrite was probably deposited during a single extended period of mineralization and fracturing. However, some pyrite veins are cut by the quartz monzonite porphyry dikes whereas other pyrite occurs as veins and disseminations in the dikes, proving that pyrite was deposited both before and after these dikes. In addition, Hernon, Jones, and Moore (1953) show pyrite deposition in the district following the intrusion of both the intermediate Tertiary and the late Tertiary dikes, and one or both of these periods may be represented at Chino. However, all the pyrite-chalcopyrite relations observed in polished sections from Chino indicate that chalcopyrite is later than or contemporaneous with pyrite in age.

## Oswaldo #1, Oswaldo #2, Kearney, and Grant County Mines

These four mines lie in the area between the Hanover-Fierro and Santa Rita stocks. Production is dominantly zinc with minor amounts of lead and copper. The Oswaldo mines are owned by the Kennecott Copper Corporation, and the Kearney and Grant County mines by the New Mexico Consolidated Mining Co. (a subsidiary of the Peru Mining Co.).

In all three mines the ore bodies are of the limestone replacement type found at Hanover, with hedenbergite, garnet, epidote, magnetite, and other tactite minerals as gangue. At both Oswaldo mines and at the Kearney mine the ore occurs largely in the Mississippian Hanover limestone unit. In the Grant County mine ore occurs in the Pennsylvanian Oswaldo formation.

The Oswaldo #1 mine is just south of the Hanover mine of the Empire Zinc Co., and the ores are very similar. Ore bodies are localized along north to northeast trending dikes, faults, and fissures.

The Oswaldo #2 mine is located directly north of the Santa Rita stock. Here again the ore is localized by dikes, fissures, and faults of northerly trend.

The Kearney mine lies between the Oswaldo #1 and #2 mines. Storms and Faust (1949, p. 3) say of the geology:

> On the Kearney property, the major zinc ore bodies occur to the north of the Santa Rita granodiorite stock, chiefly as bedded deposits in the Hanover limestone of Mississippian age, along two large steeply dipping faults and beneath a thick diorite sill. Mineralization is fairly irregular, and ore shoots vary in size and shape.
>
> Two roughly parallel faults, the Kearney and the Magnetite, which strike about northeast-southwest, seem to have been the principal pathways of ascending mineralizing solutions. The solutions came up along these faults as well as along the Clifford fault and then replaced the Hanover limestone.
>
> The chief mineralized beds, where mined, are up to 110 feet thick. However, stoping height averages only about 25 feet. The beds dip about 15 degrees to the south. Tops and bottoms of ore shoots are very irregular, tongues of ore going up into the overlying limestone and down into that beneath the ore body. The lateral extent of the ore shoots is also very irregular, the ore usually grading into low-grade material that cannot be mined at present metal prices.
>
> The principal ore-forming mineral at the Kearney is sphalerite with small amounts of galena and very small amounts of chalcopyrite. Ore mined has ranged from 5.3 to 15.7 percent zinc, with lead running from 0.35 to 1.5 percent. A very small amount of copper and a fraction of an ounce of silver a ton occurs in the ore. In May 1948 the ore averaged 7.5 percent zinc and 0.5 percent lead.

Cross sections of the mine published in Storms and Faust (1949) also show a number of pre-ore and post-ore dikes. In addition, some ore occurs in limestone breccia at the east end of the mine.

At the Grant County Mine, located about a half mile east of the Pewabic mine, the ore occurs next to a granodiorite dike. The alteration is similar to the other zinc mines just discussed and includes magnetite, pyrrhotite and hedenbergite.

The sequence of deposition at all four of these mines appears to be the same as at the Hanover and Pewabic mines from the writer's observations.

## The Groundhog Mine

The Groundhog mine, owned by the American Smelting and Refining Company, is located near the southern margin of the district. The geology has been discussed by Lasky (1936, 1942), and Lasky and Hoagland (1948).

Two types of ore have been mined at the Groundhog mine. The mine was originally developed on argentiferous zinc-lead-copper ore occuring as fissure fillings in quartz diorite sills and Mesozoic sediments. More recently the ore has been dominantly of the limestone replacement variety, similar in character to the ore mined near Hanover, although with different proportions of various ore and gangue minerals. Both types of ore are localized by the Groundhog fault zone of northeast trend. The original fault zone was intruded by granodiorite dikes, after which came further fault movement and deposition of the ore. Important post-ore movement has taken place in Tertiary time. Lasky (1936) describes a complex group of linked faults and dikes in this zone.

Of the fissure-filling type of ore, Lasky (1936 p. 96, 98) says:

> The ore consists of varitextured argentiferous mixtures of galena, sphalerite, pyrite, and chalcopyrite, accompanied by subordinate quartz and calcite. The mixtures range from fine-grained sugary, intimate intergrowths to rather coarse-grained masses

> composed chiefly of one mineral. In the Groundhog mine the ore has a suggestion of banding in galena, mixed sulfide and thin pyritic streaks parallel to the vein, and some of the galena streaks are sufficiently pure and large to be mined cleanly and shipped directly to the smelter. .... Another notable feature of the Groundhog ore is that the chalcopyrite is much more prominently associated with sphalerite than with galena. Some of the Groundhog ore contains many small druses lined with crystals of all the different vein minerals.
>
> The ore bodies are the result of continual reopening and filling of the fissures. The mineral distribution along the vein indicates that the mineral-bearing solutions were forced to take different paths at different times; and the drusy cavities in the Groundhog ores, the banding, and the original sheeting and jointing of the vein zone preserved in massive ore by streaks of early quartz and pyrite all prove that the solutions were repeatedly diverted into more open channelways at several periods.
>
> Alteration accompanying the ore stage of mineralization is mainly chloritic, though at some places there are narrow bands of bleached rock, a few feet wide at most, like the quartz-sericite-pyrite-clay alteration bands of the pre-dike stage.

Lasky (1936) gives the order of deposition as follows: "quartz, pyrite, and minor chalcopyrite; sphalerite and minor quartz; galena, chalcopyrite, and minor quartz; quartz, pyrite, and calcite."

At present most of the ore is being mined from the Hanover limestone just below the Parting shale, an occurrence geologically similar to most of the ore at Hanover. The gangue minerals include hedenbergite, specularite, pyrite, chlorite, calcite, quartz, and clay minerals. Sphalerite is the most important ore mineral. Galena and chalcopyrite are economically important but appear to be less abundant than in the fissure fillings. Lasky and Hoagland (1948, p. 21) give as the paragenesis of the limestone replacement ores:

> "Hedenbergite and (?) ilvaite; rhodonite and garnet; magnetite and specularite; abundant pyrite accompanied by chlorite; abundant sphalerite accompanied by pyrite; galena; perhaps chalcopyrite and lamellar calcite; (hydrothermal leaching); quartz; pyrite, chalcopyrite and quartz; very minor sphalerite; quartz; scalenohedral calcite; chlorite and clay (?) minerals."

Specimens collected and studied by the writer are consistent with the above paragenesis on the assumption that a group of vuggy open space fillings were deposited following the leaching.

## Other Mines South and Southwest of Hanover

Lasky (1936) discussed the geology of a number of small mines and prospects of the Bayard area in the southwestern corner of the district. At the time of Lasky's work these mines had produced only minor amounts of ore, mainly oxidized and enriched lead, silver and gold ore. Since then the Bullfrog and Slate mines of U. S. Smelting, Refining and Mining Co., have produced a large amount of zinc-lead-silver ore. The Hobo mine, not discussed by Lasky, also falls into this group. Most of the ore has been produced from fissure fillings in the quartz diorite sill exposed at the surface in most of the Bayard area. Prominent gangue minerals are pyrite, quartz and calcite with some chlorite, and clay (?) minerals.

The Peerless mine, near Central, appears to be the most westerly mine in the district with appreciable production. There, lead-zinc ore with a gangue of calcite and quartz occurs as veins in a quartz diorite sill (Soule, 1947).

At Copper Flats a small highly-altered quartz-monzonite porphyry stock intrudes the Middle Blue limestone (Mullen and Storms, 1948; Lasky and Hoagland 1948). The stock is known from diamond drilling and underground workings to decrease in diameter with depth. The limestone at the surface has been pushed into a series of anticlines and synclines, in part overturned, which encircle the mass. A thick quartz diorite sill lies beneath the Middle Blue limestone. The ore consists of replacement bodies of sphalerite with magnetite in the limestone along the contact. Small amounts of pyrite, hematite and chalcopyrite are also present.

The Combination or Blackhawk mine is located just south of the Wimsattville basin. Schmitt (1942, p. 76) says of the geology:

> The ore is intermediate in type between the Groundhog and the pyrometasomatic ores at Hanover for it contains abundant quartz and pyrite in addition to pyrometasomatic silicates, has galena associated with the sphalerite, and contains silver. There is some minor chalcopyrite. The ore-depositing fluids apparently lacked the strong replacing power of those at Hanover and ground preparation was more important in the formation of the ore bodies. Thus the important ore is found only at fault intersections and junctions. Since the faults are nearly vertical the chimneys of ore are approximately vertical. The No. 1 chimney ore shoot outcrops near the collar of the Combination shaft and is associated with a pre-ore igneous neck or plug.... The No. 2 chimney ore shoot from the surface pitches steeply downward with a fault intersection and finally unites with the No. 1 ore shoot on the 650-foot level. Along each chimney the ore favors the pure limestone beds and avoids shale, shaly limestone, and sills. The lower parts of the ore shoots are in the Hanover limestone but end abruptly downward in shaly limestone. The upper parts of the chimneys are in the alternating limestone and minor shale of the Lower Magdalena formation.

## Mines in the Fierro Area

Several kinds of ore have been mined from the area within approximately two miles of Fierro. Iron ore has been mined along the contact between the Hanover-Fierro stock and dolomite of lower Paleozoic age. Magnetite is the dominant ore mineral, although considerable amounts of hematite are present in places. Some magnetite ore contains minor amounts of pyrite, chalcopyrite, and cubanite and traces of pyrrhotite and sphalerite. Gangue minerals include olivine, wollastonite, serpentine, garnet, epidote, pyroxene, quartz, and carbonates. The writer has identified ankerite from one mine. Schwartz (1923) gives the sequence of deposition as magnetite and pyrite; chalcopyrite and cubanite; pyrrhotite; and sphalerite. Important mines in this group are the Republic Iron, Union Hill, Jim Fair, Humbolt, and Snowflake mines.

Several mines with a slightly different type of ore are found along the Barringer fault. West of Fierro at the Continental and Pearson mines, important amounts of chalcopyrite and sphalerite occur with magnetite and garnet as replacements of the upper Paleozoic limestones along the Barringer fault. The paragenesis is interpreted by the writer to be garnet, magnetite, pyrite, chalcopyrite, sphalerite, minor chalcopyrite; similar to the sequence found by Schwartz for the iron ores. Some chalcopyrite contains tiny star-shaped bodies of sphalerite, suggesting exsolution. It may be significant that most of the chalcopyrite in this area apparently was deposited before sphalerite rather than following it as in the area around Hanover, because this chalcopyrite has been found to have a distinctly different content of certain trace elements.

The wide zone in which the Barringer fault crosses the Hanover-Fierro stock is badly shattered, and the rock is altered to sericite and clay minerals accompanied by abundant pyrite. Veins and disseminations of supergene copper minerals occur in this zone, and some chalcopyrite can be found. The area resembles the porphyry copper mineralization at Santa Rita in many ways, but no large bodies of ore are known.

Northwest of Hanover Mountain a small amount of chalcopyrite occurs as veins in relatively unaltered diorite porphyry at the Super Cobre mine. Other small occurrences of chalcopyrite are known in this area.

Farther northeast along the Barringer fault is the Shingle Canyon mine owned by the U. S. Smelting, Refining and Mining Co. Lead and zinc have been mined here, in part from a limestone replacement (Duriez and Neumann, 1948). Specimens collected by the writer appear to be replacements of a limy shale.

A few miles east of the Shingle Canyon mine is the Georgetown district, where rich silver ore was mined from the Fusselman limestone just beneath the Percha shale.

At the Mountain Home mine, northwest of Hanover, galena (and sphalerite?) are associated with vesuvianite and fluorite in the Syrena and Abo formations (Schmitt, 1935b).

## Production of Metals in the Central Mining District

Because the concentrations of some trace elements in the sulfide minerals seem to show a correlation with the distribution of major ore metals in the district, an attempt has been made to collect data on the production and grade of ore. Undoubtedly many companies and individuals have more and better data of this sort than the writer, but these have not yet been made public, and the data collected seem worth presenting.

Plate 1 shows the estimated total zinc production of mines in the district. The estimates are based on yearly production totals given in the Minerals Yearbook, plus data on the relative production of mines for recent years, milling capacity, estimated grade, and other information. Published data on total production of a few mines agree relatively well with the estimates.

From the map it can be seen that the zinc deposits of the district are concentrated in a northwest trending band with the largest production from the contact of the Hanover-Fierro stock. The area between Hanover and Santa Rita, and the Groundhog mine are also very important. The Bullfrog mine and the Copper Flats deposits have produced significant amounts of zinc.

Similar estimates of the lead production of the various mines have been prepared but are not believed to be very accurate. However there is no doubt that the Groundhog mine and the Bullfrog mine are by far the largest producers of lead in the district. One or the other of these mines has led the state in lead production almost every year for the last 20 years, according to the Minerals Yearbook.

In figure 25, the Zn/Pb ratios for a number of ores have been plotted against distance to the nearest outcrop of either the Santa Rita or Hanover-Fierro stock. The ratios have been calculated from a number of published analyses of either ore samples or average ore grades for mines. The Zn/Pb ratio changes from over 100 in much of the ore in the contact zone at Hanover to about 2 at the Groundhog mine and is still lower at the Bullfrog mine. The ore of the Shingle Canyon mine northeast of Fierro contains important amounts of Pb. Mines at intermediate distances from the stocks, like the Kearney and the Combination mines, show intermediate values of the ratio. This zonal relationship has been noted by other workers. For instance Schmitt (1935b, p. 202) says:

> At Hanover any given ore-bearing fault, such as the Republic mine fault zone, will show magnetite and minor sphalerite adjacent to the contact zone and sphalerite with no magnetite and with lead less than 0.1 percent next outward. Within 1000 ft. farther outward, the lead may increase from 0.1 to 3.0 percent, whereas zinc will remain constant or increase a few percent.

Similar relations exist with respect to the distribution of silver within the district. Silver is unimportant in the Hanover area. According to Storms and Faust (1948) the ore at the Kearney Mine contains only a fraction of an ounce of silver. At the Combination mine, 2 oz. of silver is reported by Warren (1935). Lasky gives 10 oz. as the average silver content of the ore at the Groundhog mine. No grade is known for

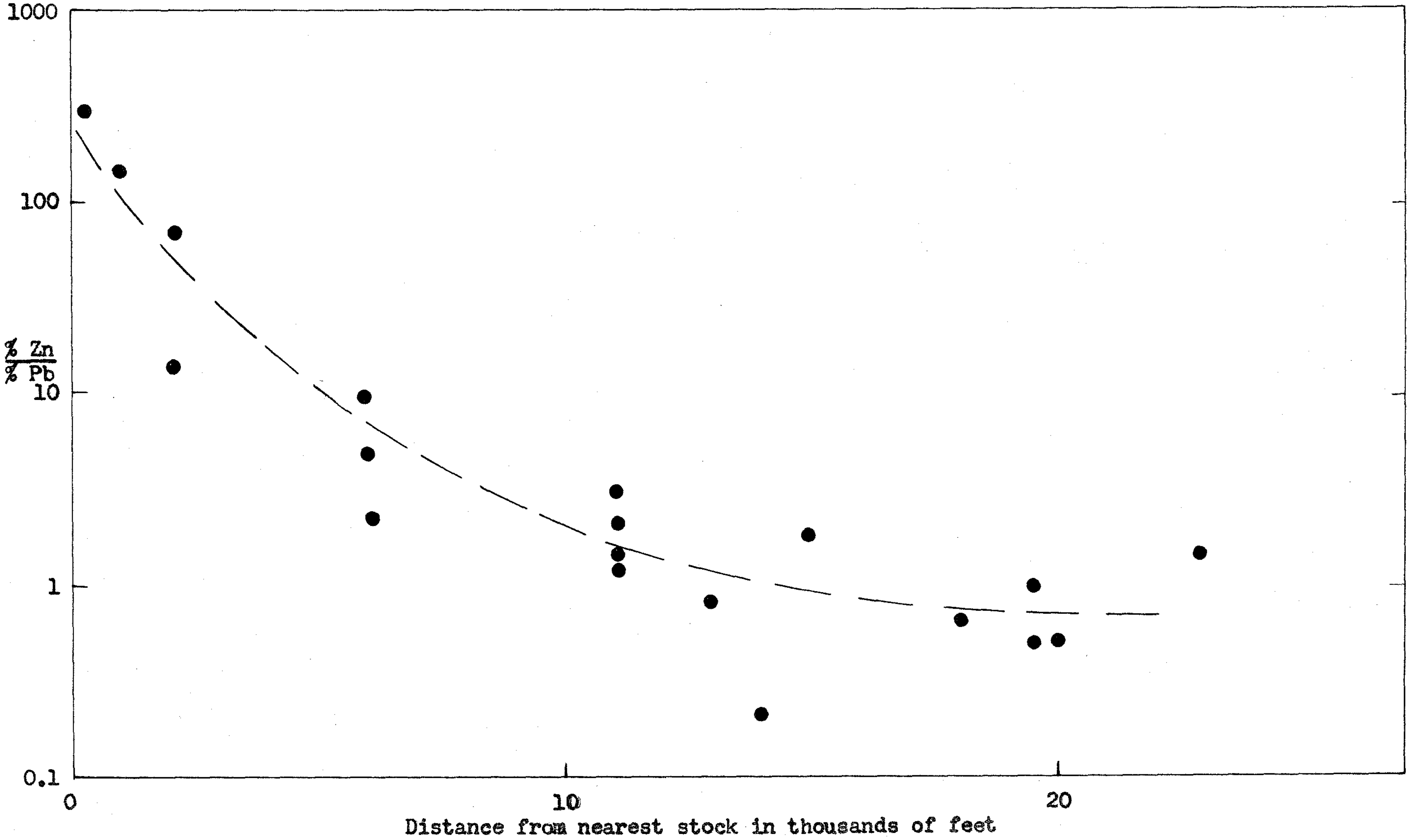


Figure 25. Zonal change in the Zn/Pb ratio of ores in the Central mining district, N. M.

the ore of the Bullfrog mine, but it has been the largest silver producer in the state during a number of years. Mines west of the Bullfrog all have silver in the ore according to the analyses at hand. Important amounts of silver were mined at Georgetown, a few miles northeast of Fierro. In addition, small amounts of gold have been mined in the southwestern part of the district, whereas it is not reported from near Hanover. Thus there appears to be a gradual increase in silver content of the ore with increased distance from the stocks. In contrast to a number of other porphyry copper deposits, gold and silver are not recovered from the ore at Chino.

Accurate estimates of the copper production of mines in the district have not been possible, but it is clear that the Chino mine has produced from 30 to 50 times as much copper as the Groundhog mine, the next biggest producer of copper. Some copper has also been produced from the Barringer fault area. Virtually all the sphalerite in the district contains blebs of chalcopyrite, but the amount of copper present in this fashion averages at most a few tenths of a percent. The distribution of copper within the district thus differs from the distribution of lead and silver in being concentrated at Chino and at the Groundhog mine to the west. However, copper is present in essentially all the ores of the district.

Zonal relations of copper to zinc do appear to exist. Leroy (1954) shows zoning from only copper minerals within and near the Santa Rita stock through mixed copper and zinc minerals farther north to a dominance of zinc minerals near the Oswaldo #2 shaft. Similar zoning probably exists to the northwest and west of the Santa Rita stock.

The cause of the well-developed zonal patterns in the district is not known. Schmitt (1935b) has suggested temperature gradients, changing composition of the mineralizing fluids, and differences in wallrock as possible causes. Probably all of these factors are in part responsible.

## The Pinos Altos District

A number of smaller mining districts are present in the Silver City region in addition to the Central mining district. Most of these districts are located near stocks of quartz-monzonite porphyry similar to the stocks of the Central mining district. Such districts include Silver City (Boston Hill and Chloride Flats), Tyrone, Lone Mountain and Pinos Altos. The Pinos Altos district is located about 8 miles west-northwest of Hanover and 7 miles north-northeast of Silver City. A variety of igneous rocks, mainly dioritic, are present in the district, but the ore appears to be most closely associated with a stock of quartz monzonite porphyry.

Two types of ore are found in the Pinos Altos region. In the area near the town of Pinos Altos, gold-bearing lead-zinc-copper ore has been mined from fissure veins of dominantly north to northeast trend in the quartz-monzonite and surrounding igneous rocks. The veins contain sphalerite, chalcopyrite, galena and gold with quartz, pyrite, calcite, barite, and rhodochrosite. Most of the value of the ore has been in gold, but sphalerite appears to be the most abundant heavy metal sulfide. Tetrahedrite was identified by the writer in one polished section.

About two miles west of Pinos Altos on the opposite side of the Continental Divide are a group of mines which have been called the West Pinos Altos district. The largest mine of the group is the Cleveland mine; others include the Atlas #2 and Houston-Thomas mines. The group of mines is located in a block of Paleozoic and Cretaceous sediments surrounded and intruded by dioritic igneous rocks. The ore bodies are replacements of limestone horizons in the Pennsylvanian. Marmatite is the dominant ore mineral with minor amounts of chalcopyrite and galena. Diorite underlies all the known ore-bearing areas, and one drill hole penetrated 600 feet of this rock, indicating the presence of a thick sill or small stock (Soule, 1948).

At the Cleveland mine, now abandoned, most of the ore occurs as replacements of two horizons in the limestone. The two ore bodies are usually separated by a few feet of unreplaced limestone. The sphalerite is coarse-grained, many grains being a centimeter in diameter. Euhedral quartz crystals occur in many specimens. Pyrite is present in all the ore, and pyrrhotite is present in much of it. The contacts of the ore with limestone are typically sharp, and a thin layer of ankerite is present between the ore and the limestone in many places. Typical ore ran 10% Zn, 1% Pb, 0.5% Cu. 1 oz. Ag, and a trace of gold.

Several varieties of pyrite occur in the ore. Some pyrite occurs as solid grains up to several millimeters in size, typically with irregular outlines. Other pyrite has a porous appearance with concentric zoning suggesting deposition as a colloid. Veins of solid pyrite cut across this colloform pyrite, and contacts of sphalerite with the colloform pyrite also cut across the zoning, suggesting that sphalerite replaced the pyrite. Pyrite also veins euhedral quartz (fig. 26). Chalcopyrite veins pyrite. A few narrow veins of late pyrite cut sphalerite.

Sphalerite occurs as coarse grains almost invariably containing relatively coarse rounded blebs of chalcopyrite. In some sections, blebs and lamellae of pyrrhotite are also present. Chalcopyrite veins the sphalerite in many sections (fig. 27). Grains of pyrrhotite several millimeters in size are present in some sections. They are clearly veined by chalcopyrite. In several sections marcasite is present with the pyrrhotite and the marcasite occurs as lamellae or lenses replacing pyrrhotite apparently along a parting, because within a single crystal of pyrrhotite all the marcasite lamellae are parallel (fig. 29, 31).

Other sections contain no pyrrhotite but show lamellar aggregates of marcasite which are inferred to represent pyrrhotite. In some examples the lamellar material is pyrite, not marcasite, as in fig. 30. Similar textures have been described by Edwards (1947, p. 100), Noble (1950), and others, and were also observed by the writer at the Pewabic and other mines in the Hanover area. The texture is of interest because it may throw some light on the stability relations of pyrite and marcasite. Allen, Crenshaw, and Johnson (1912) concluded that pyrite was the stable form of $FeS_2$ at all temperatures, and that the inversion of marcasite to pyrite took place rapidly above about 400° C. However, Buerger (1934) proposed on the basis of the best chemical analyses available that marcasite was slightly deficient in sulfur relative to $FeS_2$. If Buerger is correct, marcasite lies between pyrrhotite and pyrite in composition, and even if not truly stable relative to pyrite plus pyrrhotite, might be expected to form by the alteration of pyrrhotite according to Ostwald's principle, since marcasite would be closer to pyrrhotite than pyrite in composition. Thus the observation that pyrrhotite not uncommonly alters to marcasite rather than directly to pyrite, the "stable" form, suggests that Buerger's hypothesis of sulfur deficiency may be correct. Of course it is also possible that this pyrrhotite-marcasite relation is caused by similarity of crystal structure or composition of altering fluids.

Chalcopyrite in many of the polished sections of Cleveland mine ore contains star-shaped bodies of sphalerite, possibly originating by exsolution, (fig. 27, 28). Galena replaces sphalerite, pyrite and probably chalcopyrite. Two polished sections (CEN-321 and 60) contain a mineral similar in appearance to galena in ordinary light, but distinctly anisotropic. Qualitative spectrographic analyses show lead, copper, bismuth and silver as major constituents. An X-ray powder pattern does not fit any known mineral exactly, but resembles cosalite and benjaminite. The mineral is believed to be a silver-bearing cosalite. It may be the source of the bismuth in the bismuth-bearing gold ore shipped from the district (Soule, 1948).

The sequence of deposition is interpreted to be:

Euhedral quartz —?— Colloidal pyrite —— Pyrite —— Pyrrhotite —?— Sphalerite —— Chalcopyrite

Galena cosalite (?) —— Pyrite.

The age of pyrrhotite and chalcopyrite is doubtful relative to sphalerite, but chalcopyrite definitely veins pyrrhotite. Marcasite replaces pyrrhotite and is veined by the last generation of pyrite. It is probably later than sphalerite, but relations to chalcopyrite and galena are uncertain.

Figure 26. Photomicrograph of CEN-58. Pyrite veins quartz (x 100).

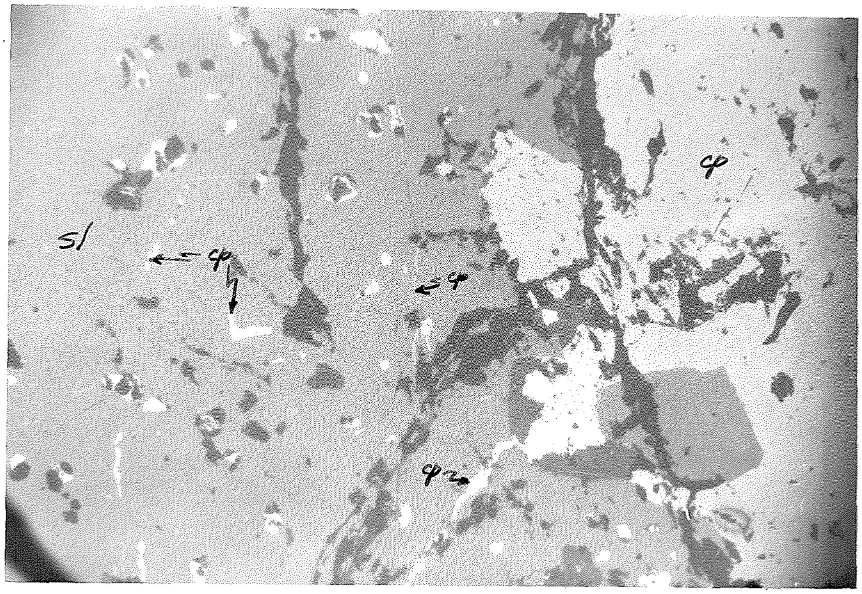


Figure 27. Photomicrograph of CEN-60. Chalcopyrite as veins and blebs in sphalerite, and a grain of chalcopyrite containing star-shaped sphalerite bodies at upper right (x 100).

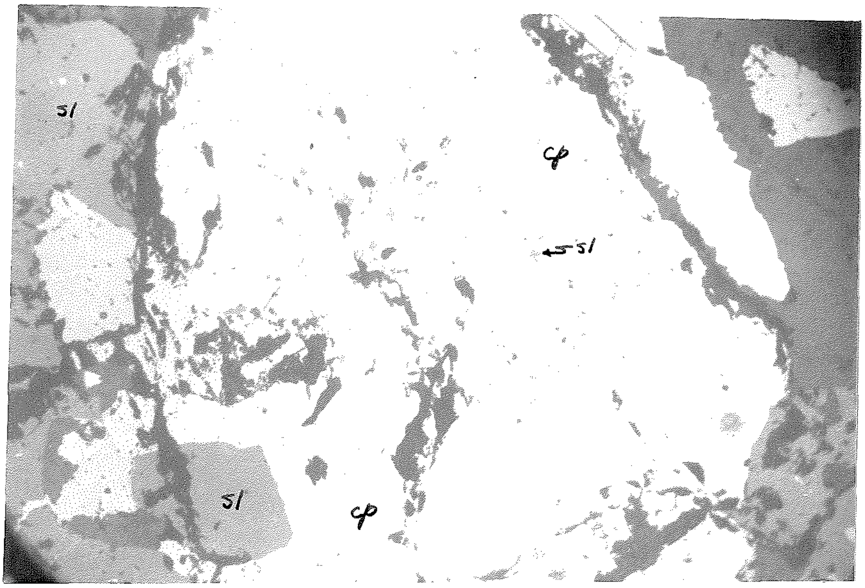


Figure 28. Photomicrograph of CEN-60. Star-shaped bodies of sphalerite in chalcopyrite (x 100).

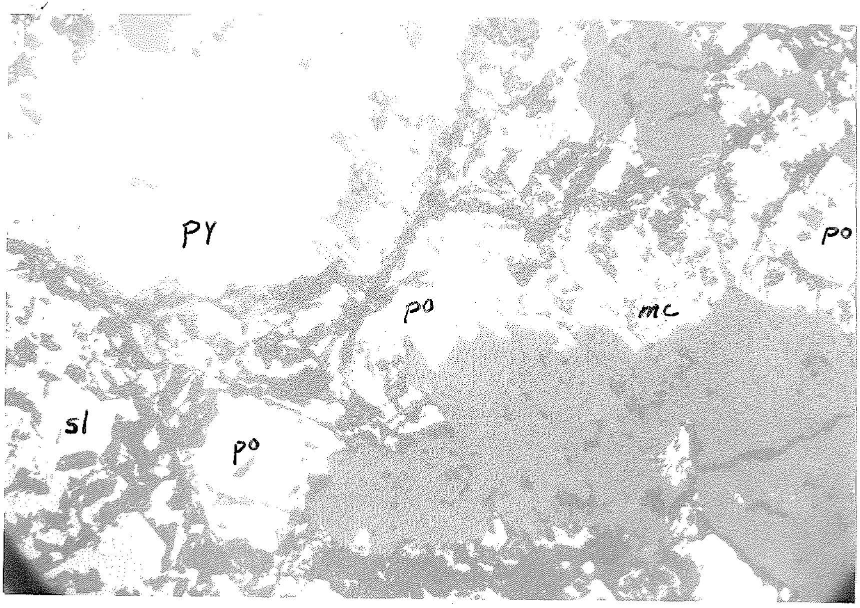


Figure 29. Photomicrograph of CEN-61. Lamellar marcasite replacing pyrrhotite, with porous-appearing pyrite (x 100).

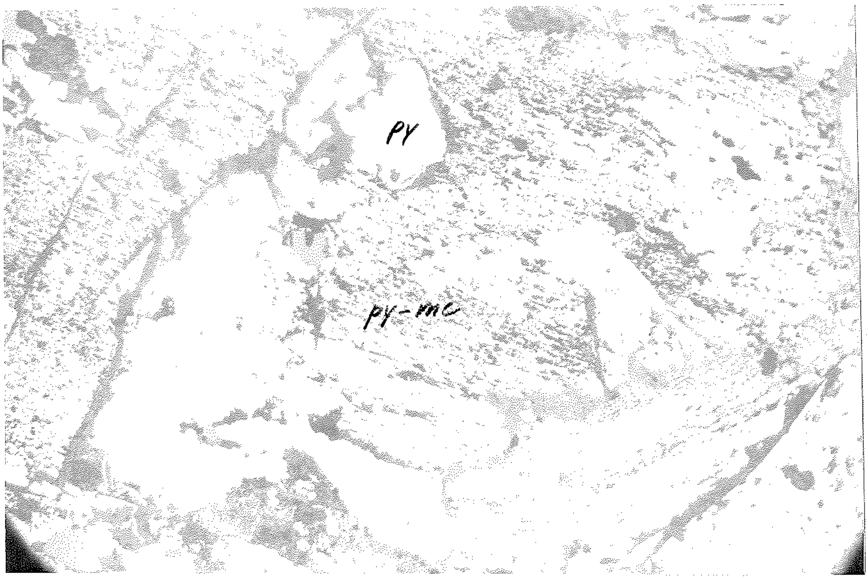


Figure 30. Photomicrograph of CEN-61. Lamellar aggregate of pyrite and marcasite probably originating by alteration of pyrrhotite (x 100).

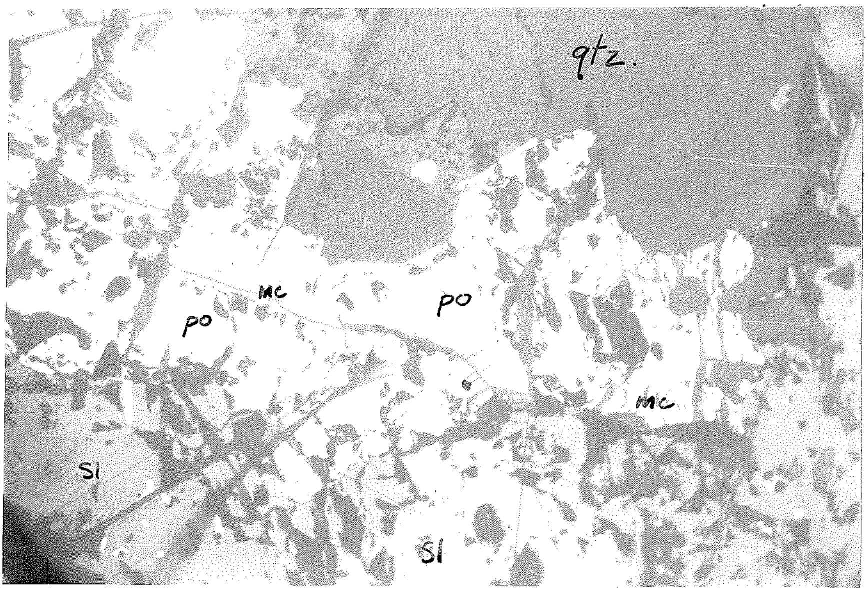


Figure 31. Photomicrograph of CEN-61. Lamellar marcasite replacing pyrrhotite (x 100).

# GEOLOGY OF THE BINGHAM MINING DISTRICT

## Introduction

The Bingham mining district is located on the east slope of the Oquirrh Range about 25 miles southwest of Salt Lake City, Utah. The district is best known for the production of copper from the great Utah Copper open pit mine of the Kennecott Copper Corporation, but in addition, a large quantity of copper ore and lead-silver-zinc ore has been produced from underground mines surrounding the porphyry copper deposit. The following resume of the geology is based largely on published discussions by Boutwell, Keith, and Emmons (1905), Hunt (1924, 1933), Hunt and Peacock (1948), and J. P. Hunt (1957). Figure 32 is a geologic map of the district from Hunt and Peacock (1948).

The district lies in a thick section of Pennsylvanian sediments intruded by two stocks of granitic to quartz monzonitic composition. The sediments throughout most of the district dip gently, forming an open syncline plunging to the northwest. However, the southwest limb of the syncline dips steeply or is overturned in certain parts of the mining district (see figures 33 and 34). Quartzite is the dominant rock type of the sedimentary series, but limestone and calcareous sandstone make up about a fourth of the sequence. The bulk of the ore produced by the underground mining operations has been closely associated with these limestone members of the section. In general, the limestones are somewhat lenticular in habit but some do persist for thousands of feet along the strike. Names have been given to several limestone horizons which have been important in localizing the ore. They are, in order from youngest to oldest, the Mayflower-Fortuna-Winnebago (or Parnell-Petro) series, the Commercial (Yampa) limestone, the Jordan (Highland Boy)

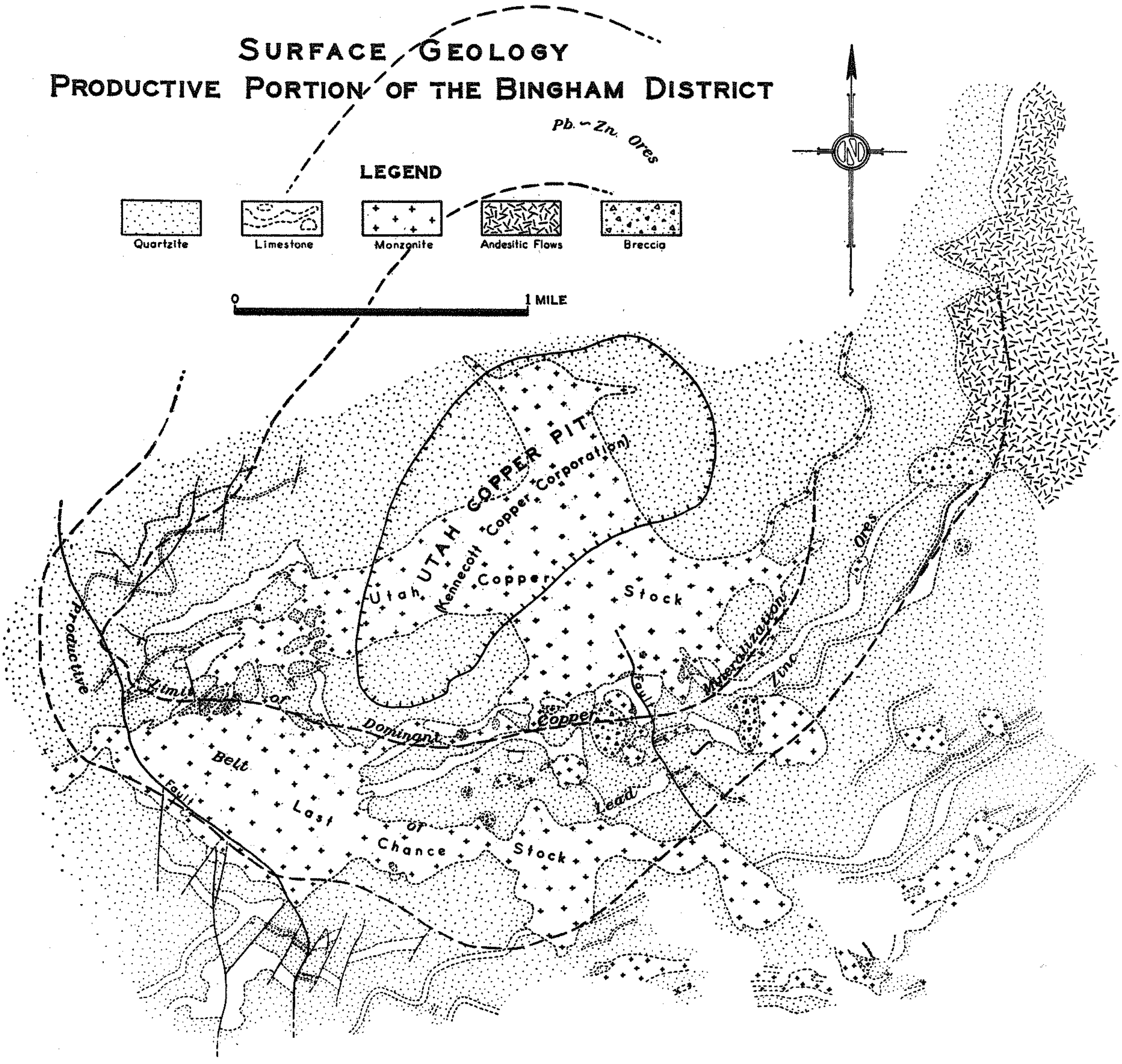


Figure 32. Geologic map of the Bingham mining district, Utah (from Hunt and Peacock, 1948).

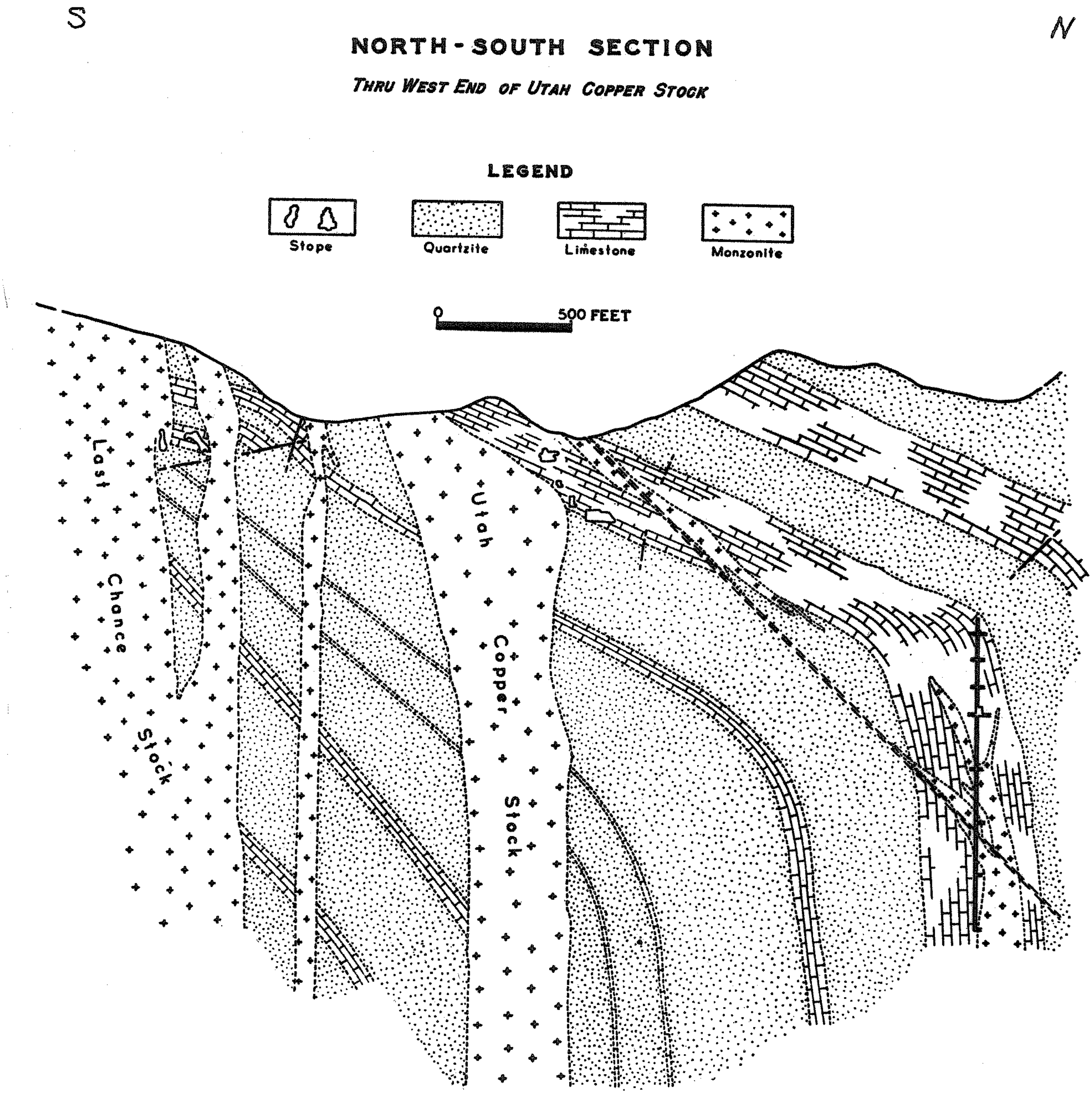


Figure 33. North-south cross-section through the west side of the Bingham mining district, Utah (from Hunt and Peacock, 1948).

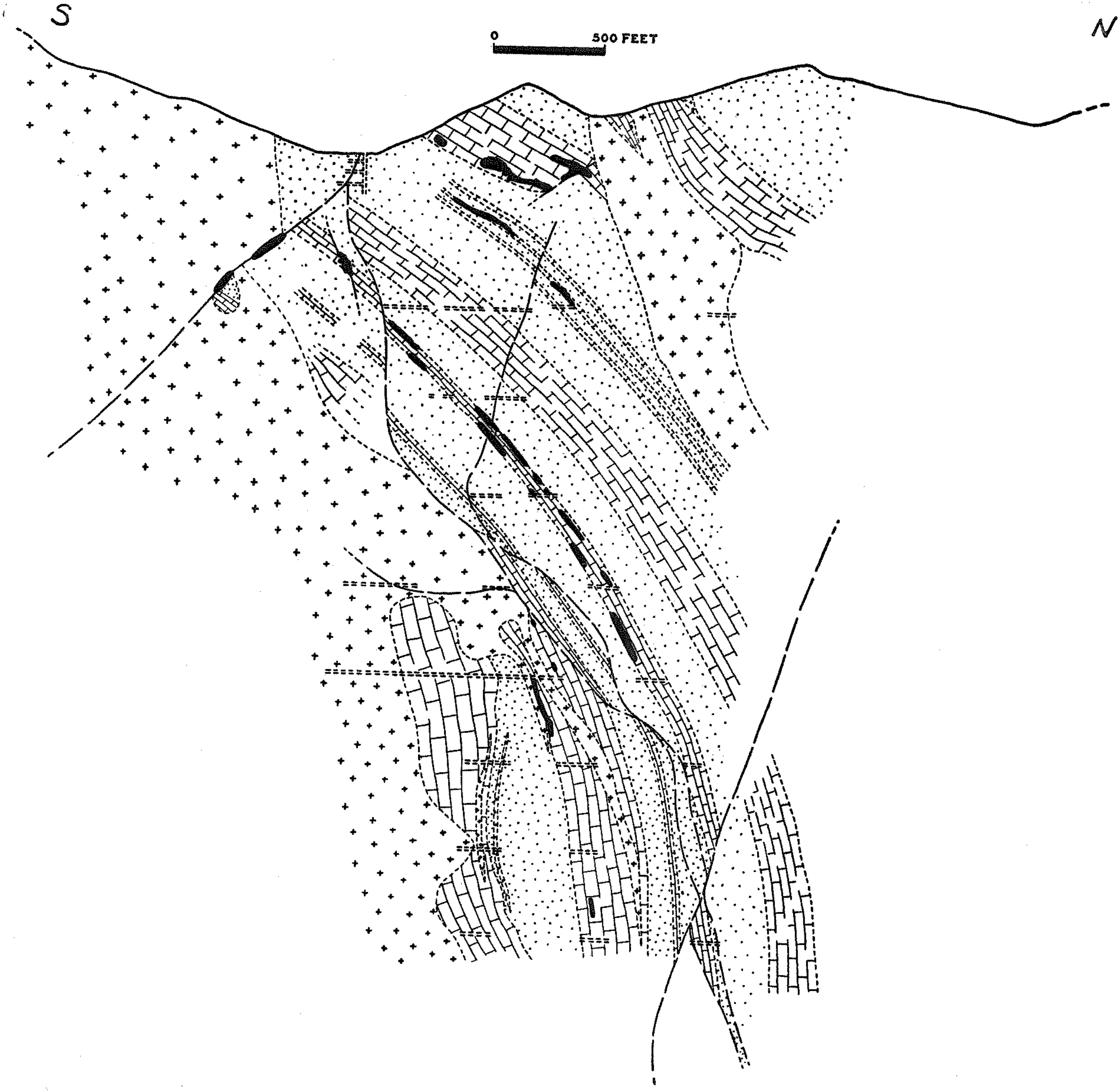


Figure 34. North-south cross-section through the U. S. section, U. S. Smelting, Refining and Mining Company property at Bingham, Utah (from Peacock, 1952).

Limestone, and the Alphabetical series.

The Utah Copper stock, intruded near the axis of the syncline, forms a center around which the ores and wallrock alteration appear to be zoned. Two rock types, the light porphyry and the dark porphyry, are easily distinguished within the stock, and more detailed study has led to the recognition of additional variations. According to Stringham (1953), true granite constitutes the bulk of the exposed igneous rock, but local variants include such extremes as syenite, quartz diorite, and diorite. Many specimens of the stock are characterized by abundant biotite.

The Last Chance stock to the south of the Utah Copper stock is also compositionally rather variable but quartz monzonite is probably most abundant. Pyroxene and amphibole are present in addition to biotite, but megascopically the rock appears similar to the Utah Copper stock. The close relationship of the two stocks is also indicated by dikelike connections between the two stocks. The Last Chance stock is relatively unaltered compared to the Utah Copper stock.

A number of breccia pipes cut the sediments south and east of the Utah Copper stock. At least some of the breccia pipes are post-stock and pre-ore in age. Some are also clearly later than the Tertiary andesitic volcanics along the east margin of the range. Gilluly (1932) concluded that monzonitic intrusive rocks and latitic extrusive rocks in the Fairfield and Stockton quadrangles to the south were intruded during a single period of igneous activity. The similarity to the rocks at Bingham suggested to Gilluly a similar contemporaneity of extrusive and intrusive activity at Bingham. This conclusion is opposed to that of Emmons (Boutwell, Keith, and Emmons, 1905), who believed the igneous activity was pre-Tertiary.

A number of periods of faulting have been distinguished within the district (Hunt, 1933). Faulting took place before intrusion of the stocks, between the times of intrusion and ore deposition, during ore deposition, and following ore deposition. Movement apparently occurred a number of times along some faults. In addition to the faults cutting across the bedding, a number of faults are parallel to the bedding.

## The Utah Copper Mine

The Utah Copper open pit mine has now been in operation about 50 years, and during this period approximately 500,000,000 tons of ore have been mined, with an average grade of a little less than one percent copper, a little molybdenum, a few hundredths of an ounce of silver, and a few thousandths of an ounce of gold. The ore is largely restricted to the Utah Copper stock. Some quartzite and limestone near the margin of the stock make ore, but the grade generally drops off near the contact of the stock.

The principal copper mineral is chalcopyrite, with smaller amounts of bornite, chalcocite, digenite and enargite. The copper minerals occur in veinlets of all sizes and as disseminated grains replacing the solid rock. Pyrite is abundant in most of the rock, although it appears to be subordinate to chalcopyrite in some higher grade areas. The most prominent alteration mineral is biotite, but studies by Stringham (1953), show kaolinite, illite, sericite, chlorite, allophane, and other minerals. Supergene enrichment and alteration are relatively minor.

In many parts of the pit, quartz veins up to several centimeters in width, typically with euhedral quartz crystals projecting from the walls into open spaces, contain chalcopyrite in the open spaces and intergrown with the quartz in the center part of the vein. Molybdenite flakes occur along the margins of many of these veins. Similar veins without chalcopyrite, or with chalcopyrite in greater abundance than quartz, can also be found. Pyrite is present in many of these quartz veins, and polished sections disclose marcasite in some. In the sediments and lower grade areas, quartz veins with pyrite but no chalcopyrite are common. Two of the three specimens of enargite seen by the writer occurred in quartz veins. Minor bornite and chalcocite occur with chalcopyrite in some veins. Biotite intergrown with the quartz and chalcopyrite is not uncommon, and a number of thin sections show sanidine (potash feldspar with low 2V) along vein margins. The character of most of the quartz veins indicates formation mainly by open space filling.

Disseminated copper minerals probably account for the bulk of the copper in the mine, although it is difficult in many cases to distinguish true disseminations from poorly developed veinlets. Bornite, chalcocite, and digenite appear to be more abundant as disseminated grains than in the quartz veinlets described above. Chalcopyrite is the dominant disseminated ore mineral, however. Bornite and either chalcocite or digenite are commonly associated and in many specimens rim grains of chalcopyrite. According to Stringham (1953), and J. P. Hunt (1957), bornite is more abundant in the granite porphyry in the bottom of the pit. Some molybdenite also occurs as disseminated grains.

Several altered limestone units are present in the pit, and chalcopyrite occurs in these along with pyrite, garnet, magnetite, hematite, actinolite and other minerals.

Small amounts of sphalerite and galena were found in several of the heavy mineral separates. Veins containing these minerals are reported to cut through the stock, although no examples could be found at the time of the writer's field work. A polished section of an enargite vein disclosed two unidentified minerals intergrown with the enargite, in addition to chalcopyrite and pyrite.

## Underground Mines

Underground mining operations encircle the Utah Copper pit on all but the north side. The ores mined by these operations include replacements of limestone units; veinlike bodies in and along fissures, bedding-planes and intrusive contacts; and veins cutting sediments, the Last Chance stock, or other bodies of igneous rock. Table 2, from Hunt and Peacock (1948), shows the production and grade of ore mined between 1909 and 1947.

Table 2

Ore produced by underground mining operations, 1909-1947
Bingham mining district, Utah
(after Hunt and Peacock, 1948)

| | Tons | Oz. Au | Oz. Ag | %Pb | %Zn | %Cu |
|---|---|---|---|---|---|---|
| Lead ore | 3,750,000 | 0.065 | 5.21 | 1.99 | --- | 0.59 |
| Lead-zinc ore | 9,794,000 | 0.062 | 4.91 | 8.88 | 5.0 | 0.29 |
| Lead (copper) zinc ore | 215,000 | 0.037 | 1.77 | 2.25 | --- | 1.54 |
| Gold-silver siliceous ore | 1,243,000 | 0.135 | 4.15 | 0.90 | 0.78 | 0.95 |
| Copper ore | 7,421,000 | 0.012 | 1.34 | 0.03 | --- | 2.44 |

In the western section of the district, particularly in the Highland

Boy and Utah Apex mines, copper ore occurs as replacements of the limestone. Hunt (1924) gives an excellent description of these ores. The copper is in the form of chalcopyrite, with an abundance of pyrite. Nonopaque gangue minerals include garnet, wollastonite, diopside, tremolite, and carbonate minerals. Pyrrhotite is reported by Butler (1920, p. 357). The limestone units within about 1500 feet of the Utah Copper stock are characteristically silicated, but farther away from the stock, the limestone has been merely recrystallized to a white marble. Still farther away, it retains its original dark color and fine grain size. The transition from white marble to black limestone in this section of the districe is closely paralleled by changes in the ore from pyritic copper ore to lead or lead-zinc ore. The boundaries between the alteration or ore types are relatively sharp and the changes take place in three dimensions along a surface roughly parallel to the contact of the stock. The lead ores contain galena with varying amounts of pyrite and sphalerite and minor amounts of copper and silver minerals. Ore bodies along bedding fissures and cross-cutting fissures have produced some ore, but the amount is subordinate to the ore of the replacement type.

In the United States Smelting, Refining and Mining Company's properties, both the U. S. section south and southeast of the Utah Copper stock and the Lark section to the east of the stock have produced dominantly lead, zinc, and silver. In the U. S. section, a number of limestone units have been followed down the dip for over three thousand feet. Fissures and other structural disturbances in the foot and hanging walls of the limestone units have been important in localizing the ore. Northeast-trending fissures cutting sediments and the Last Chance stock also contain ore.

The ore within the bedding fissures occurs as shoots plunging down the dip of the structures toward the Utah Copper stock. Shoots of pyrite coincide with the ore shoots in places but in other places diverge from the shoots of ore minerals. Figure 37 from Hunt (1957), shows similar shoots in the Lark section. The ore along bedding fissures has replaced the limestone but generally the replacement is restricted to the vicinity of the controlling fissure and does not replace the entire thickness of limestone.

The important ore minerals are galena and sphalerite. In places chalcopyrite or tetrahedrite-tennantite is present in notable amounts. Rarer minerals include pyrrhotite, marcasite, bornite, covellite, chalcocite, enargite, specularite, realgar, orpiment, cinnibar, stibnite, boulangerite, native silver and native gold. Gold is associated with pyrite and silver with galena or tetrahedrite-tennantite, (Hunt and Peacock, 1948). Oxidized ores occur near the surface, but oxidation has rarely penetrated more than 200' below the surface.

Most of the limestone units within the mine have been silicated or marbleized, although relatively less altered black limestone can be found. Hunt (1957) has studied the alteration minerals present in the fissures and adjoining wallrock in several parts of the mine. Minerals identified include garnet, diopside, wollastonite, feldspar, dioctahedral and trioctahedral micas of several types, dioctahedral and trioctahedral montmorillonoids of several types, including montmorillonite and saponite, several kaolin-group minerals, chlorite, vermiculite, talc, quartz, tridymite, crystobalite, opal, calcite, dolomite, rhodocrosite and gypsum. Temperature classification of the deposits according to either the sulfide or the non-sulfide minerals leads to the conclusion that a large range of temperature is represented by the ore and alteration. The appearance of ores seen by the writer suggests that in the deeper levels of the mine replacement processes were more intense than in the upper levels, where much open space filling took place.

The samples from the U. S. section analyzed in this study come from replacements of three limestone units and from five cross-fissures or fissure systems. From oldest to youngest (and on any one level from south to north), the limestone units are the D limestone, the B limestone, and the Highland limestone. The cross fissures, mostly striking northwesterly and dipping steeply, are the East fissure group, the Gem fissure, the Last Chance fissure and several splits, the Niagara fissure, the Holden fissure, and the Galena fissure (roughly from west to east).

Ore in the U. S. section is mostly medium to coarse grained, the sphalerite and galena crystals ranging from a millimeter to several centimeters in size. Some ore is vuggy, with euhedral sulfide minerals projecting into the cavities. Banding parallel to the fissure or bedding is present in some ores, and if present, is usually relatively coarse and is defined by changes in mineralogy. In the Galena fissure, however, thin color banding occurs within zones of light-colored sphalerite, and is accompanied by thinly banded mineralogical changes. In the other ores, the generally dark color of the sphalerite may vary, but rather than being banded, the color is concentrically zoned within single crystals or shows irregular areas of dark and light sphalerite. In the suite of specimens from the Last Chance fissure much of the sphalerite shows concentric color zoning within single crystals, having light sphalerite in the center and dark sphalerite on the margins of grains. Two poorly developed examples of the reverse kind of zoning were noted, however. Color variations of sphalerite from other structures are of the irregular type where present, except one concentrically-zoned example from the B limestone footwall fissure. Sphalerite in polished sections frequently is seen to contain zonally arranged blebs of chalcopyrite.

Age relations of the sulfide minerals appear to be complicated. The sequence pyrite-sphalerite-tetrahedrite-galena fits the relations observed for the bulk of these minerals. The relations of chalcopyrite in various sections place it through the entire sequence of deposition from sphalerite through galena, and possibly before sphalerite also. Pyrite as veins and small masses shows a similar range in age from beginning to end of the sequence. Marcasite was deposited late in the sequence. The larger grains of chalcopyrite seem to have been deposited after sphalerite and before galena, but occurrences of large chalcopyrite grains are relatively rare in the sections examined.

In the Lark section east of the Utah Copper stock the ore comes largely from replacements and bedding fissures along three limestone units, the Jordan, Commercial and Lark limestones. Smaller amounts of ore are produced from cross fissures. The limestones dip gently northwesterly toward and past the Utah Copper stock. Figure 35 shows shoots of ore and of pyrite plunging down the dip of the bedding toward the stock. The ore being mined at present is mainly lead-zinc ore, but chalcopyrite is present in some pyrite shoots and also in some galena and sphalerite ore. Much of the ore in the Lark section is associated with black limestone relatively less altered than limestones in the U. S. section. According to the writer's observations at the mine and in the laboratory, most sphalerite from the Lark section is relatively light in color and low in iron content. The sequence of deposition appears to be similar to that given for the U. S. section; at least such a sequence fits essentially all the relationships observed except that some tetrahedrite follows rather than precedes galena.

One of the more notable features of the Bingham district is the well-developed zoning in the limestone alterations and in the ores.

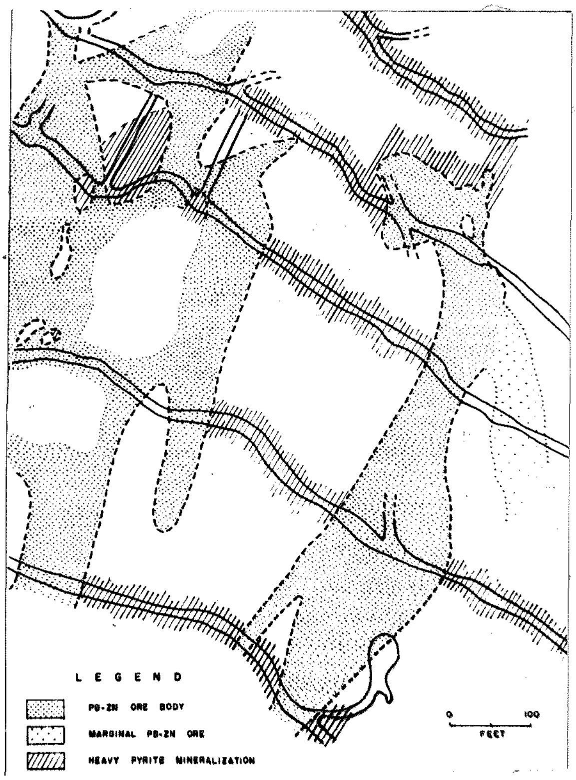


Figure 35. Composite plan of a portion of a major vein in the Lark mine showing form of the ore shoot and abundant pyrite mineralization. The vein dips towards the bottom of the page. (From J. P. Hunt, 1957).

Figure 32, after Hunt and Peacock (1948), shows the zoning in the ores. In the center of the district is the Utah Copper stock with its disseminated copper ore, and accompanying pyritization, biotization, silicification and other alterations. In the sediments surrounding the stock is a zone of higher grade pyritic copper ore in recrystallized or silicated limestone. Lead and lead-zinc ore occurs beyond the copper ore in relatively less altered limestone on the east and west, and in marbleized and silicated limestone on the south. In the southern portion of the U. S. section and the adjacent westerly portion of the Utah Metals mine and elsewhere near the fringes of the district, lead-zinc ores with notable amounts of silver have been mined.

The proportions of major metals in the sediments are not equal in all sectors of the district. On the west side of the district, the ratio of copper to lead is estimated at about 2 to 1, whereas to the south in the area of the U. S. section, the ratio is about 1 to 4 (Hunt and Peacock, 1948). The zonal relations of the ore and the limestone alterations do not exactly match either. Lead ore in the U. S. section occurs in silicated or marbleized limestone whereas in the eastern and western sectors of the district the lead ore is largely confined to relatively less altered limestone. However, these are only minor deviations from the overall zoning around the Utah Copper stock. There is no suggestion of zoning centered on the Last Chance stock.

According to Hunt (1924), the observed relations of copper ore and lead ore indicate that some lead ores are later than copper ores where an age difference is evident. The writer has observed chalcopyrite both older and younger than galena, but it is probable that Hunt's statement is true for the bulk of the ores.

## SAMPLE PREPARATION

All the chalcopyrite, sphalerite, and pyrite analyses of samples from the Central Mining District, New Mexico, were made on material drilled out of polished sections by the method described by Burnham (1955). Samples of sphalerite and a few samples of chalcopyrite from Bingham were obtained in the same way. Briefly, the method involves making a standard polished section of a small piece of the sample, and, after examining the section with regard to mineralogy and paragenesis, drilling 5 to 25 milligrams of material from the polished section, obtaining the purest possible material. A dental drill tipped with an S.S. White No. 2 carbide burr having a diameter of about one millimeter is used.

Any impurities or possible impurities are noted and taken into account in the interpretation of the analysis. The maximum estimated amount of opaque mineral impurities in the majority of the samples was one percent. A few sphalerite samples were estimated to contain up to 2% chalcopyrite as blebs, and a few chalcopyrite samples were estimated to contain 2-3% sphalerite. Gangue mineral impurities were occasionally included in the samples to a slightly greater extent, but most samples contained less than 1% gangue mineral impurities. Comparisons of measured lead content with the estimated galena impurities indicate that most estimates were too high. This method of sample preparation was found to result in generally purer samples and a better knowledge of the kind and amount of impurities present than the other methods tried, in addition to being much less time consuming. No difficulty was ever traced to contamination introduced by the process of making the polished section or from the drill.

In most of the chalcopyrite specimens from Bingham the chalcopyrite was dispersed as small grains through a relatively large volume of rock or gangue material, and an attempt to use the polished section technique produced a large proportion of mounts with little or no chalcopyrite in grains large enough to drill out. Therefore chalcopyrite mineral separates were prepared by the use of heavy liquids and magnetic separation. Selected portions of the samples were crushed to pass 50 mesh, and the minus 100 mesh grains were sieved off. The retain 100 mesh material was treated with bromoform, which removed the quartz, feldspar, and other minerals of low specific gravity, leaving a concentrate composed mainly of chalcopyrite, pyrite, molybdenite, biotite, and bornite. This concentrate was then passed through a Frantz Isodynamic Magnetic Separator. Biotite was more magnetic than chalcopyrite, and pyrite and molybdenite were much less magnetic and could be almost completely removed. Some difficulty was experienced with bornite, chalcocite, various intergrowths of these minerals, and with grains consisting of more than one mineral, because these grains overlapped chalcopyrite in their effective magnetic susceptibility. As a result, a few samples had to be discarded. Most of the samples were given an additional treatment with methylene iodide. Polished sections of grain mounts were made of splits from the chalcopyrite separates used for the trace element analysis. Pyrite, molybdenite, and marcasite were less than ½% in all samples. A few samples contained up to several percent of bornite, chalcocite, or gangue minerals, but the majority contained less than a percent. Appreciably more time was required for this method than the polished section method, but it allowed the use of a greater number and variety of samples.

Pyrite samples from Bingham were separated by hand picking coarsely crushed grains under the binocular microscope. This technique was found to be relatively time consuming, resulted in no better sample purity than the other methods, and resulted in less information about the mineralogy and paragenesis of the specimen than the polished section technique. However, the tendency of pyrite to occur as small cubes embedded in other minerals made it difficult to apply the polished section technique because of the small size of most grains and the tendency for the drill to "fall off" the hard pyrite grains into the surrounding softer material.

## ANALYTICAL METHODS

### Trace Elements in Chalcopyrite and Sphalerite

The chalcopyrite and sphalerite samples were analyzed spectrographically for trace elements by essentially the same procedure described by Burnham (1955). Slight modifications giving improved sensitivity and reproducibility were made in the analysis of samples from Bingham. The spectrographic procedures and equipment used for the Central mining district samples are summarized below.

Spectrograph: A Jarrel-Ash 21 foot Wadsworth-mounted grating type instrument with a dispersion of 5.2 Å. per millimeter in the first order.

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

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

Wavelength Range: 2300-4800 A. in the first order.

Excitation: A D.C. arc adjusted to give 13 amperes with the electrodes short circuited. The analytical gap is 4 millimeters. The central two millimeters is focused on a diaphragm, and this image is in turn focused on the slit with a vertical cylindrical lens.

Exposure: Slit width of 25 microns. Neutral density quartz filters are used to reduce the amount of light transmitted. At the end of 50 seconds of exposure, the camera is advanced and the sample burned to completion.

Plate calibration: Method of Dieke and Crosswhite (1943).

Electrode charge: 5 milligrams of sample and 15 milligrams of matrix. For chalcopyrite the matrix contains 50% $SiO_2$, 10% $Na_2CO_3$, and 40% ZnO. For sphalerite the matrix contains 50% $SiO_2$, 10% $Na_2CO_3$, 25% ZnO, and 15% CuO.

Internal standardization: Zinc, copper and iron are used as internal standards in the analysis of chalcopyrite, and zinc and copper in the analysis of sphalerite.

Standards: Spectrographically pure oxides added to a base of nearly pure chalcopyrite from Ajo, Arizona, and to a zinc sulfide phosphor. The standards are those prepared and used by Burnham (1955).

Analytical lines: See table 3.

Sensitivities: See table 4.

In the samples from the Central mining district, all elements were evaluated using the spectra recorded during the first 50 seconds of the burn only. The second portion of the burn was used only to check for interferences. For the samples from Bingham the method was modified to use the second portion of the burn for evaluation of nickel, cobalt, manganese, and silver. To decrease the extremely dark background, a two step filter was inserted into the optical path at the slit, and the transmission of the quartz filters was increased. The spectra produced through the clear step of the filter during the first 50 seconds of the burn were used to evaluate the more volatile group of elements, and the spectra produced through the dark step of the filter during the second portion of the burn were used to evaluate cobalt, nickel, manganese, and silver. This procedure resulted in an improved reproducibility for the less volatile group of elements, as well as improved sensitivity for nickel, cobalt, and manganese.

Table 3

Analytical Lines

| | | Internal standard line | |
|---|---|---|---|
| Element | Wave length | Chalcopyrite | Sphalerite |
| Ag | 3382.9 A. | Cu 3307.9 A. | Cu 3307.9 A. |
| As | 2780.2 | --------- | Zn 2670.5 |
| | 2860.5 | Zn 2670.5 | --------- |
| Bi | 3067.7 | Zn 2670.5 | Zn 2670.5 |
| | 2898.0 | Zn 2670.5 | Zn 2670.5 |
| Cd | 3261.1 | Zn 2670.5 | --------- |
| | 3403.0 | --------- | Zn 3018.4 |
| Co | 3044.0 | Cu 3169.7 | Cu 3169.7 |
| | 3453.5 | Cu 3169.7 | Cu 3169.7 |
| Ga | 2943.6 | --------- | Zn 2670.5 |
| Ge | 3039.1 | Zn 2670.5 | Zn 2670.5 |
| In | 3039.4 | --------- | Zn 2670.5 |
| | 3256.1 | Zn 2670.5 | Zn 2670.5 |
| Mn | 2798.3 | Fe 2791.5 | Cu 3169.7 |
| | 2949.2 | Fe 2791.5 | --------- |
| | 2933.1 | --------- | Cu 3169.7 |
| Mo | 3170.3 | Cu 3169.7 | Cu 3169.7 |
| Ni | 3414.8 | Fe 2791.5 | Cu 3169.7 |
| | 3050.8 | Fe 2791.5 | --------- |
| Pb | 2614.2 | Zn 2670.5 | Zn 2670.5 |
| | 2833.1 | Zn 2670.5 | Zn 2670.5 |
| Sb | 2877.9 | --------- | Zn 2670.5 |
| | 2598.1 | Zn 2670.5 | --------- |
| Sn | 3034.1 | Zn 2670.5 | Zn 2670.5 |
| Tl | 2767.9 | Zn 2670.5 | Zn 2670.5 |

## Table 4

Sensitivities of spectrographic determinations in ppm.

| Element | Central Mining District Cpy. | Sphal. | Py. | Bingham Mining District Cpy. | Sphal. | Py. |
|---|---|---|---|---|---|---|
| Ag | 1 | 1 | 1 | 1 | 1 | 1 |
| As | 300 | 300 | 100 | 100 | 300 | 100 |
| Bi | 3 | 3 | 10 | 1 | 1 | 30 |
| Cd | 10 | 30 | 30 | 10 | 30 | 30 |
| Co | 10 | 10 | 10 | 1 | 1 | 1 |
| Ga | - | 3 | 30 | - | 2 | - |
| Ge | 3 | 3 | 10 | 1 | 2 | 3 |
| In | 2 | 3 | 10 | 2 | 3 | 30 |
| Mn | 3 | 30 | 3 | 3 | 3 | 10 |
| Mo | 2 | 1 | 1 | 2 | 2 | 3 |
| Ni | 10 | 3 | 1 | 1 | 2 | 1 |
| Sn | 3 | 3 | 10 | 3 | 3 | 10 |
| Sb | 100 | 100 | 100 | 100 | 100 | 100 |
| Tl | - | 10 | - | - | 10 | - |
| Pb | (3) | (3) | 10 | (3) | 3 | 10 |
| Au | - | - | 10 | - | - | 10 |
| Cr | - | - | 10 | - | - | 10 |

The reproducibility of the method has been evaluated in two ways. Both methods make use of the concept of lognormal distribution of error in spectrographic analysis as discussed by Ahrens (1954). In the first method, eight analyses each of the chalcopyrite sample BOR-1 and the sphalerite sample PEW-8 were used as data. These samples were analyzed at intervals during a period of more than a year. The same samples were also analyzed by Burnham during his work, and thus afford a comparison between his analyses and those of the writer. For each element, the standard deviation of the logarithm of the concentration has been computed, and the results are shown in table 5. The standard deviation computed in this manner from the logarithms of the concentrations has been denoted by Ahrens (1954), as $\lambda$.

In the second method, the differences between duplicate analyses have been used to compute a value of $\lambda$. According to Dixon and Massey (1951, p. 239) an unbiased estimate of the standard deviation may be obtained by multiplying the difference between two observations from a normally distributed population by the factor 0.886. About 95% of the chalcopyrite and sphalerite samples in this study were analyzed in duplicate. The values of $\lambda$ for each duplicate analysis have been averaged for all of the samples containing the element to arrive at the figure given in table 5. The method involves the assumption that the reproducibility of the analytical procedure is the same for all concentration ranges represented in the samples. The writer believes from inspection of the data that this assumption is not strictly true, but that $\lambda$ is in general somewhat larger at concentrations near the detection limit than at concentrations 10 or 100 times as great, mainly because of difficulty in making the background correction. However, the value given does represent an average for the

## Table 5

### a. Reproducibility for chalcopyrite - CEN samples

| Element | λ from BOR-1 | λ from pairs | C |
|---|---|---|---|
| Bismuth | - | 0.107 | 25% |
| Cadmium | 0.139 | 0.102 | 24 |
| Cobalt | - | 0.186 | 45 |
| Indium | 0.158 | 0.117 | 27 |
| Manganese | 0.104 | 0.115 | 27 |
| Nickel | 0.071 | 0.127 | 30 |
| Silver | 0.186 | 0.182 | 43 |
| Tin | 0.121 | 0.074 | 17 |
| Molybdenum | - | 0.126 | 29 |

Table 5 (Cont.)

b. Reproducibility for sphalerite

| Element | λ from PEW-8 | λ from pairs CEN samples | C | λ from pairs BIN samples | C |
|---|---|---|---|---|---|
| Bismuth | 0.128 | 0.104 | 16% | 0.098 | 22% |
| Cadmium | 0.069 | 0.061 | 14 | 0.050 | 12 |
| Cobalt | 0.217 | 0.115 | 27 | 0.108 | 25 |
| Germanium | - | 0.118 | 28 | 0.087 | 20 |
| Gallium | - | 0.206 | 50 | 0.102 | 23 |
| Indium | 0.120 | 0.119 | 28 | 0.096 | 22 |
| Manganese | 0.080 | 0.131 | 30 | 0.069 | 16 |
| Molybdenum | - | 0.146 | 34 | - | - |
| Nickel | 0.078 | 0.112 | 26 | 0.203 | 49 |
| Silver | 0.200 | 0.128 | 30 | 0.085 | 20 |
| Tin | - | 0.075 | 18 | 0.086 | 20 |

(The values given as C, the coefficient of variation , have been computed from the value of λ from pairs by averaging the positive and negative percent deviations. The value of λ for the average of duplicate analyses of a sample is 0.707 times the values in the table.)

samples actually analyzed rather than the value for a single concentration as obtained by replicate analyses of a single sample. Also, a comparison of the reliability of the standard deviation obtained by this method and the single sample method discussed above shows that $\lambda$ computed from n samples in duplicate is about as accurate an estimate of $\lambda$ as n/2 replications of a single sample. Thus a better value of $\lambda$ is more easily obtained in practice by the method of duplicates.

For all the samples from the Central mining district, and the sphalerite samples from Bingham, the duplicate analyses were made on separate plates, generally a day or two apart, and the reproducibility obtained from these duplicate analyses is believed to represent the reproducibility of the method over a period of several weeks or months. In general, the values of $\lambda$ computed from the two standard samples are slightly larger than for the duplicates, apparently because of changes in the equipment and conditions over the longer periods of time. In the case of BOR-1, two of the analyses were made by the modification of the procedure used for the chalcopyrite from Bingham. Except for a small decrease in the amount of silver found in the latter two analyses, no long-term trends were found in the values. Most of the samples of a particular mineral from one mining district were analyzed in a batch within a period of two to four months, therefore the reproducibility computed from pairs is believed to be close to the true value. In general, the method has a coefficient of variation of 20-30%. The standard deviation of the average concentration for the analyses made in duplicate would, of course, be 0.707 times the value given in table 5, or 10-20% of the amount present.

The poor reproducibility for cobalt in chalcopyrite and for germanium and gallium in sphalerite is believed to be partly caused by concentrations near the detection limit in most of the samples analyzed, and the resulting difficulty in making the background correction. For some elements, especially gallium, indium, and manganese, the method of internal standardization is not entirely satisfactory. Possibly the use of a different internal standard would improve the reproducibility for these elements. The analysis of silver was accomplished by measuring the width of the silver line at 3383A., using the width of a copper line as an internal standard. Apparently this procedure is not completely satisfactory, although the same method worked excellently for cadmium in sphalerite. In some samples it is possible that the amounts of silver in the duplicate analyses were not equal.

Table 6 gives the concentrations obtained for the samples BOR-1 and PEW-8 by Burnham (1955) as compared to those found in the present work, and also a comparison of analyses from Fryklund and Fletcher (1956) with splits of the same samples analyzed during this work. These splits were kindly furnished by Harry Bastron of the U. S. Geological Survey. It should be recognized that spectrochemical analysis is known to give results which are reproducible, but do not accurately measure the concentration present in the sample. Comparisons of samples analyzed by the same procedure and equipment are not affected by this type of error, but comparison of analyses done in different laboratories can lead to significant errors, as suggested by the comparison with the analyses of the samples of Fryklund and Fletcher shown in table 6.

## Trace Elements in Pyrite

Pyrite standards were prepared by adding spectrographically pure oxides of arsenic, antimony, bismuth, cadmium, chromium, cobalt, copper,

Table 6

A. Comparison with results of Burnham (1955)

1. Chalcopyrite sample BOR-1

| | Ag | Cd | In | Mn | Sn |
|---|---|---|---|---|---|
| Burnham (1955) | 600 | 50 | 80 | 7 | 2000 |
| This work | 490 | 45 | 83 | 4.9 | 1800 |

2. Sphalerite sample PEW-8

| | Ag | Bi | Co | Cd | In | Mn | Ni |
|---|---|---|---|---|---|---|---|
| Burnham (1955) | 20 | 4 | 300 | 1000 | 60 | 1000 | 20 |
| This work | 12 | 4.6 | 330 | 1200 | 11 | 2200 | 6.8 |

B. Comparison with results of Fryklund and Fletcher (1956)

| Sample | Cd | | Co | | Ga | | Ge | |
|---|---|---|---|---|---|---|---|---|
| | CIT | USGS | CIT | USGS | CIT | USGS | CIT | USGS |
| 53-159S | 4500 | 4100 | 2 | 10 | - | 10 | - | 20 |
| 53-160S | 2800 | 2100 | 20 | 30 | 50 | 10 | 3 | 20 |
| 53-162S | 3100 | 2400 | 10 | 30 | 60 | 10 | - | 20 |
| 53-166S | 1900 | 1500 | 50 | 70 | 30 | 6 | 6 | 20 |
| 54-212S | 2300 | 3400 | 40 | 50 | 15 | 6 | 4 | 20 |
| 54-214S | 3800 | 4200 | 30 | 40 | 40 | 20 | 30 | 50 |

| Sample | In | | Mn | | % FeS | |
|---|---|---|---|---|---|---|
| | CIT | USGS | CIT | USGS | CIT | USGS |
| 53-159S | - | 30 | - | 9 | ? | 0.54 |
| 53-160S | 10 | 30 | 2500 | 600 | 7.21 | 7.55 |
| 53-162S | 8 | 30 | 400 | 70 | 1.68 | 1.42 |
| 53-166S | 20 | 30 | 1700 | 400 | 14.9 | 12.1 |
| 54-212S | 40 | 30 | 6000 | 9600 | 18.9 | 17.3 |
| 54-214S | 10 | 30 | 2500 | 2400 | 8.33 | 9.4 |

USGS = Fryklund and Fletcher (1956).
CIT = This work.

gallium, germanium, indium, lead, manganese, molybdenum, nickel, silver, thallium, tin, titanium, and vanadium and metallic gold to a base of pyrite obtained from a large single crystal found in the mineral collection of the California Institute of Technology. This pyrite does not contain detectable amounts of any of the above elements. The locality from which the crystal was collected is not known. For the 1% and 0.32% standards, three separate sets of mixtures were made up containing a maximum of eight elements, in order to minimize the matrix effect of the oxides on each other. For 0.1% and below, all elements are contained in a single standard.

After some experimentation, the pyrite samples from the Central mining district were analyzed by a procedure almost identical to the method used for chalcopyrite from that district. The same matrix of $SiO_2$, $Na_2CO_3$, and ZnO was mixed with the samples in a matrix to sample ratio of 3 to 1. The other conditions and procedures remained the same. Zinc and iron were used as internal standards. The sensitivities obtained are not as good as for sphalerite or chalcopyrite. The reason for this slightly poorer sensitivity is not clear. The addition of copper to the matrix did not seem to improve the sensitivity.

Pyrite samples from Bingham were analyzed by essentially the same method employed for the chalcopyrite and sphalerite samples from Bingham, using a two-step filter, 80% transmission, and both portions of the burn.

## Iron In Sphalerite

The amount of iron in sphalerite is known to vary considerably, and for this reason alone it is worthy of as much attention as trace element concentrations. In addition, Kullerud (1953) has published a phase diagram for the system FeS-ZnS and has proposed that the amount of iron in sphalerite under certain conditions is a measure of the temperature of deposition. Therefore it seemed desirable to develop a method for the analysis of iron in sphalerite.

The characteristics desired for such a method were that it be relatively rapid, reproducible to ± 5% or less of the amount of iron present, usable on samples as small as ten milligrams, and non-destructive. The last two requirements were necessary in order that the same sample could be used for emission spectrographic analyses following the iron determination.

Kullerud (1953) used x-ray diffraction and emission spectrographic methods for the determination of iron in sphalerite. Fryklund and Fletcher (1956) used an emission spectrographic method. A few trial runs using x-ray diffraction indicated that the method was slow. Emission spectrographic methods would destroy the sample and probably not give the required accuracy. Evaluation of iron in the spectra recorded for the trace element work gave extremely erratic results.

The recent acquisition of a Norelco x-ray fluorescence spectrograph by the Division of Geological Sciences allowed the use of this method of chemical analysis. A very satisfactory method, meeting all the requirements, has been developed by Mr. A. A. Chodos and the writer.

Ten milligram samples of sphalerite are weighed into a flat-bottomed circular cavity (1/32" deep x 1/4" dia.) drilled into a lucite holder. The samples are spread to give a roughly even thickness within the cavity, but no great pains are taken. The use of the Zn/Fe intensity ratio eliminates the necessity for internal standards, binders, briquetting, and other involved sample preparation procedures. No effect of sample weight on the ZnS/FeS ratio could be detected in samples ranging from 3 to 15 mg.

Weighing the sample is necessary only to limit the counting rates of the Geiger tube.

The spectrograph is equipped with a high purity tungsten x-ray tube (Phillips FA-60). About 60% of the analyses were made using a sodium chloride crystal and an argon Geiger tube. The x-ray tube was operated at 35kv. and 24ma. for these analyses. The peak maxima for Fe $K_\alpha$ and for Zn$K_\alpha$ second order are used. The peak maxima are determined from time to time by counting over the peaks and found to reproduce within about 0.02° 2θ over periods of several weeks and longer. The second order zinc peak was chosen in order to keep the counting rates of the Geiger tube below 800 counts per second to avoid coincidence errors. For each peak, 25,600 counts were taken and for each background 6,400 counts. The background was measured on both sides of each peak and averaged.

More recently the analyses have been carried out with a Norelco gas flow proportional counter. For these analyses a lithium fluoride crystal has been used with a wider collimator (0.020" instead of 0.005") to broaden the peaks. The x-ray tube is operated at 45kv. and 25ma. giving higher counting rates but otherwise comparable results. The analysis time is about 15 minutes per sample.

Originally, synthetic mixtures of zinc sulfide phosphor, pyrite and iron powder were used for standards. The results from chemically analyzed samples furnished by Bruce Doe and by V. Fryklund and H. Bastron of the U. S. Geological Survey indicated a small systematic difference between the wet chemical analyses and our results. The reason for the discrepancy is not clear. The present standards consist of nine sphalerite samples analyzed by the writer and E. Godijn for iron and zinc by wet chemical procedures. The older x-ray fluorescense results have been corrected for this change in standards.

For the wet chemical analyses about 0.5 grams of sample was dissolved in concentrated boiling HCl or fused in potassium pyrosulfate. Iron was double precipitated as the hydroxide, reduced in a silver reductor, and titrated with ceric ammonium sulfate to a ferroin endpoint. Zinc was determined on the iron filtrate by precipitation as zinc ammonium phosphate and ignition at $900^{\circ}$ C. to zinc pyrophosphate. Several of the samples were analyzed for iron without separation of the zinc and gave the same results within the limits of error. Two samples were analyzed for iron by both Rose and Godijn with identical results. Table 7 gives the sphalerite analyses, including spectrochemical analyses for Mn and Cd. Sample Doe #11 is believed to contain a small amount of calcite. The same may be true of samples USGS 53-162S and 53-160S. The zinc analyses may be a little high for samples Sphalerite III and CEN 266, because of coprecipitation of potassium in the zinc ammonium phosphate precipitates.

The working curve is plotted as the Zn/Fe intensity ratio against the ZnS/FeS concentration ratio. This is the mutual standard concept introduced by Couillette (1943). It has been used by Mortimore and Romans (1953) for x-ray fluorescence analysis. The procedure in this case gives an almost linear working curve. In computing the percent FeS from the ZnS/FeS ratio the assumption is made that FeS + ZnS equals 100% (i.e. $\%\mathrm{FeS} = \frac{100}{1 + \mathrm{ZnS}/\mathrm{FeS}}$). This assumption neglects the small amounts of Mn and Cd present, as well as impurities not containing iron or zinc. The error resulting from ignoring Mn and Cd is negligible. The ability to ignore iron-free and zinc-free impurities, such as calcite or quartz, is an advantage because the results are equivalent to those from a pure sphalerite sample.

## Table 7

## Chemical analyses of sphalerites #

| | TS-68 | CEN-214 | S. III | Doe 11 | S. II | S. I | CEN-266 |
|---|---|---|---|---|---|---|---|
| ZnS | 81.2 | 90.3 | 97.6 * | 83.6 | 98.82 | n.d. | 97.2 * |
| FeS | 18.17 | 8.61 | 3.19 | 11.52 | 0.40 | 0.33 | 3.24 |
| CdS | 0.23 | 0.15 | 0.33 | 0.15 | 0.51 | 0.60 | 0.19 |
| MnS | 0.3 | 0.21 | 0.02 | 0.95 | | | 0.06 |
| Insol. | | | | 1.16 | 0.04 | | |
| Total | 99.90 | 99.27 | 101.14 | 97.38 | 99.77 | | 100.69 |

| | 53-162S | 53-160S |
|---|---|---|
| ZnS | 89.3 | 95.25 |
| FeS | 7.21 | 1.68 |
| CdS | 0.35 | 0.30 |
| MnS | 0.09 | 0.09 |
| Insol. | | |
| Total | 96.95 | 97.32 |

*Possibly too high because of co-precipitation of potassium from the potassium pyrosulfate flux used.

n.d. Not determined.

# Iron and zinc determined by wet chemical procedures, Mn and Cd determined spectrographically.

Repeated analysis of the standards gave a coefficient of variation of 3% except for the concentration range below 1% where the coefficient of variation is 5 - 10%.

The possibility of absorption or enhancement of the iron or zinc lines by other elements present in the sample has been investigated using mixtures. The presence of copper in the sample might increase the intensity of the iron radiation, and the presence of manganese might reduce the intensity of the zinc radiation. One percent of $Mn_3O_4$ mixed with a sample produced no definite change in the percent FeS found. Ten percent $Mn_3O_4$ produced a decrease of about 12% in the amount of iron found. Ten percent CuO produced a slightly smaller change. Because the greatest amount of Mn found in sphalerites analyzed during the present study is a little over one percent, the absorption and enhancement effects are believed to fall within the limits of the analytical procedure.

## DATA

Data on trace elements in chalcopyrite and sphalerite are listed in tables 8 through 11. The concentrations are given in parts per million by weight (ppm.) of the element, except for iron in sphalerite, which is given in weight percent FeS.

A dash (-) indicates the element was not detected. In a few cases, an element was present in amounts greater than could be analyzed with the standards or working curves in use. The concentrations in these cases are indicated by a greater than ( > ) symbol followed by the maximum concentration which could be analyzed. Some samples were not analyzed for certain elements, and are indicated by an asterisk (*). A few analyses by Burnham have been included, and are marked by a dagger ( † ). For a few samples no meaningful average could be obtained owing to disagreement of the duplicate analyses or other reasons; these are indicated by a query (?).

The analyses are given to one significant figure, with the addition of 1.5, 15, 150, etc. This addition has been made because the spectrographic error is believed to be approximately proportional to the amount present, as mentioned previously, and the difference between 10 and 15 ppm. can thus be distinguished about as accurately as the difference between 7 and 10 ppm. Cadmium is given to two significant figures.

Standards for lead were not made up for chalcopyrite, and had not yet been made up for sphalerite at the time the samples from the Central mining district were analyzed. Therefore, the intensity of a lead line was noted, or intensity ratios with zinc were measured, and these data combined with the later standards for lead in sphalerite were used to make an estimate of the lead content of the samples. These estimates are given as an "X" followed by a number of zeros indicating the range to a factor of ten within which the lead content is estimated to be. Thus, X00 indicates a lead content between 100 and 1000 ppm.

The following elements were looked for but not found in the samples:

Chalcopyrite, Central mining district: As, Ge, and Sb.

Sphalerite, Central mining district: As, Au, Sb, and Tl.

Chalcopyrite, Bingham mining district: Sb, (except BIN-608), Tl.

Sphalerite, Bingham mining district: Au, Tl.

Vanadium was detected in a few sphalerites from the Central mining district, but because the analytical error appeared to be very large, and some vanadium was present in the electrodes used, no values are given.

Table 8

Trace Elements in Chalcopyrite from the Central Mining District

| | Ag | Bi | Cd | Co | In | Mn | Mo | Ni | Pb | Sn |
|---|---|---|---|---|---|---|---|---|---|---|
| Group I | | | | | | | | | | |
| CEN-30 | - | - | - | 40 | - | 4 | - | 15 | XO | 40 |
| CEN-31-1 | - | - | - | - | 2 | 30 | - | - | XO | 60 |
| CEN-31-2 | - | - | - | 40 | 4 | 50 | - | 10 | XO | 70 |
| CEN-31-3 | - | - | - | 20 | 2 | 8 | - | 10 | XO | 70 |
| CEN-32-1 | - | - | - | 15 | - | 8 | - | - | XO | 50 |
| CEN-32-2 | - | - | - | 20 | - | 5 | - | - | XO | 50 |
| CEN-32-3 | - | - | - | 20 | - | 10 | - | - | XO | 50 |
| CEN-32-4 | - | - | - | 30 | - | 15 | - | - | XO | 50 |
| CEN-42-1 | - | - | - | 40 | 2 | - | 700 | 10 | XO | 60 |
| CEN-42-2 | - | - | - | 15 | 3 | 10 | 80 | 10 | XO | 60 |
| CEN-45-1 | 15 | - | - | 60 | 4 | 6 | 10 | 60 | XOO | 60 |
| CEN-45-2 | 10 | - | - | 60 | 5 | 4 | 10 | 40 | XOO | 60 |
| CEN-65 | - | - | - | 15 | 3 | 20 | 15 | - | XO | 10 |
| CEN-67 | 3 | - | - | - | - | 7 | 4 | - | - | 15 |
| CEN-71 | 10 | - | - | (2) | 20 | 700 | 3 | - | - | 50 |
| CEN-72 | - | - | - | 15 | 8 | 50 | 7 | 30 | - | 15 |
| CEN-75 | 15 | - | - | - | 4 | 50 | 9 | - | XO | 40 |
| CEN-576 | 4 | - | - | 20 | 5 | 10 | 5 | - | XO | 90 |
| CEN-579 | 15 | - | 20 | 150 | - | 3 | 30 | 100 | XO | 20 |
| CEN-580 | 15 | 7 | 50 | (6) | 40 | 1000 | - | 8 | XOO | 6 |
| SR-16 | 10 | - | - | 30 | 3 | 100 | - | 15 | XO | 9 |
| Group II | | | | | | | | | | |
| CEN-3 | 7 | - | - | (1.5) | 50 | 60 | - | - | XOO | 70 |
| CEN-17 | 40 | 6 | - | - | - | 90 | 4 | - | XOOO | - |
| CEN-343-1 | - | - | - | - | 60 | 60 | - | - | XO | 40 |
| CEN-343-2 | - | - | - | - | 60 | 20 | 3 | - | XO | 40 |
| CEN-343-3 | - | - | - | - | 40 | 20 | - | - | XO | 30 |
| CEN-343-4 | - | - | - | - | 50 | 20 | - | - | XO | 40 |
| CEN-343-5 | 2 | 3 | - | - | 70 | 30 | - | - | XO | 40 |
| CEN-349 | - | - | - | - | 15 | 600 | - | - | XOO | 20 |
| CEN-354-1 | 7 | 6 | - | - | 60 | 3 | - | - | - | 100 |
| CEN-354-2 | 8 | - | - | - | 50 | 15 | - | - | - | 90 |
| CEN-354-3 | 40 | 4 | - | - | 60 | 8 | 3 | - | - | 100 |
| CEN-354-4 | 30 | - | - | - | 50 | 7 | - | - | - | 90 |
| CEN-354-5 | 8 | 40 | - | - | 50 | - | - | - | - | 90 |
| CEN-354-6 | 40 | 5 | - | - | 40 | 15 | 4 | - | - | 80 |
| CEN-368 | 600 | 30 | 10 | - | 70 | 100 | - | - | XO | 100 |
| CEN-369 | 15 | 4 | - | - | 200 | 3 | - | - | - | 150 |
| CEN-503 | 30 | - | - | (1.5) | 30 | 40 | 10 | - | XOO | 100 |
| CEN-506 | 40 | - | - | 15 | 60 | 300 | - | - | - | 80 |
| CEN-514 | 10 | - | - | - | 15 | 15 | - | - | XOO | 50 |

Table 8 (Cont.)

| | Ag | Bi | Cd | Co | In | Mn | Mo | Ni | Pb | Sn |
|---|---|---|---|---|---|---|---|---|---|---|
| Group III | | | | | | | | | | |
| CEN-243 | 300 | - | - | 100 | 100 | 800 | 4 | 150 | - | 30 |
| CEN-358A | 150 | 200 | - | 300 | - | 90 | - | 10 | X00 | - |
| CEN-358B | 70 | 300 | 40 | 30 | - | 150 | 4 | 150 | X00 | 6 |
| CEN-551 | 20 | 20 | 10 | 80 | 60 | 150 | - | 20 | X0 | 15 |
| CEN-552 | 150 | - | 30 | 900 | 30 | 200 | - | 90 | - | 3 |
| CEN-553 | 150 | - | - | 40 | 100 | 200 | - | 20 | X0 | 15 |
| CEN-554 | 15 | 40 | - | 300 | 70 | 300 | - | 40 | X0 | 10 |
| Group IV | | | | | | | | | | |
| CEN-185 | 50 | - | 15 | - | 4 | 500 | 4 | - | X000 | 3 |
| CEN-218 | 20 | - | 10 | - | 5 | 150 | - | - | X0 | 7 |
| CEN-225 | 7 | 40 | 50 | - | 3 | 500 | - | - | X00 | 3 |
| CEN-531A | 100 | 300 | - | - | - | 100 | - | - | X000 | - |
| CEN-537 | 50 | 30 | - | - | 10 | 2000 | - | - | - | - |
| CEN-539 | 50 | 20 | 40 | - | - | 150 | - | - | X0 | - |
| CEN-546 | 300 | - | - | 15 | 50 | 3000 | 20 | 20 | X0 | 4 |
| OS-1[†] | 100 | - | - | (6) | - | 400 | - | - | * | - |
| CEN-570 | 200 | 90 | 30 | - | - | 100 | - | - | X0 | - |
| CEN-577 | 90 | 40 | 20 | 10 | 20 | 400 | 6 | - | X0 | - |
| CEN-578 | 150 | - | 20 | 15 | - | 4 | 200 | 20 | - | - |
| CEN-390 | 2 | 50 | 70 | 30 | 8 | 800 | 20 | - | X00 | - |
| CEN-390A | 150 | - | 20 | - | 5 | 500 | 4 | - | - | - |
| CEN-516 | 50 | - | - | - | 40 | 400 | - | - | - | 15 |
| CEN-518A | 5 | 6 | - | - | 9 | 600 | 9 | - | X000 | 4 |
| CEN-520 | 90 | 10 | 100 | 7 | 5 | 600 | - | 20 | X000 | - |
| CEN-377 | - | - | 70 | 40 | - | 600 | - | 20 | X00 | - |
| BH-14[†] | 20 | 20 | - | 10 | - | 200 | - | 4 | * | - |
| CEN-348 | 30 | - | - | - | 8 | 300 | - | - | - | - |
| Group V | | | | | | | | | | |
| CEN-6 | 30 | - | - | - | - | 2 | - | - | X00 | - |
| CEN-261A-1 | 300 | - | - | - | 4 | 3 | - | - | - | 4 |
| CEN-261A-2 | 150 | - | - | - | 5 | 1 | - | - | X0 | 5 |
| CEN-261A-3 | 150 | - | - | - | 3 | 2 | - | - | - | 5 |
| CEN-261A-4 | 200 | - | - | - | 4 | 15 | - | - | - | 4 |
| CEN-261A-5 | 200 | - | - | - | 4 | 9 | - | - | - | 4 |
| CEN-262A | 70 | 5 | 200 | - | 6 | 500 | - | - | X000 | - |
| CEN-263A-1 | 500 | - | - | - | 4 | 9 | - | - | - | 4 |
| CEN-263A-2 | 400 | 70 | - | 20 | 3 | 9 | - | - | X000 | 4 |
| CEN-263A-3 | 600 | 10 | - | - | 7 | 10 | 3 | - | X00 | 5 |
| CEN-263A-4 | 200 | - | - | - | - | 3 | - | - | - | 4 |

Table 8 (Cont.)

| | Ag | Bi | Cd | Co | In | Mn | Mo | Ni | Pb | Sn |
|---|---|---|---|---|---|---|---|---|---|---|
| CEN-269 | 80 | 80 | 100 | - | 4 | 300 | - | - | X000 | - |
| CEN-271 | 100 | - | 20 | - | 4 | 300 | - | - | X000 | - |
| CEN-275 | 80 | - | - | - | - | 30 | 4 | - | X0 | - |
| CEN-371 | 80 | - | - | - | - | 200 | - | - | - | 4 |
| G-3† | 40 | - | - | 3 | 10 | 7 | 3 | 9 | * | - |
| G-4† | 20 | - | - | 4 | - | 10 | - | 3 | * | - |
| G-6† | 20 | - | - | 1 | - | 6 | 4 | 2 | * | - |
| G-11† | 100 | 60 | - | 20 | 2 | 300 | - | - | * | 8 |
| SR-15† | 1000 | - | 100 | 20 | - | 100 | - | - | * | - |
| Cleveland Mine | | | | | | | | | | |
| CEN-60 | 300 | 200 | 100 | - | 20 | 200 | - | - | X00 | 20 |
| CEN-286 | 400 | - | 30 | - | 20 | 4 | - | - | - | 30 |
| CEN-287 | 400 | - | 50 | - | 20 | 40 | 5 | - | - | 10 |
| CEN-289A-1 | 300 | - | 40 | - | 30 | 40 | 5 | - | - | 30 |
| CEN-289A-2 | 300 | - | 30 | - | 30 | 10 | 3 | - | - | 20 |
| CEN-290 | 300 | - | 30 | - | 15 | 700 | - | 10 | X0 | 7 |
| CEN-320 | 700 | - | 40 | 50 | 30 | 5 | 6 | 150 | - | 40 |
| CEN-321 | 500 | 30 | 100 | 20 | 15 | 200 | - | - | X0 | 8 |
| CEN-360 | 200 | - | - | - | 20 | 2 | - | - | X0 | 8 |
| Pinos Altos | | | | | | | | | | |
| CEN-334 | 150 | 70 | 3 | - | 4 | 30 | - | 10 | X00 | 5 |
| CEN-337-1 | 400 | 5 | - | - | 30 | >1000 | - | - | X0 | 5 |
| CEN-337-2 | 200 | 6 | - | 60 | 5 | 300 | - | - | X00 | 6 |
| CEN-338 | 800 | 200 | 15 | - | 6 | 300 | - | - | X000 | 7 |

Table 9

Trace Elements in Sphalerite from the Central Mining District

| | Ag | Bi | Cd | Co | Ga | Ge | In | Mn | Mo | Ni | Pb | Sn | FeS(%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Hanover Mine | | | | | | | | | | | | | |
| CEN-168-1 | 15 | 6 | 1100 | 300 | - | - | 40 | 5000 | - | 7 | * | 4 | * |
| CEN-168-2 | 10 | 3 | 1500 | 200 | - | - | 50 | 4000 | - | ? | * | 4 | * |
| CEN-168-3 | 7 | 4 | 1500 | 200 | - | - | 60 | 4000 | - | 6 | * | - | 16.5 |
| CEN-168-4 | 8 | 3 | 1500 | 300 | - | - | 60 | 5000 | - | 7 | * | - | * |
| CEN-168-5 | 15 | 4 | 1700 | 300 | - | - | 50 | 4000 | - | 10 | * | - | 16.6 |
| CEN-168-6 | 15 | 2 | 1800 | 200 | - | - | 50 | 3000 | - | 10 | * | - | * |
| CEN-168-7 | 15 | 3 | 1600 | 300 | - | - | 40 | ? | - | 10 | * | - | * |
| CEN-168-8 | 15 | 4 | 1500 | 300 | - | - | 50 | 4000 | - | 9 | * | - | * |
| CEN-171 | * | * | * | * | * | * | * | * | * | * | * | * | 15.9 |
| CEN-174 | 2 | 1.5 | 1900 | 400 | - | - | - | 7000 | - | 3 | XO | - | 6.23 |
| CEN-177 | 15 | 10 | 1600 | 200 | - | - | 8 | 3000 | - | 15 | XOO | - | 5.65 |
| CEN-178 | 150 | 300 | 1600 | 300 | - | - | - | >10,000 | - | 8 | XOOO | - | 5.33 |
| CEN-180 | 1.5 | 5 | 1600 | 200 | - | - | - | 6000 | ? | 7 | XOO | - | 7.25 |
| CEN-183 | 1.5 | 2 | 1600 | 300 | - | - | - | 4000 | - | 6 | - | - | 7.0 |
| CEN-186 | 60 | 150 | 1300 | 60 | - | - | 4 | 7000 | - | 4 | XOOO | - | * |
| CEN-188 | 50 | 20 | 1700 | 50 | - | - | 20 | 6000 | - | 5 | XOOO | - | 7.87 |
| CEN-189 | 1.5 | 3 | 1400 | 300 | - | - | 15 | 4000 | - | 10 | - | - | 6.63 |
| CEN-190 | 1.5 | 4 | 1300 | 200 | - | - | 80 | 2000 | 3 | 7 | - | - | 10.86 |
| CEN-193-1 | 2 | 2 | 1100 | 150 | - | - | - | 5000 | 6 | - | - | - | 9.08 |
| CEN-193-2 | 5 | - | 1400 | 150 | - | - | 6 | 4000 | 3 | - | - | - | 11.6 |
| CEN-193-3 | 40 | 2 | 1300 | 100 | - | - | - | 4000 | - | - | - | - | * |
| CEN-194 | 1.5 | 3 | 1500 | 200 | - | - | - | 4000 | - | 8 | - | - | 6.06 |
| CEN-195 | 8 | 5 | 1100 | 100 | - | - | - | 5000 | 6 | 8 | - | - | 8.20 |
| CEN-196 | 4 | 30 | 1200 | 400 | - | - | 8 | 3000 | 20 | 15 | XO | - | * |
| CEN-197 | 3 | 4 | 1400 | 200 | - | - | 5 | 3000 | 70 | - | - | - | 5.88 |

Table 9 (Cont.)

| | Ag | Bi | Cd | Co | Ga | Ge | In | Mn | Mo | Ni | Pb | Sn | FeS(%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| CEN-198 | 10 | 90 | 1300 | 300 | - | - | 40 | 3000 | - | 30 | X00 | - | 8.78 |
| CEN-199 | 90 | 200 | 1300 | 150 | - | - | 30 | 8000 | 5 | 6 | X000 | - | 5.19 |
| CEN-203 | 4 | 5 | 1500 | 500 | - | - | - | 5000 | - | 5 | X0 | - | 6.32 |
| CEN-204 | 10 | 10 | 1700 | 40 | - | - | 40 | 4000 | - | 5 | X00 | - | * |
| CEN-207 | 1.5 | 8 | 1400 | 300 | - | - | 10 | 1000 | - | 9 | X00 | - | 6.00 |
| CEN-208 | 2 | 10 | 1100 | 400 | - | - | 10 | 2000 | 15 | 10 | X00 | - | 6.73 |
| CEN-209 | 40 | 4 | 1400 | 15 | - | - | 20 | 5000 | - | 9 | X000 | 8 | 8.93 |
| CEN-211 | 4 | 10 | 1300 | 150 | - | - | 80 | 1000 | - | 5 | X0 | - | 6.85 |
| CEN-212 | 2 | 5 | 1100 | 200 | - | - | 10 | 3000 | - | 6 | X00 | - | * |
| CEN-213 | 5 | 200 | 1200 | 300 | - | - | 5 | 2000 | - | 10 | - | - | 12.8 |
| CEN-213A | 10 | 30 | 1300 | 100 | - | - | - | 2000 | - | 6 | X00 | - | 7.93 |
| CEN-214 | 6 | 10 | 1200 | 300 | - | - | 90 | 1500 | - | - | * | - | 8.61 |
| CEN-216 | 10 | 8 | 1300 | 60 | - | - | 40 | 3000 | - | 5 | X000 | 40 | 8.78 |
| CEN-218 | 2 | 1.5 | 1400 | 100 | - | - | 100 | 4000 | - | - | X0 | - | 5.29 |
| CEN-219 | 10 | 70 | 1300 | 400 | - | - | 9 | 3000 | - | 9 | X00 | - | 5.65 |
| CEN-220 | 4 | 15 | 1300 | 400 | - | - | 5 | 1500 | - | 10 | X00 | - | 7.64 |
| CEN-221 | 70 | 300 | 1100 | 100 | - | - | - | 4000 | - | 7 | X000 | 4 | * |
| CEN-222 | 4 | 4 | 1200 | 300 | - | - | - | 5000 | - | 8 | X00 | - | 4.21 |
| CEN-227 | 70 | 20 | 1100 | 15 | - | - | 8 | 4000 | - | 9 | X00 | - | 9.47 |
| CEN-229-1 | 15 | 20 | 1100 | 300 | - | - | 6 | 3000 | 20 | 10 | X0 | - | 10.3 |
| CEN-229-2 | 3 | 10 | 1100 | 200 | - | - | - | 4000 | 20 | 6 | X0 | - | * |
| CEN-230 | 3 | 6 | 1400 | 200 | - | - | 9 | 4000 | - | 15 | X00 | - | 5.71 |
| CEN-233 | 4 | 80 | 1200 | 200 | - | - | 4 | 1000 | - | 7 | X00 | - | 5.05 |
| CEN-533 | 30 | 60 | 1100 | 80 | - | - | - | 5000 | - | - | * | - | 7.35 |
| CEN-534 | 200 | 800 | 2000 | 400 | - | - | - | 7000 | - | 20 | 2000 | - | 5.88 |
| CEN-535 | 20 | 150 | 1500 | 200 | - | - | 4 | 9000 | - | 30 | 200 | - | 7.58 |
| CEN-536 | 10 | 20 | 1500 | 300 | - | 2 | - | 10000 | - | 10 | 100 | - | 7.25 |
| CEN-537 | 30 | 50 | 1100 | 400 | - | - | 4 | 7000 | - | 20 | 700 | - | 7.25 |
| CEN-538 | 2 | 50 | 1200 | 500 | - | - | 15 | 3000 | - | - | X0 | - | 5.32 |
| CEN-538A_1 | 20 | 20 | 1300 | 400 | - | - | - | 5000 | - | - | X0 | - | 7.70 |

Table 9 (Cont.)

| | Ag | Bi | Cd | Co | Ga | Ge | In | Mn | Mo | Ni | Pb | Sn | FeS(%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| CEN-538A-2 | 1.5 | 5 | 1200 | 200 | - | - | - | 2000 | - | - | - | - | 7.05 |
| CEN-538A-3 | 30 | 15 | 1200 | 200 | - | - | 5 | 2000 | - | - | XO | - | 8.85 |
| CEN-541 | 1.5 | 40 | 1300 | 400 | - | - | - | 5000 | - | - | XO | - | 5.55 |
| CEN-542 | 1.5 | 50 | 1300 | 500 | - | - | 5 | 7000 | - | - | XOO | - | 5.16 |
| CEN-543 | 1.5 | 4 | 1100 | 400 | - | - | 8 | 7000 | - | - | XO | - | 7.00 |
| CEN-544 | 4 | 10 | 1000 | 200 | - | - | - | 2000 | - | - | XOO | - | 8.05 |
| CEN-545 | 1.5 | 9 | 1300 | 600 | - | - | 7 | 6000 | - | - | - | - | 6.75 |
| CEN-531-1 | - | 3 | 1600 | 15 | 4 | 3 | 20 | 1500 | - | 3 | XO | 4 | 4.35 |
| CEN-531-2 | - | 1.5 | 1300 | 30 | - | 3 | 20 | 4000 | - | 8 | XO | - | 7.57 |
| CEN-531-3 | - | 2 | 1600 | 100 | - | - | 20 | 9000 | - | 10 | XO | - | 12.1 |
| CEN-531-4 | - | 2 | 1600 | 30 | - | 3 | 30 | 6000 | - | 15 | XO | - | 12.1 |
| CEN-531-5 | - | 4 | 1500 | 100 | - | - | 10 | 4000 | - | 10 | XO | - | 7.70 |
| CEN-531-6 | - | 1.5 | 1600 | 100 | - | - | 15 | 4000 | - | 15 | XO | - | 7.05 |
| CEN-531-7 | 90 | 200 | 1400 | 150 | - | - | 10 | 5000 | - | 15 | XOOO | - | 5.41 |
| CEN-531-8 | - | 4 | 1400 | 100 | - | - | 20 | 4000 | - | 10 | XO | - | 8.85 |
| CEN-531-9 | 1 | 3 | 1400 | 150 | - | - | 10 | 5000 | - | 15 | XO | - | 10.65 |
| CEN-531-10 | 2 | 4 | 1700 | 20 | - | - | 7 | 3000 | - | 3 | XO | - | 7.63 |
| CEN-531A | 100 | 300 | 1600 | 100 | - | - | - | >10,000 | - | 20 | 3000 | - | 17.9 |
| CEN-530 | 70 | 150 | 1600 | 300 | - | - | 4 | 4000 | - | 15 | 3000 | - | 8.00 |
| HAN-6 | 40 | 2 | 1100 | 300 | - | - | 3 | 800 | - | 10 | - | - | 13.9 |
| HAN-5 | * | * | * | * | * | * | * | * | * | * | * | * | 9.52 |
| <u>Pewabic Mine</u> | | | | | | | | | | | | | |
| CEN-149 | 20 | 200 | 1900 | 600 | - | - | 10 | 4000 | - | 20 | 300 | - | 18.5 |
| CEN-150 | 1.5 | 10 | 1400 | 400 | - | - | 7 | 3000 | 15 | 15 | XO | - | 9.80 |
| CEN-151 | 3 | 2 | 1100 | 300 | - | - | 10 | 1500 | - | 6 | XOO | 3 | 14.9 |
| CEN-152-1 | 2 | 1.5 | 1500 | 90 | - | - | 60 | 3000 | - | 8 | - | - | 17.9 |
| CEN-152-2 | 1.5 | 1.5 | 1300 | 70 | - | - | 40 | 2000 | - | 6 | XO | 4 | 18.6 |
| CEN-152-3 | 1 | - | 1400 | 80 | - | - | 40 | 2000 | - | 5 | XO | - | 17.8 |

Table 9 (Cont.)

| | Ag | Bi | Cd | Co | Ga | Ge | In | Mn | Mo | Ni | Pb | Sn | FeS(%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| CEN-152-4 | 1 | 1.5 | 1400 | 100 | - | - | 50 | 3000 | - | 5 | XO | - | 17.9 |
| CEN-153 | 2 | 1.5 | 1400 | 200 | - | - | 40 | 2000 | - | 5 | - | - | 11.1 |
| CEN-158 | 1 | 2 | 1400 | 400 | - | - | 150 | 2000 | - | 6 | - | - | 10.9 |
| PEW-8 | 10 | 5 | 1200 | 300 | - | - | 10 | 2000 | - | 7 | * | - | 11.4 |
| PEW-9 | 2 | 3 | 1200 | 400 | - | - | 20 | 1500 | - | 9 | XO | - | 14.4 |
| <u>Kearney Mine</u> | | | | | | | | | | | | | |
| CEN-236 | 9 | 150 | 1100 | 300 | - | - | 20 | 2000 | - | 10 | XOO | - | 6.70 |
| CEN-237 | 10 | 80 | 1200 | 60 | - | - | 20 | 3000 | - | 5 | XOO | - | 7.25 |
| CEN-238 | 3 | 2 | 1600 | 80 | - | - | 70 | 8000 | - | 7 | - | - | 6.8 |
| CEN-239 | 1.5 | 5 | 2200 | 200 | - | - | 5 | 3000 | - | 9 | XO | - | 5.20 |
| CEN-240 | 3 | 10 | 1200 | 100 | - | - | - | 1000 | - | 6 | XOO | - | 5.89 |
| CEN-241-1 | 1.5 | 15 | 1100 | 30 | - | - | 40 | 3000 | - | - | XO | - | 6.45 |
| CEN-241-2 | 1.5 | 5 | 1200 | 40 | - | - | 60 | 4000 | - | - | XO | - | |
| CEN-241-3 | - | 1.5 | 1200 | 50 | - | - | 40 | 4000 | - | 4 | XO | - | |
| CEN-241-4 | 1 | 10 | 1300 | 50 | - | - | 40 | 4000 | - | 4 | XO | - | |
| CEN-241-5 | 4 | 20 | 1300 | 50 | - | - | 40 | 5000 | - | 5 | XOO | - | |
| CEN-577 | 20 | 40 | 1300 | 150 | - | - | 70 | 2000 | - | 6 | 1500 | - | 11.3 |
| CEN-578 | 60 | 10 | 1500 | 200 | - | - | 4 | 1500 | - | 15 | - | - | 15.9 |
| <u>Oswaldo #2 Mine</u> | | | | | | | | | | | | | |
| CEN-390 | 300 | 700 | 1100 | 300 | - | - | 4 | 9000 | - | 15 | XOOO | - | * |
| CEN-518 | ? | 20 | 1100 | 400 | - | - | 30 | 5000 | - | - | XOO | - | 7.10 |
| CEN-519 | 30 | 4 | 1300 | 100 | - | - | 10 | 2000 | - | - | XOO | - | 10.9 |
| CEN-520 | 70 | 100 | 1200 | 300 | - | - | 10 | 9000 | - | - | XOOO | - | 21.8 |
| CEN-521 | 5 | 50 | 1200 | 400 | - | - | 20 | 400 | - | - | XOO | - | 10.4 |
| CEN-522 | 1.5 | 2 | 1300 | 400 | - | - | 15 | 2000 | - | - | - | - | 7.25 |
| CEN-528 | 1.5 | 3 | 1500 | 400 | - | - | 40 | 4000 | - | - | - | - | 8.27 |

Table 9 (Cont.)

|  | Ag | Bi | Cd | Co | Ga | Ge | In | Mn | Mo | Ni | Pb | Sn | FeS(%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Grant County Mine |  |  |  |  |  |  |  |  |  |  |  |  |  |
| CEN-160 | 20 | 100 | 1300 | 300 | - | - | 60 | 2000 | - | 5 | X00 | - | 17.1 |
| CEN-162 | 5 | 1.5 | 1400 | 300 | - | - | 20 | 1500 | - | 10 | X00 | - | 13.9 |
| Groundhog Mine |  |  |  |  |  |  |  |  |  |  |  |  |  |
| CEN-255 | 40 | 10 | 1500 | 50 | - | - | 15 | 2000 | - | 3 | X00 | 6 | 6.90 |
| CEN-256 | 40 | 70 | 1600 | 50 | - | - | 15 | 3000 | - | 6 | X000 | - | 6.46 |
| CEN-257 | 10 | 8 | 1100 | 150 | - | - | 40 | 2000 | - | 6 | X00 | - | 9.42 |
| CEN-263A | 100 | 5 | 1100 | 60 | - | - | 30 | 3000 | - | 6 | X0 | - | * |
| CEN-264 | 15 | 1.5 | 1300 | 20 | - | - | - | 1500 | - | 10 | X000 | - | 6.41 |
| CEN-265 | 6 | 6 | 1700 | 20 | 20 | - | 20 | 1000 | - | 5 | X000 | 6 | 5.22 |
| CEN-266-1 | 4 | - | 1500 | 30 | - | - | 300 | 200 | - | 9 | X0 | 20 | 2.74 |
| CEN-266-2 | 4 | 1 | 1600 | 20 | - | - | 300 | 400 | - | 5 | X0 | 15 | 3.03 |
| CEN-266-3 | 4 | - | 1600 | 20 | - | - | 300 | 400 | - | 6 | X00 | 40 | 3.54 |
| CEN-266-4 | 3 | - | 1500 | 20 | - | - | 300 | 400 | - | 6 | X0 | 10 | 3.20 |
| CEN-266-5 | 3 | - | 1700 | 30 | - | - | 300 | 700 | - | 7 | X00 | 10 | 3.40 |
| CEN-267-1 | 3 | - | 2200 | 30 | 20 | - | 3 | 300 | - | 6 | - | - | 0.84 |
| CEN-267-2 | 2 | 1 | 1800 | 20 | 30 | - | 6 | 2000 | - | 5 | X0 | 7 | 4.90 |
| CEN-268 | 2 | - | 1500 | 15 | - | - | 4 | 1000 | - | 4 | X0 | - | 4.00 |
| CEN-269 | 8 | 2 | 1500 | 80 | - | - | 40 | 1000 | - | 5 | X0 | - | 3.12 |
| CEN-271 | 100 | 100 | 1400 | 100 | - | - | 20 | 3000 | - | - | 4000 | - | 4.00 |
| CEN-274 | 150 | 900 | 1400 | 200 | - | - | 20 | 4000 | - | 4 | X000 | - | 4.72 |
| CEN-275 | 90 | 15 | 1200 | 40 | 6 | - | 6 | 6000 | - | 7 | X000 | - | * |
| CEN-371 | - | 10 | 1100 | 150 | - | - | - | 1000 | - | 15 | 150 | - | 3.78 |
| G-3 | 4 | 1 | 1800 | 30 | 7 | - | 7 | 3000 | - | 6 | - | - | 3.06 |
| SR-15 | 7 | 2 | 1800 | 300 | 3 | - | 9 | 1500 | - | 5 | - | - | 5.62 |

Table 9 (Cont.)

| | Ag | Bi | Cd | Co | Ga | Ge | In | Mn | Mo | Ni | Pb | Sn | FeS(%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Other Mines | | | | | | | | | | | | | |
| CEN-377 | 50 | 30 | 1300 | 100 | - | - | 4 | 5000 | - | 10 | X000 | - | 6.63 |
| BH-18 | 10 | 2 | 1100 | 10 | - | - | 80 | 3000 | - | 5 | X00 | - | 19.8 |
| CEN-348 | 3 | 1 | 1500 | 30 | - | - | - | 8000 | - | 7 | X00 | - | 3.16 |
| CEN-374A | 50 | - | 1500 | 30 | 4 | - | - | 1500 | - | 4 | X00 | - | * |
| CEN-376 | 50 | 1.5 | 1600 | <10 | - | - | 1000 | 1500 | - | - | X0 | - | 4.90 |
| CEN-513 | 40 | - | 1400 | - | - | - | 600 | 600 | - | - | X00 | 10 | 5.40 |
| CEN-547 | 3 | - | 2000 | 100 | 50 | 7 | 15 | 900 | - | - | X000 | - | 1.91 |
| CEN-378 | 30 | - | 1300 | 40 | 8 | - | - | 1000 | - | - | X000 | - | * |
| CEN-579 | 30 | 40 | 1100 | 30 | - | - | 80 | 3000 | - | 30 | 2000 | 8 | 10.6 |
| CEN-359 | 1 | 1.5 | 1300 | 700 | - | - | 70 | 8000 | - | 8 | - | - | 17.7 |
| CEN-507 | 1.5 | - | 1100 | 800 | - | - | 100 | >10,000 | - | - | X0 | - | 18.9 |
| CEN-341 | 15 | 1 | 1100 | 20 | 15 | - | 15 | 1000 | - | 4 | X0 | - | 1.96 |
| Copper Flats-Barringer fault areas | | | | | | | | | | | | | |
| CEN-355 | 3 | 1.5 | 500 | 500 | - | - | 7 | 5000 | - | 15 | - | - | * |
| CEN-355A | 1.5 | - | 400 | 500 | 4 | - | 60 | 3000 | - | 15 | X0 | - | high |
| CEN-356 | 4 | 2 | 300 | 400 | - | - | 400 | 2000 | - | 30 | X000 | - | * |
| CEN-243 | 2 | 15 | 700 | 200 | - | 5 | 30 | 6000 | - | 40 | X0 | - | 22.1 |
| CEN-358B | 3 | 2 | 1000 | 300 | - | - | - | 1500 | - | 7 | X00 | - | 2.86 |
| CEN-554 | 30 | 20 | 800 | 1000 | - | - | 70 | 9000 | - | - | - | - | 15.5 |
| Cleveland Mine | | | | | | | | | | | | | |
| CEN-58 | 10 | 6 | 2100 | 150 | 3 | - | 70 | 8000 | - | 5 | X0 | - | 22.0 |
| CEN-60 | 9 | 3 | 2100 | 80 | - | - | 80 | 5000 | 4 | 5 | X00 | - | 24.1 |
| CEN-61 | 20 | 15 | 1600 | 100 | - | - | 80 | >10,000 | - | 40 | - | - | 22.8 |

Table 9 (Cont.)

| | Ag | Bi | Cd | Co | Ga | Ge | In | Mn | Mo | Ni | Pb | Sn | FeS(%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| CEN-62 | 5 | 1 | 2100 | 15 | 20 | - | 15 | 9000 | - | 5 | X00 | - | 19.9 |
| CEN-63 | 10 | 15 | 2000 | 20 | 50 | - | 40 | 10,000 | - | 10 | X00 | - | 21.2 |
| CEN-64 | 3 | 30 | 1900 | 700 | 6 | - | 30 | 7000 | 8 | 10 | X00 | - | 15.7 |
| CEN-285A | 3 | - | 1800 | 150 | 3 | - | 70 | 8000 | - | - | X0 | - | 22.2 |
| CEN-286 | 5 | 4 | 2100 | 70 | 15 | - | 150 | 8000 | - | 6 | X00 | - | 19.3 |
| CEN-287 | 10 | 50 | 2000 | 150 | - | - | 100 | 8000 | - | 5 | X00 | - | 22.6 |
| CEN-289A | 10 | 1.5 | 1800 | 100 | 6 | - | 60 | 10,000 | - | 4 | X0 | - | 22.5 |
| CEN-320 | 5 | 4 | 2100 | 700 | 9 | - | 20 | 7000 | - | 10 | X0 | - | 18.0 |
| CEN-321 | 50 | 200 | 2600 | 150 | 20 | - | 80 | 5000 | - | 2 | X0 | - | 20.0 |
| Pinos Altos district | | | | | | | | | | | | | |
| CEN-281 | 90 | 40 | 2600 | 10 | 40 | - | 150 | 2000 | - | 5 | X00 | - | 15.6 |
| CEN-334-1 | 2 | - | 2800 | 50 | - | - | - | 300 | - | - | X0 | - | * |
| CEN-334-2 | 3 | 1 | 3000 | 40 | 6 | - | 10 | 300 | - | 5 | X0 | - | 4.76 |
| CEN-337 | 5 | - | 2600 | 60 | 20 | - | - | 10 | 6 | 5 | - | - | 0.37 |
| CEN-338 | 40 | - | 2600 | 80 | - | - | 4 | 30 | - | ? | - | - | <1.0 |
| CEN-361 | 6 | - | 2400 | 10 | 15 | - | 70 | 4000 | - | 5 | X0 | - | <1.0 |
| CEN-363-1 | 1.5 | - | 2900 | 70 | - | - | 30 | 50 | - | - | X0 | - | 0.43 |
| CEN-363-2 | 1 | - | 2600 | 50 | - | - | - | 20 | - | 7 | - | - | * |

## Table 10

### Trace Elements in Chalcopyrite from Bingham Mining District

|  | Ag | As | Bi | Cd | Co | Ge | In | Mn | Mo | Ni | Sn | Pb |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Utah Copper |  |  |  |  |  |  |  |  |  |  |  |  |
| BIN-502 | 5 | - | - | - | 3 | - | - | - | - | 3 | 200 | X |
| BIN-504 | 60 | - | 1.5 | - | 1 | 15 | 15 | 20 | 6 | 10 | 20 | X |
| BIN-506 | 200 | - | 8 | - | 2 | - | 50 | 500 | - | 7 | 20 | XO |
| BIN-507 | 50 | - | - | - | 4 | - | 10 | - | 400 | 3 | 150 | XO |
| BIN-509 | 40 | - | - | - | - | - | 10 | - | 700 | 1.5 | 200 | XO |
| BIN-510 | 6 | - | 20 | - | 1.5 | 1.5 | - | 3 | 2 | 30 | 40 | X |
| BIN-511 | 30 | - | - | - | 20 | - | - | 30 | 8 | 80 | 200 | X |
| BIN-513 | 2 | - | - | - | 6 | - | - | - | 20 | 8 | 50 | XO |
| BIN-514 | 1.5 | - | - | - | 8 | 5 | - | - | 50 | - | 600 | X000 |
| BIN-515 | 9 | - | - | - | 20 | - | - | 1 | 10 | 8 | - | XO |
| BIN-516 | 7 | - | - | - | 5 | 2 | - | 9 | 50 | 20 | 300 | X |
| BIN-517 | 1.5 | - | - | - | 3 | - | 3 | 1 | 300 | 15 | 150 | X |
| BIN-518 | 30 | - | 150 | - | 3 | - | 60 | - | >1000 | 70 | 100 | XO |
| BIN-519 | - | - | - | - | 8 | - | 7 | - | 5 | 1 | 200 | X |
| BIN-520 | 1 | - | - | - | 5 | - | - | - | 300 | 10 | 150 | X |
| BIN-521 | - | - | - | - | 3 | - | 3 | - | 4 | 4 | 300 | XO |
| BIN-522 | 7 | - | 20 | - | 3 | - | - | - | 500 | 3 | 200 | X |
| BIN-523V | 40 | - | 150 | - | 5 | - | 10 | - | 500 | 100 | 500 | X00 |
| BIN-523R | 100 | - | 900 | - | 1 | - | 150 | - | >1000 | 100 | 150 | X00 |
| BIN-525 | 20 | - | 30 | - | 3 | - | - | - | 500 | 100 | 90 | X |
| BIN-527 | 1.5 | - | - | - | - | - | - | - | 15 | 4 | 50 | X |
| BIN-533 | 15 | - | - | - | 1 | - | - | - | 100 | 30 | 100 | X |
| BIN-534 | 30 | - | - | - | 1.5 | - | - | - | 4 | 10 | 60 | X |
| BIN-535 | 6 | 400 | - | - | 3 | - | 15 | - | 700 | 20 | 200 | X00 |
| BIN-536 | - | - | - | - | 3 | - | 15 | - | 50 | - | 200 | XO |
| BIN-537 | 50 | - | 200 | - | 1.5 | - | - | 9 | 20 | 5 | 200 | X000 |
| BIN-538 | 20 | - | 90 | - | 3 | - | 3 | 20 | 400 | 30 | 100 | XO |
| BIN-543 | 40 | - | - | - | 4 | - | - | 10 | 3 | 4 | 90 | X |
| BIN-544 | 4 | - | - | - | - | - | - | - | 1000 | 6 | 500 | - |
| BIN-546 | 7 | - | - | - | - | - | - | - | 4 | 5 | 400 | X |
| BIN-550 | 10 | - | - | - | - | - | - | - | 9 | 4 | 300 | XO |
| BIN-551 | 3 | - | - | - | 3 | - | - | - | 100 | 20 | 200 | XO |
| BIN-553 | 80 | - | - | - | 10 | 3 | 5 | 2 | 5 | 9 | 80 | X |
| BIN-557 | 15 | - | - | - | 8 | - | - | - | 30 | 15 | 100 | X |
| BIN-561 | - | - | - | - | 3 | - | 15 | - | 300 | 10 | 200 | X |
| BIN-563 | 30 | - | - | - | 1 | - | - | - | 300 | - | 100 | X |
| BIN-566 | 4 | 200 | - | - | 50 | - | - | - | 10 | 600 | 200 | XO |
| BIN-567 | 30 | 300 | 200 | - | 3 | 300 | - | - | 6 | 50 | 200 | X |
| BIN-567D | 100 | 800 | >1000 | - | 9 | 900 | 20 | - | 1000 | 30 | 200 | X |
| BIN-568 | 20 | - | 60 | - | 1.5 | - | 30 | - | 1500 | 6 | 150 | XO |
| BIN-569 | 20 | - | 100 | - | 6 | - | 50 | - | >1000 | 50 | 70 | XO |
| BIN-570 | - | - | - | - | 2 | - | - | - | 5 | 4 | 200 | X |

Table 10 (Cont.)

| | Ag | As | Bi | Cd | Co | Ge | In | Mn | Mo | Ni | Sn | Pb |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Underground mines | | | | | | | | | | | | |
| BIN-576 | 30 | - | - | - | - | - | 1000 | - | - | - | 200 | X0 |
| BIN-577 | >100 | - | - | - | - | - | 100 | - | 2 | - | 150 | X000 |
| BIN-578 | 50 | - | - | - | 1 | - | 1000 | 40 | - | - | 200 | X0 |
| BIN-608 | 70 | 200° | - | 30 | - | - | 90 | 150 | 3 | - | 150 | X000 |
| BIN-612 | 20 | - | - | 50 | - | - | 150 | 200 | - | - | 400 | X0 |
| BIN-661 | 20 | 200 | - | 90 | 1.5 | - | 60 | 200 | 1 | - | 270 | X |
| BIN-712 | > 100 | 150 | - | - | - | 15 | - | - | 20 | 60 | 60 | X000 |
| BIN-751 | >100 | - | - | - | - | - | 300 | - | 3 | - | 400 | X00 |
| BIN-7† | 30 | - | 8 | 7 | - | - | 50 | 70 | - | - | 200 | * |
| BIN-8† | 200 | - | 2000 | 20 | - | - | 100 | 300 | - | - | 900 | * |
| BIN-12† | 200 | - | 200 | - | - | - | 40 | 20 | - | - | 400 | * |

° Also 200 ppm. Sb.

## Table 11

### Trace Elements in Sphalerite from the Bingham Mining District

| | Ag | As | Bi | Cd | Co | Ga | Ge | In | Mn | Mo | Ni | Pb | Sb | Sn | FeS (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Galena and Holden fissures | | | | | | | | | | | | | | | |
| BIN-580-1 | >100 | - | 1.5 | 5200 | 1 | 70 | 3 | - | 5000 | - | - | 900 | 800 | 80 | 3.45 |
| BIN-580-2 | >100 | - | 1.5 | 2900 | 1 | 70 | 5 | 4 | 5000 | - | 1.5 | 300 | 600 | 15 | 0.55 |
| BIN-581 | 90 | - | 3 | 3900 | 1 | 60 | 2 | 10 | 5000 | - | 4 | 600 | 300 | 70 | 0.69 |
| BIN-583 | 70 | - | 1.5 | 3000 | - | 150 | 8 | 30 | 2000 | 4 | - | 400 | 500 | 20 | 0.51 |
| BIN-585 | 20 | - | - | 2700 | 6 | 40 | - | 100 | 1500 | - | 9 | 1000 | 300 | 200 | 2.13 |
| BIN-586-1 | 20 | - | 2 | 2600 | 2 | 200 | 7 | 4 | 2000 | - | 1.5 | 150 | 100 | 15 | 0.33 |
| BIN-586-2 | 10 | - | 2 | 3100 | - | 80 | - | 4 | 3000 | - | 1.5 | 90 | - | 8 | 0.25 |
| BIN-586-3 | 9 | - | 2 | 2900 | - | 30 | - | 20 | 200 | 5 | - | 2000 | - | 50 | 0.93 |
| BIN-589-1 | 100 | - | 1.5 | 3300 | 1 | 150 | 5 | 30 | 5000 | 4 | - | 200 | 500 | 30 | 0.33 |
| BIN-589-2 | 20 | - | 2 | 2700 | - | 50 | - | 20 | 2000 | - | - | 300 | - | 1000 | 0.68 |
| BIN-592 | >100 | 1500 | 4 | 3600 | 1.5 | 90 | - | 30 | 1500 | 6 | 4 | 5000 | 1500 | 100 | 1.52 |
| BIN-595-1 | 70 | - | 3 | 3900 | - | 80 | 5 | 40 | 1000 | 9 | 3 | 500 | 150 | 40 | 1.22 |
| BIN-595-2 | 40 | - | 3 | 4200 | - | 40 | - | 100 | 1000 | 5 | 2 | 700 | 150 | 300 | 6.75 |
| BIN-596-1 | >100 | 300 | 4 | 5400 | - | 100 | - | 100 | 1000 | - | 2 | 600 | 500 | 100 | 1.19 |
| BIN-596-2 | 150 | - | 3 | 5300 | 1.5 | 40 | - | 150 | 700 | - | 4 | 400 | 400 | 100 | 1.25 |
| BIN-596-3 | >100 | 1500 | 2 | 3100 | - | 60 | - | 15 | 5000 | - | 6 | 600 | 1500 | 10 | <0.25 |
| BIN-596-4 | 20 | - | 3 | 3700 | - | 50 | - | 3 | 1500 | - | 4 | 300 | - | 20 | 2.06 |
| BIN-596-5 | 7 | - | 3 | 3500 | - | 60 | - | 20 | 3000 | - | 3 | 100 | - | 30 | 0.38 |
| BIN-596-6 | 150 | - | 3 | 3700 | - | 80 | - | 8 | 4000 | - | 4 | 1000 | 400 | 15 | <0.25 |
| BIN-596-7 | 90 | - | 3 | 3100 | - | 60 | - | 40 | 5000 | - | 4 | 400 | - | 400 | 4.88 |
| BIN-596-8 | >100 | - | 5 | 2700 | 4 | 90 | - | 15 | 4000 | - | - | 3000 | 600 | 200 | 0.61 |
| BIN-599 | 80 | - | 2 | 3800 | 1 | 100 | 4 | 20 | 2000 | - | - | 1500 | 500 | 150 | 1.61 |
| BIN-600 | 20 | - | - | 2700 | - | 30 | - | 4 | 2000 | - | 9 | 1000 | - | 500 | 0.54 |

Table 11 (Cont.)

| | Ag | As | Bi | Cd | Co | Ga | Ge | In | Mn | Mo | Ni | Pb | Sb | Sn | FeS (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Highland limestone | | | | | | | | | | | | | | | |
| BIN-577 | 4 | - | 1.5 | 2400 | - | - | - | 100 | 1000 | - | - | 4000 | - | 100 | 2.26 |
| BIN-579 | 8 | - | 6 | 2800 | 2 | 30 | - | 50 | 2000 | - | 4 | 300 | - | 30 | 0.99 |
| B limestone | | | | | | | | | | | | | | | |
| BIN-617 | 10 | - | - | 3300 | 2 | 4 | - | 50 | 3000 | - | - | 800 | - | 20 | 8.50 |
| BIN-625 | 30 | - | - | 3900 | - | 20 | - | 400 | 3000 | - | - | 7000 | - | 90 | 8.55 |
| BIN-626 | 6 | - | 1 | 3500 | - | 4 | - | 90 | 2000 | - | 4 | 300 | - | 10 | 12.4 |
| BIN-646 | 5 | - | - | 3000 | - | 10 | - | 150 | 4000 | - | - | 150 | - | - | 14.5 |
| BIN-647 | 6 | - | - | 3300 | - | 9 | - | 15 | 3000 | - | - | 300 | - | 20 | 12.8 |
| BIN-654 | 30 | - | - | 3400 | - | 5 | - | 40 | 2000 | - | - | 1500 | - | 8 | 13.8 |
| BIN-655 | 7 | - | 1 | 3700 | - | 9 | - | 5 | 3000 | - | 2 | 500 | - | 5 | 14.0 |
| BIN-671-1 | 100 | - | 4 | 5100 | - | 20 | - | - | 4000 | - | 4 | 6000 | - | 100 | 8.27 |
| BIN-671-2 | 6 | - | - | 3100 | 1 | 10 | - | 200 | 4000 | - | 5 | 600 | - | 80 | 5.55 |
| BIN-676 | 100 | - | - | 3600 | 3 | 4 | - | 100 | 2000 | - | 60 | 4000 | - | 70 | 11.9 |
| BIN-677 | 5 | - | 3 | 4100 | - | 6 | - | 200 | 4000 | - | 6 | 300 | - | 15 | 8.88 |
| BIN-678-1 | 7 | - | - | 3200 | - | 2 | - | 150 | 3000 | - | - | 60 | - | 3 | 6.37 |
| BIN-678-2 | 40 | - | - | 2700 | - | - | - | 100 | 1500 | - | - | 100 | - | 5 | 5.47 |
| BIN-695 | 4 | - | 3 | 3200 | - | 1.5 | - | 4 | 2000 | - | 4 | 100 | - | 100 | 6.06 |
| BIN-697 | 200 | - | 8 | 2900 | 1.5 | 20 | 3 | 3 | 5000 | - | 7 | 9000 | 90 | 300 | 2.42 |
| BIN-698 | 9 | - | 7 | 3000 | 3 | - | - | 80 | 4000 | - | 8 | 600 | - | 300 | 2.78 |
| BIN-699 | 5 | - | 3 | 3000 | - | 9 | - | 150 | 3000 | - | 3 | 150 | - | 40 | 9.61 |
| BIN-700 | 7 | - | - | 3700 | 1 | 90 | - | 30 | 9000 | - | 1 | 300 | - | 200 | 0.55 |
| BIN-755 | 15 | - | 1 | 3000 | 1 | 2 | - | 150 | 1500 | - | - | 1500 | - | 15 | 8.00 |

Table 11 (Cont.)

| | Ag | As | Bi | Cd | Co | Ga | Ge | In | Mn | Mo | Ni | Pb | Sb | Sn | FeS (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Last Chance fissure | | | | | | | | | | | | | | | |
| BIN-572 | 20 | - | - | 3400 | - | 5 | - | 15 | 4000 | - | 2 | 90 | 90 | - | 16.7 |
| BIN-605 | 3 | - | - | 4200 | - | 8 | - | 10 | 6000 | - | 3 | 100 | - | 15 | 11.4 |
| BIN-614 | 2 | - | 4 | 3600 | - | 10 | - | 3 | 5000 | - | 3 | 70 | - | 5 | 17.1 |
| BIN-619 | 15 | - | 1 | 2900 | 1.5 | 5 | - | 10 | 4000 | - | 7 | 2000 | - | 6 | 7.15 |
| BIN-620 | 7 | - | 1 | 3200 | 3 | - | - | 30 | 2000 | - | 10 | 600 | - | 7 | 11.8 |
| BIN-622 | 30 | - | 2 | 4200 | 8 | 4 | - | 15 | 3000 | - | 10 | 4000 | - | 15 | 9.15 |
| BIN-629 | 150 | - | 30 | 3300 | - | 6 | - | 20 | 4000 | - | 5 | 6000 | - | 15 | 11.0 |
| BIN-630 | 1 | - | - | 3900 | 5 | 3 | - | 30 | 3000 | - | 10 | 300 | - | 15 | 7.95 |
| BIN-635 | 1.5 | - | 3 | 2800 | 4 | 3 | - | 15 | 3000 | - | 15 | 200 | - | - | 9.30 |
| D limestone | | | | | | | | | | | | | | | |
| BIN-621 | 8 | - | 3 | 3500 | - | 9 | - | 30 | 2000 | - | 2 | 60 | - | 10 | 11.8 |
| BIN-645 | 8 | - | 4 | 4100 | 1 | 4 | - | 100 | 3000 | 5 | - | 80 | - | 3 | 11.3 |
| BIN-651 | 4 | - | - | 3800 | - | 20 | - | 10 | 6000 | - | 4 | 400 | - | 20 | 16.1 |
| Niagara fissure | | | | | | | | | | | | | | | |
| BIN-638 | 3 | - | - | 3900 | 5 | 5 | - | 200 | 4000 | - | 4 | 500 | - | - | 13.6 |
| BIN-644 | >100 | 3000 | 15 | 2300 | 6 | 8 | - | 150 | 4000 | - | 7 | 200 | 2000 | 10 | 15.4 |
| BIN-674 | 3 | - | 4 | 3600 | - | 90 | - | 60 | 4000 | - | - | 70 | - | 300 | 7.25 |
| East fissure | | | | | | | | | | | | | | | |
| BIN-660 | 15 | - | - | 3800 | 2 | 30 | - | 20 | 5000 | - | 2 | 600 | - | 80 | 15.1 |
| BIN-662 | 9 | - | 3 | 3300 | 2 | 100 | - | 15 | 1500 | - | 5 | 800 | - | 150 | 4.20 |
| BIN-664 | 20 | - | 6 | 3200 | 1 | 30 | - | 100 | 3000 | - | 5 | 700 | - | 8 | 9.08 |

Table 11 (Cont.)

| | Ag | As | Bi | Cd | Co | Ga | Ge | In | Mn | Mo | Ni | Pb | Sb | Sn | FeS (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| BIN-666-1 | 10 | - | 5 | 4300 | - | 40 | - | 10 | 3000 | - | 5 | 150 | - | 40 | 13.2 |
| BIN-666-2 | 2 | - | - | 3700 | - | 30 | - | 7 | 1000 | - | 3 | 80 | - | 100 | 4.34 |
| BIN-656 | 6 | - | 4 | 3500 | - | 10 | - | 80 | 6000 | - | 15 | 300 | - | 7 | 16.5 |
| Lark vein | | | | | | | | | | | | | | | |
| BIN-701 | 9 | - | 1 | 2900 | - | 80 | 4 | 8 | 5000 | - | - | 200 | - | - | 0.58 |
| BIN-704 | 70 | - | 3 | 3200 | - | 50 | - | 20 | 7000 | 4 | 9 | 5000 | - | 20 | 0.94 |
| BIN-706 | 30 | - | 1 | 4800 | - | 90 | 1 | - | 9000 | - | 1 | 300 | - | 5 | 0.26 |
| BIN-712 | 5 | - | 1.5 | 2900 | - | 100 | - | 4 | 7000 | - | - | 300 | - | 20 | 0.57 |
| Commercial limestone | | | | | | | | | | | | | | | |
| BIN-723 | 70 | - | 1 | 4400 | 3 | 50 | - | - | 9000 | - | 10 | 1500 | - | 5 | 0.88 |
| BIN-732-1 | 60 | - | - | 3000 | 1.5 | 300 | 15 | 40 | 4000 | - | - | 1500 | - | 15 | 1.69 |
| BIN-732-2 | 30 | - | - | 2200 | - | 40 | - | 100 | 1000 | - | - | 3000 | - | 20 | 1.83 |
| Jordan limestone | | | | | | | | | | | | | | | |
| BIN-734 | 30 | - | - | 1700 | - | 2 | - | 150 | 4000 | - | - | 3000 | - | 80 | 2.08 |

## CONSIDERATIONS OF SAMPLING AND STATISTICS

Several papers have recently been published discussing the application of statistics to trace element studies. These include Ahrens (1954), Shaw and Bankier (1954), Chayes (1954), and Miller and Goldberg (1955). A statistical approach has been used in a number of ways in this work. However, in the opinion of the writer as well as that of several of the authors quoted above, much care must be used in the application and interpretation of statistics to trace element data.

A concept important in statistical treatment of data is that of the population or universe under consideration. The population is composed of all individuals having certain specified characteristics. For instance, if we want to know the average concentration of a trace element in chalcopyrite from a certain geographic area, then the population consists of _all_ the chalcopyrite existing in that area. An alternative concept of the population for this case is to consider the district to be divided into a large number of small equal areas or volumes, with whatever chalcopyrite exists within each area or volume being considered a unit in the population. The first definition seems preferable to the writer.

The population should be distinguished from the sample we may take of the population. The sample consists of a relatively small number of individuals taken from the population for purposes of necessity or economy.

A problem arises in selecting from the population a sample small enough to be handled by the means at our disposal, yet with properties representative of the population as a whole. Ideally, the population should be sampled in a random manner in order to avoid any bias. Random sampling of sulfide minerals from a specified population is likely to be difficult or impossible for a number of reasons. In most mining districts it can be assumed that an appreciable fraction of the ore has not yet been discovered. Some of the ore has probably been mined and is no longer available. Other quantities of ore may be known but may not now be accessible because of closed mine workings or the like. Some material may not be amenable to the sample preparation techniques available. Parts of the population may no longer exist because of erosion, oxidation, alteration, or other processes. For these reasons it is in general not possible to sample sulfide minerals randomly or in any other rigorous fashion. In general, the specimens collected for this study were chosen more on the basis of availability than in an attempt to obtain a random sampling. In some cases a definite attempt was made to obtain anomalous or unusual samples.

An important characteristic of the population is the frequency distribution for the property in question. Most statistical tests have been worked out for populations with a normal or Gaussian distribution of values. Other frequency distributions recognized in nature include Poisson and lognormal. Ahrens (1954) states as a fundamental law of geochemistry that "the concentration of an element is lognormally distributed in a specific igneous rock." By "specific igneous rock" Ahrens apparently means a rock type such as granite or diabase. He also discusses tin in mica as an example of lognormal distribution of an element in a mineral, and suggests that a lognormal distribution may be found fairly generally for trace elements in minerals. The examples given in the paper consist of a number of histograms for trace element concentrations in diabase and in granite. Most of the histograms are badly skewed when concentrations are plotted directly but are more symmetrical when the logarithms of the concentrations are plotted.

Miller and Goldberg (1955) discuss the paper by Ahrens and conclude that most of his examples are neither normally or lognormally distributed (although it is not clear exactly what criteria were used in the rejection of the hypothesis of normal or lognormal distribution). These writers conclude "that the elements in geochemical universes are not all distributed as log-normal or any other single function." They set up a model which might give rise to a lognormal distribution in nature. This model is based on the Central Limit Theorem.

The Central Limit Theorem states that the cumulative effect of a number of independent random factors on the property of interest is a normal distribution under certain assumptions. One of the assumptions is that the number of factors is large and that the effect of any one factor is small. It seems very probable that in many geological processes involving trace elements, the effect of one or two factors may be much larger than any of the others. This condition might result in a frequency distribution with more than one maximum, or some other type of distribution which was clearly not normal or lognormal. The writer believes that the distribution of tin in chalcopyrite from the Central mining district is an example of this condition.

Because concentrations of trace elements in specific minerals or rock types are able to vary by large factors (in contrast to variations in major elements) a logarithmic transformation of the concentrations might be expected to decrease the skewness of the values and thus give a result more nearly normal than the raw data, regardless of the true frequency distribution. In addition, the effects of many chemical and physical processes are proportional to the amount present, thus tending to preserve a logarithmic distribution.

Most statistical tests assume a normal distribution of the population, but according to Cochran (1947) moderate deviations from normality do not seriously affect the conclusions of the tests. Therefore, the writer has used lognormal plots and transformations in some of the discussion to follow. This does not imply that the frequency function is truly lognormal, but it is believed that the logarithmic transformation results in a frequency distribution that is close enough to normal that the testing procedures give correct results. In several cases, non-parametric tests have been used to avoid the necessity for making an assumption of normal distribution.

However, because of the difficulties of sampling the writer does not consider that the statistical tests by themselves constitute proof of the hypotheses being tested. The extrapolation of the test results to the total population must be accompanied by consideration of whether the sample is representative and how well other assumptions of the test are met. A firm conclusion can be reached only if consideration of all the statistical and geological factors indicates a lack of complications. The evaluation of factors outside the statistical procedure must in many cases be qualitative, and the conclusion reached thus rests on less rigorous arguments than might superficially appear to be the case. In the following pages an attempt has been made to discuss the recognized points of weakness in the statistical conclusions.

# TRACE ELEMENT VARIATION IN SULFIDES WITHIN SINGLE CRYSTALS, SINGLE POLISHED SECTIONS, AND ORE BODIES

Previous work on trace element variations within single crystals of sulfide minerals has been published by several workers, including Frondel, Newhouse, and Jarrell (1942) and Burnham (1955). Frondel, Newhouse, and Jarrell (1942) studied large crystals of galena by spectrographic and staining techniques. They found compositional differences between planes parallel to crystal faces and between the loci traced out by various crystal faces during growth. In only a few samples do the differences in silver and copper concentrations between the (111) and (001) face loci of galena appear to exceed a factor of two (the original values are given in terms of logarithms of the intensity ratio , and the writer has estimated the difference in concentration on the basis of the normal approximately 1:1 relationship between log intensity and log concentration). Larger differences are reported for a few selected samples, however.

Burnham (1955) carried out a series of analyses of two sphalerite and two chalcopyrite crystals. One sphalerite crystal was collected from the Hanover mine of the Empire Zinc Company, from which many specimens were collected during this study. The results of Burnham's analyses are reproduced in figure 36. Burnham says (p. 59):

> 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 constant within the brown part of the crystal, but undergoes 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 responsible for the change in color. Hence it would appear that the same or closely related factors govern the distribution of both manganese and iron in sphalerite. Silver also appears to decrease in amount toward the outer part of the crystal, but the decrease,

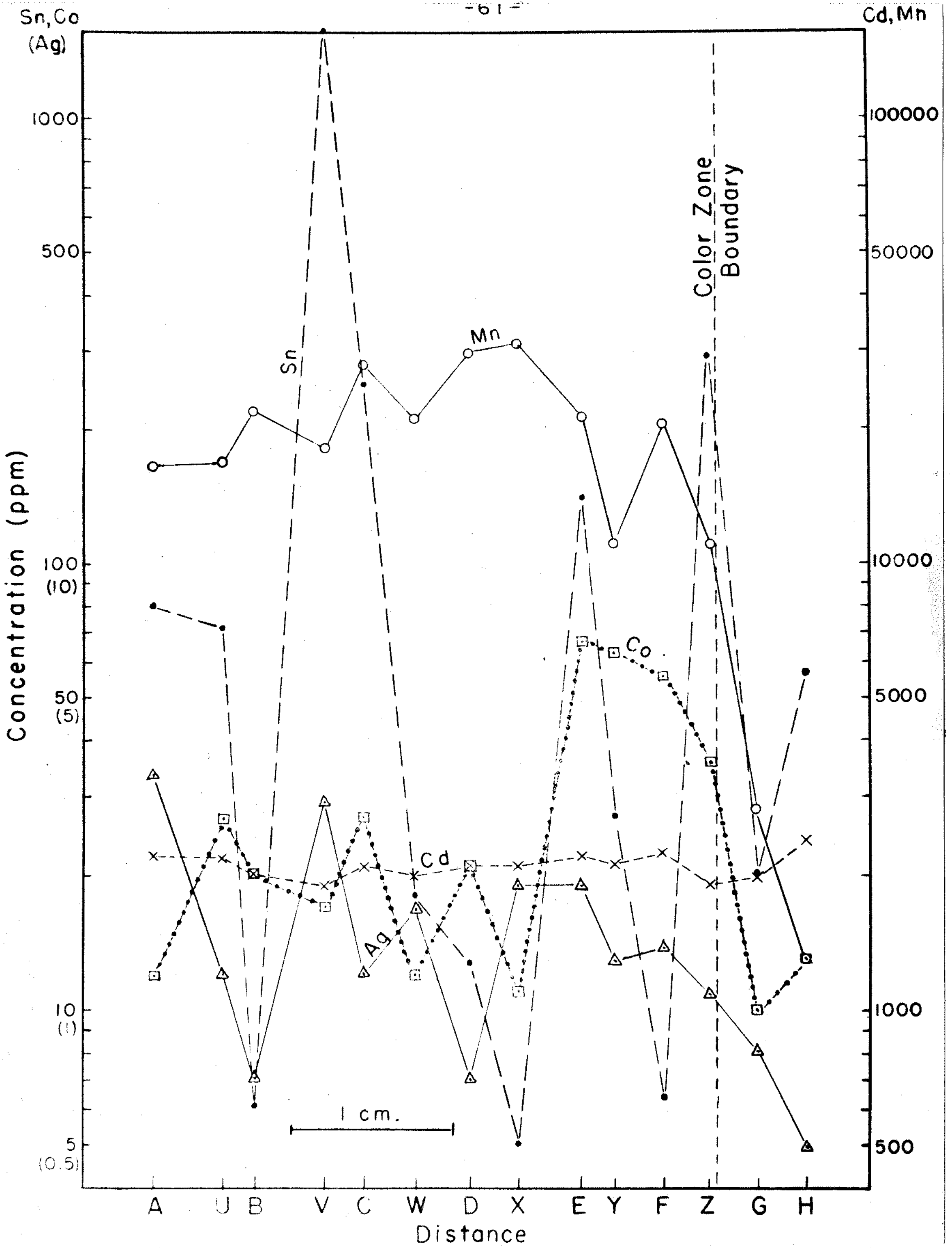


Figure 36. Trace element variation in single crystal of sphalerite analyzed by Burnham (1955).

> if any, 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.

He discusses the causes of the variations and concludes that except for tin, the variations are probably the result of changes in the composition of the fluids from which the crystal was deposited. The erratic behaviour of tin he attributed to the possible presence of cassiterite in small cavities in the specimen.

A specimen of botryoidal sphalerite from Tintic, Utah, was found by Burnham to show large variations in trace element content but with an overall pattern for most elements of decreases from the initial values, then increases near the outer surface of the crystal. The two chalcopyrite crystals were found to be relatively poor in trace elements, but showed uniformity of silver and indium content. Tin was found in a few analyses of one of the crystals but was believed to be derived from the surface tarnish or the near surface regions of the crystal.

Fryklund and Fletcher (1956) published analyses of the interior and exterior of a single crystal of sphalerite which showed no significant difference for most elements.

Figure 37 shows the results of a series of analyses of a sphalerite crystal (CEN-531) collected from the Hanover mine. The crystal occurred with similar material lining a cavity about one foot in diameter in a zinc ore body south of the Hanover-Fierro stock. The cavity occurred in slightly vuggy sphalerite with grain size up to several centimeters. This sphalerite was associated with small amounts of calcite, quartz, hematite, pyrite, galena,and chalcopyrite. About six inches above the cavity a sharp contact separated the coarse-grained sphalerite from sphalerite with a grain size of 1-2 mm, intergrown with about 20% quartz and minor calcite,

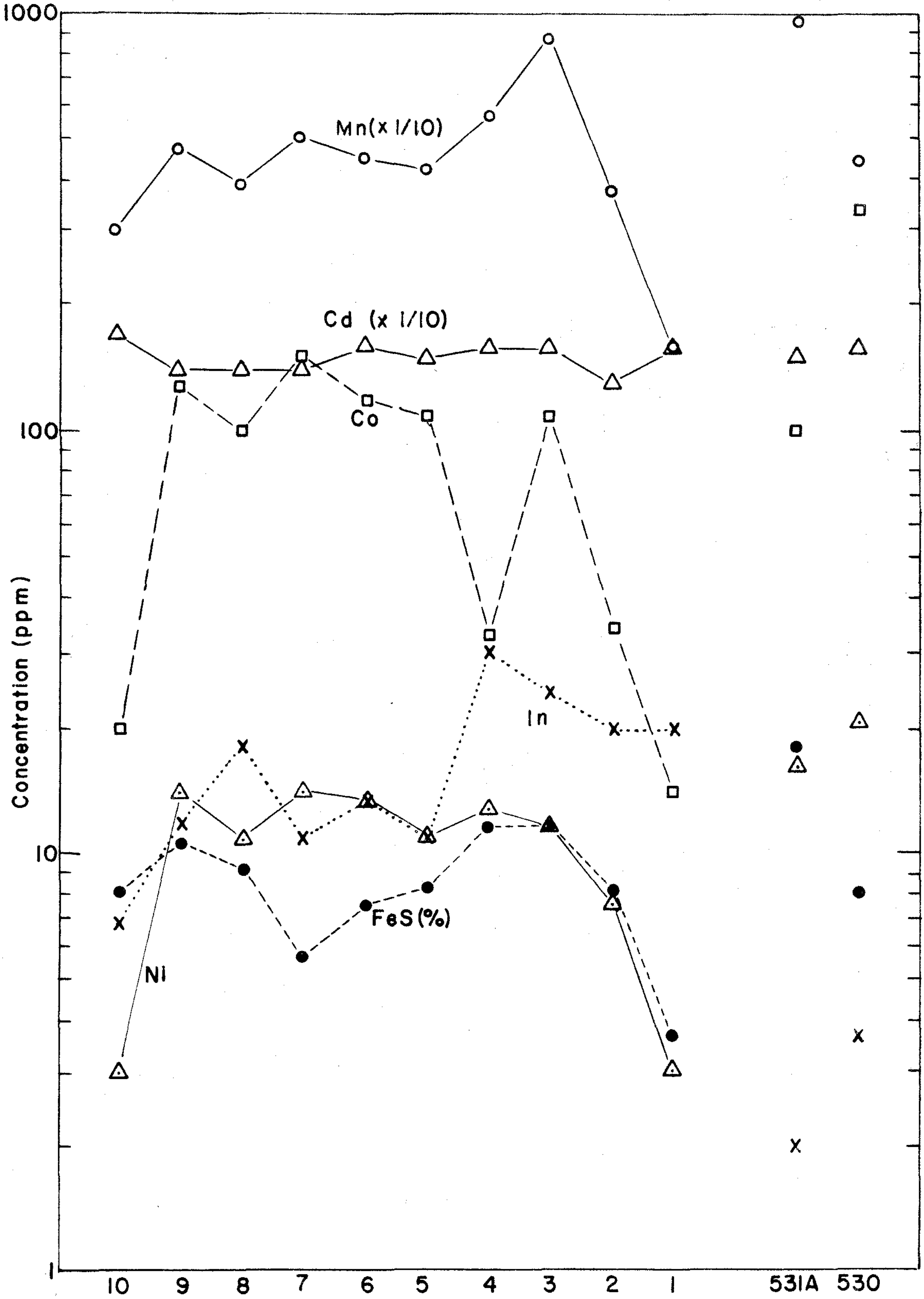


**Figure** 37

Variation in trace element content of sphalerite single crystal CEN-531 and two adjacent samples.

hematite, pyrite, galena, and chalcopyrite. Analyses of the coarse-grained (CEN-531A) and fine-grained (CEN-530) sphalerite accompany the single crystal data in figure 37.

Within the cavity the sphalerite is associated with a number of other minerals. Marcasite, quartz, siderite, manganiferous (?) calcite, calcite, and chalcopyrite were deposited as euhedral crystals in the sequence listed. Galena is also present.

As shown in figure 38 the sphalerite crystal exhibits a distinct color zoning from light to dark brown. The color variations are believed to result from differences in the amount of iron present in the sphalerite. The boundaries between the zones are sharp when observed with a hand lens. All other crystals examined from the same cavity show color zoning. A polished section of the crystal revealed two small areas of galena in about the middle of the crystal. A line of chalcopyrite blebs parallels the color zoning in a position believed to correlate with analysis CEN-531-6. A little marcasite is present near the base of the crystal. The galena and marcasite probably replaced the sphalerite. The chalcopyrite might have been deposited during the period of growth of the sphalerite, or later by selective replacement along a particularly favorable zone in the crystal.

The samples of the crystal were taken as much as possible from the locus of growth of a single crystal face, but for samples 1, 2, 6, and 7, it was necessary to take some material from adjacent face loci in order to obtain sufficient material. The position of the samples was chosen on the basis of the color zoning. In the case of iron, and probably other elements, some of the samples lap over sufficiently into adjacent zones to decrease the contrast between zones.

Figure 38A. Photograph of a single crystal from the Hanover mine, sample CEN-531, showing the color zoning (x2).

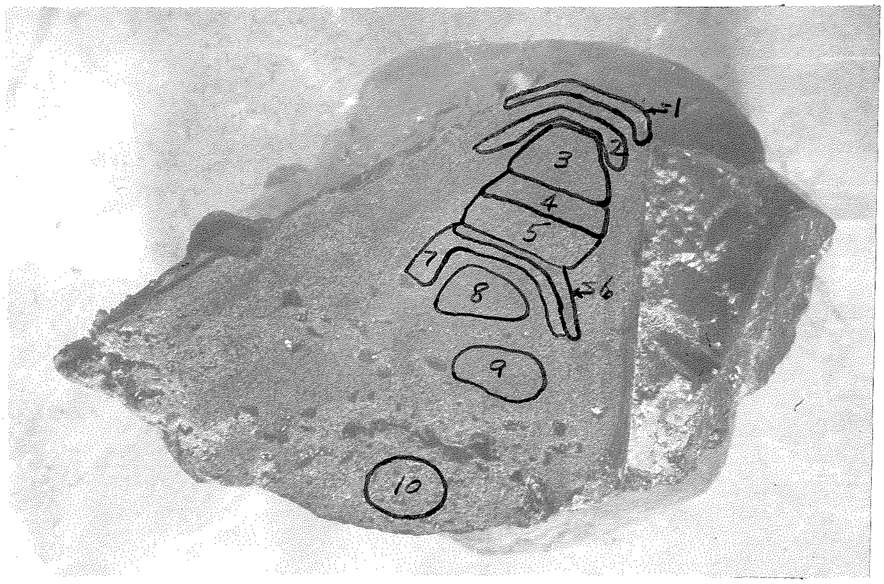


Figure 38B. Photograph of same crystal as above, showing the location of samples drilled from the crystal.

The cadmium content, as in the crystal analyzed by Burnham, is constant throughout. Iron, manganese, nickel, and cobalt show lower concentrations near the base and surface of the crystal than in the central zones. However, sample 4 has a low cobalt concentration without corresponding lows for nickel, manganese, and iron. The sharp differences in iron concentration are believed to be better shown by the color changes than by the analyses. Indium content increases slightly from near the base, levels off at 10-15 ppm., then jumps abruptly to 20-30 ppm. near the surface. Manganese stands out by virtue of a high concentration in sample 3. The germanium concentration is near the detection limit but seems to increase toward the surface of the crystal.

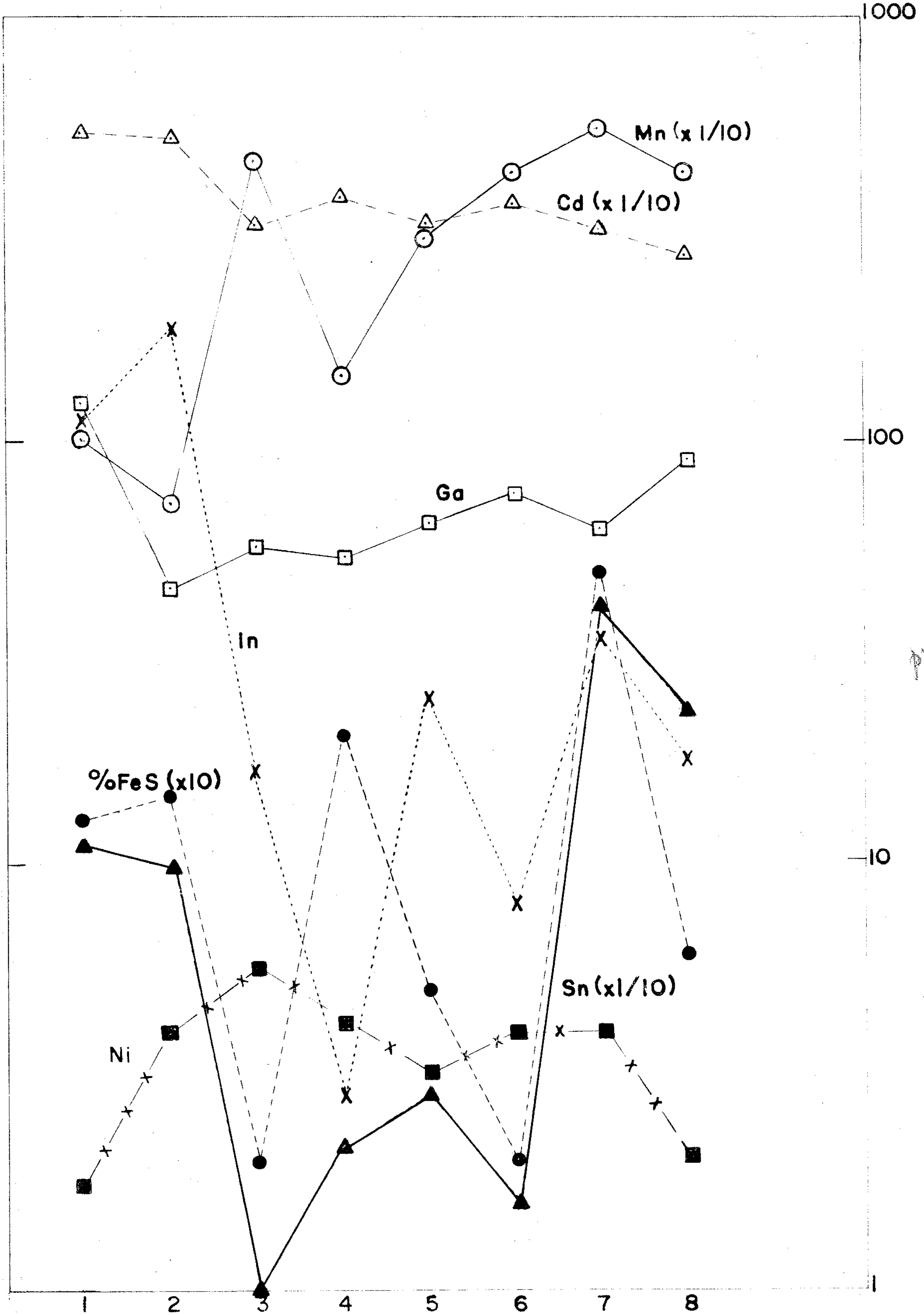
Analyses of the sphalerite surrounding the cavity (CEN-530 and 531A) differ from the single crystal analyses in having significantly lower indium in both, much higher manganese and iron in 531A, and higher cobalt in 530. Judging from the color of the sphalerite, the iron concentration in some of specimen CEN-531A is not as high as in the analyzed material.

The analyses indicate that although several elements may show similar variations (e.g. iron, manganese, cobalt, and nickel), many elements vary independently of other elements in part. Except for manganese and iron, Burnham (1955) found similar characteristics in the sample he analyzed from Hanover.

It is possible that the low trace element concentrations in sample 10 are the result of leaching, suggested by the porous appearance of some of the sphalerite. If so, the sharp color zoning indicates that leaching did not occur in the central part of the crystal. The low concentrations in sample 1 might have been produced by leaching but because samples 1 and 2 are separated by a thin dark band it seems unlikely that leaching has affected sample 2.

If the iron analyses are used to obtain a temperature from Kullerud's (1953) work on the FeS-ZnS system, the temperatures range from less than 140° C. to about 425° C. Sample CEN-531A gives about 575° C. As will be discussed in a later section, the writer believes that the temperature was this high or higher because the sphalerite was not saturated with iron sulfide when deposited. Although small temperature fluctuations may have occurred during the growth of the crystal, it is difficult to understand how the temperature variations could be as large as those indicated by the iron content. Variations in the amount of iron in the hydrothermal fluid seem a much more reasonable cause of the variation. Similar variations in the composition of the fluid are believed to be responsible for the differences in trace element content. It is significant that the postulated temperature of at least 425° C. near the end of the period of crystal growth was not sufficient to homogenize the trace or major element concentrations in the crystal during the period this temperature was maintained.

In figure 39 is plotted a series of analyses of a color-banded sphalerite vein from the U. S. Mine at Bingham. The series of samples extends almost across a vein of sphalerite an inch wide, beginning from one wall of the vein. Present in the hand specimen are about 20% galena, 10% rock or gouge altered to a mixture of quartz, calcite, and a micaceous mineral, and small amounts of tetrahedrite and chalcopyrite. Calcite and quartz also fill fractures and small open spaces within the vein. In addition to the banded sphalerite vein mentioned above, a one inch vein of sphalerite showing a more intricate color pattern parallels the first vein and is separated from it by a half centimeter of altered rock. Analysis BIN-596-8



ppm?

Figure 39. Variation in trace element content across sphalerite vein, sample BIN-596.

was taken from this second sphalerite vein. The banding in the sphalerite of both veins is interrupted by galena and tetrahedrite, which appear to have replaced the sphalerite. In the polished section from which the samples were drilled, several rows of small pyrite grains parallel the banding in the vicinity of sample 1. Other pyrite cuts across the banding. Chalcopyrite is present as rows of blebs and as larger grains. Pyrite is interpreted to have been deposited before, during and after sphalerite, but galena and tetrahedrite followed sphalerite. Some chalcopyrite replaces sphalerite; possibly all of it does.

As before, the cadmium content is the most constant of the elements although a small decrease is indicated between samples 2 and 3. The gallium concentration is also relatively constant. The variations shown by iron, indium, and tin are large and erratic, but show similarities to each other. Manganese concentrations are variable but tend to increase toward sample 7. Lead and antimony are present in some samples, probably as galena and tetrahedrite. The silver content is probably strongly controlled by impurities.

Unfortunately, the specimen offers no convincing evidence on the relative ages of sphalerite in samples 5, 6, and 7. Samples 1 - 5 were drilled from sphalerite deposited in that order. Samples 6 and 7 may represent a continuation of this sequence, or material from the opposite half of a symmetrical vein. However, crystals making up the vein extend across several bands, and one crystal actually extends from the band of sample 4 to the band represented by sample 7, suggesting that sample 7 is the youngest.

The variations of trace element content in the sequence are in general much larger than those found in the specimen from Hanover, and are more nearly comparable in size to those found by Burnham in the sphalerite from

Tintic. The amounts and kinds of impurities present do not seem to furnish an explanation for most of the variations. Change in the composition of the fluids from which the sphalerite was deposited again seems the most reasonable explanation.

In an effort to ascertain the amount of variation to be expected within small specimens of ore other than visibly-zoned material, several suites of chalcopyrite and sphalerite from different parts of the same polished section have been analyzed. The analyses of ten suites of this type from chalcopyrite specimens of the Central mining district are plotted in figures 40 to 45.

The variability observed in the tin analyses can be entirely accounted for by analytical error. The same is true for the variations in the indium analyses, except CEN-263A (probably a single crystal), CEN-337, and possibly CEN-343. The spread of silver contents in sample 263A is only slightly larger than that expected from the analytical procedure. In CEN-354 the low silver concentrations are correlated with one end of the polished section and the higher values with the opposite end. The variations observed in cobalt, manganese, molybdenum, and nickel are greater than the analytical error, but at the lower concentrations present in most of the samples, the possible importance of impurities cannot be denied. The variation in bismuth content of CEN-263A is probably caused by the presence of galena, but such an explanation cannot be made for CEN-354 or 337.

In summary, the data presented above are consistent with a relatively small variability of tin, indium and silver within pure samples of the chalcopyrite from varied geologic environments within the district. Although impurities may be responsible for many of the variations in other

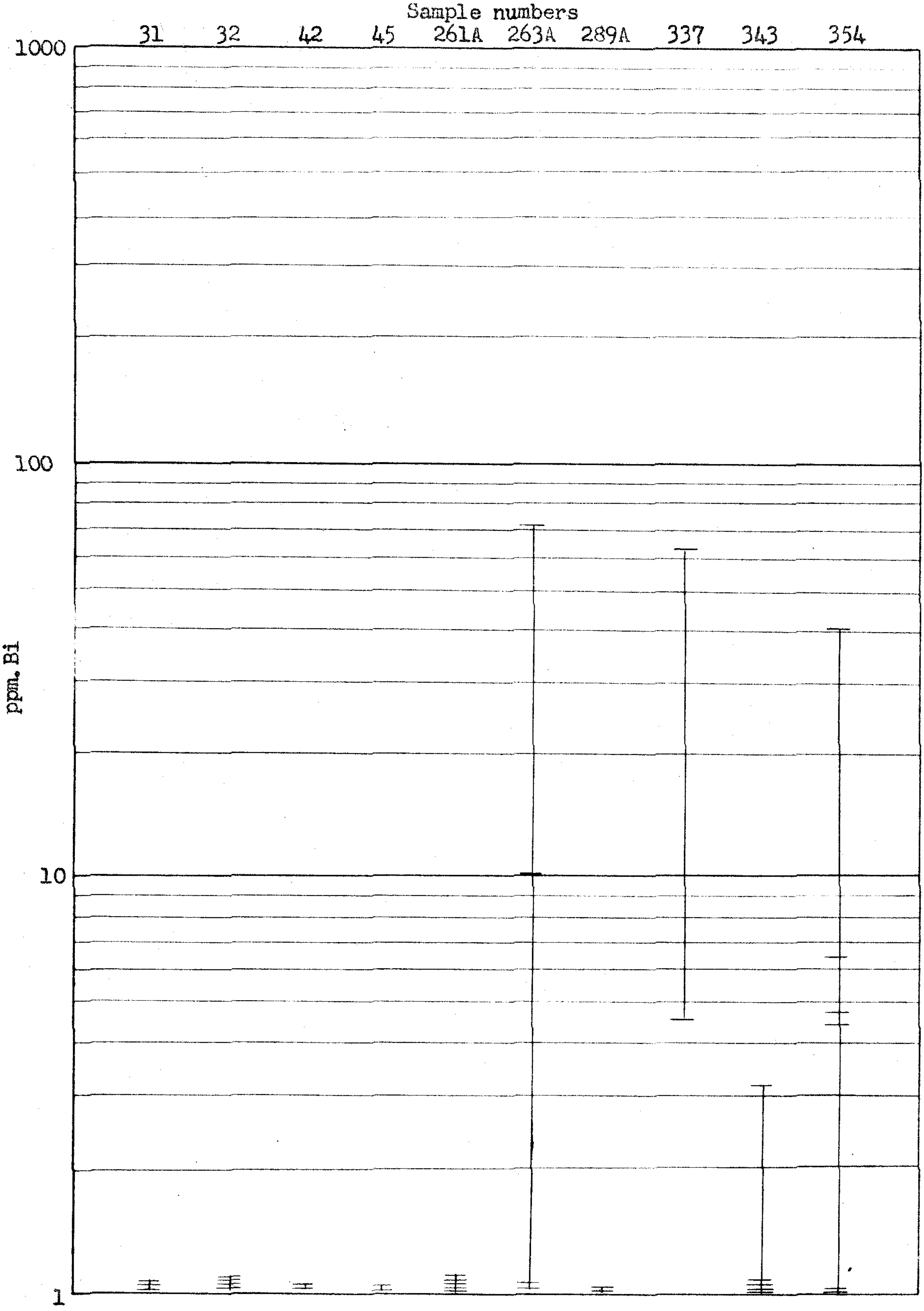


Figure 40. Variation of bismuth content within polished sections of chalcopyrite, Central mining district, New Mexico.

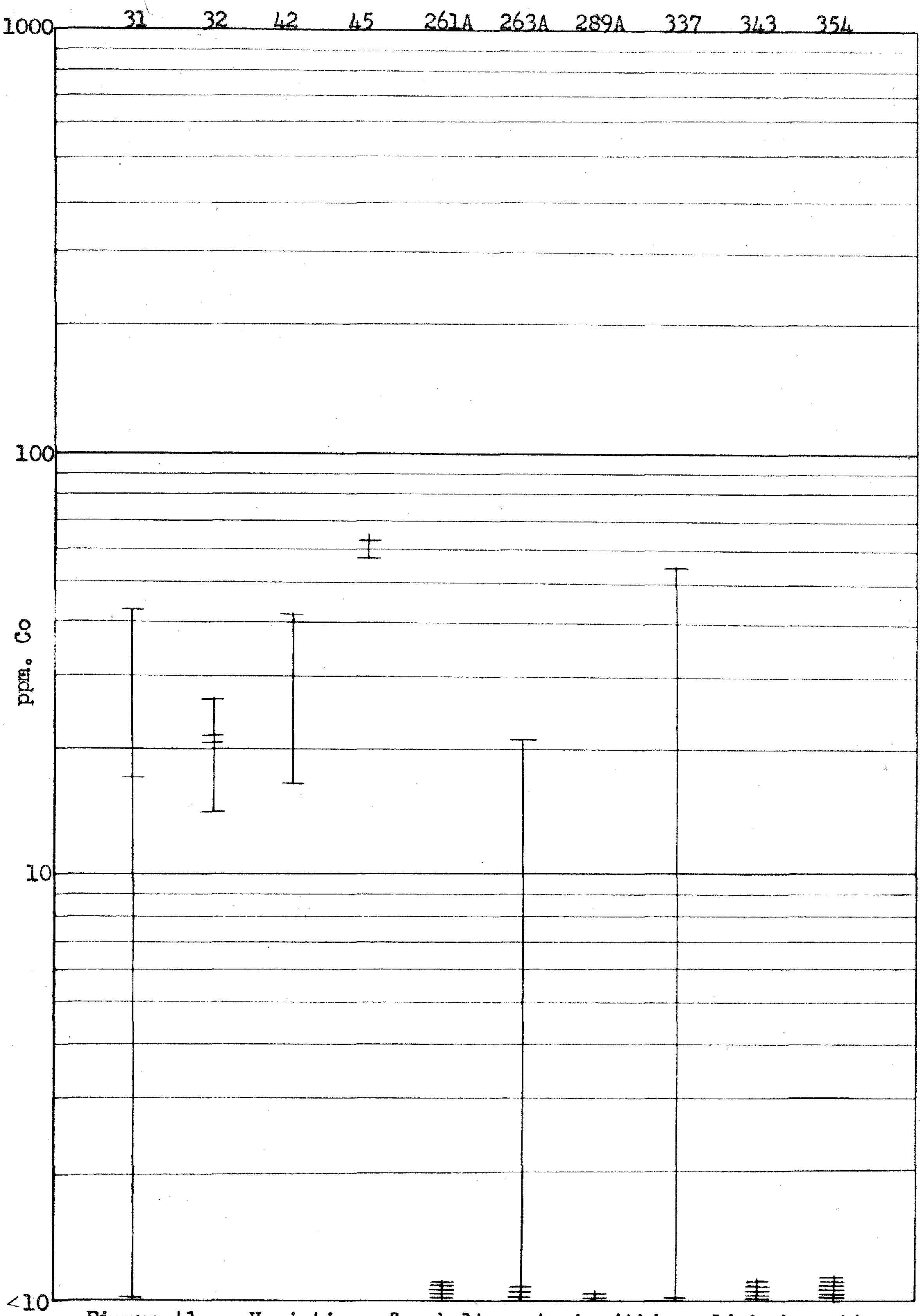


Figure 41. Variation of cobalt content within polished sections of chalcopyrite, Central mining district, New Mexico.

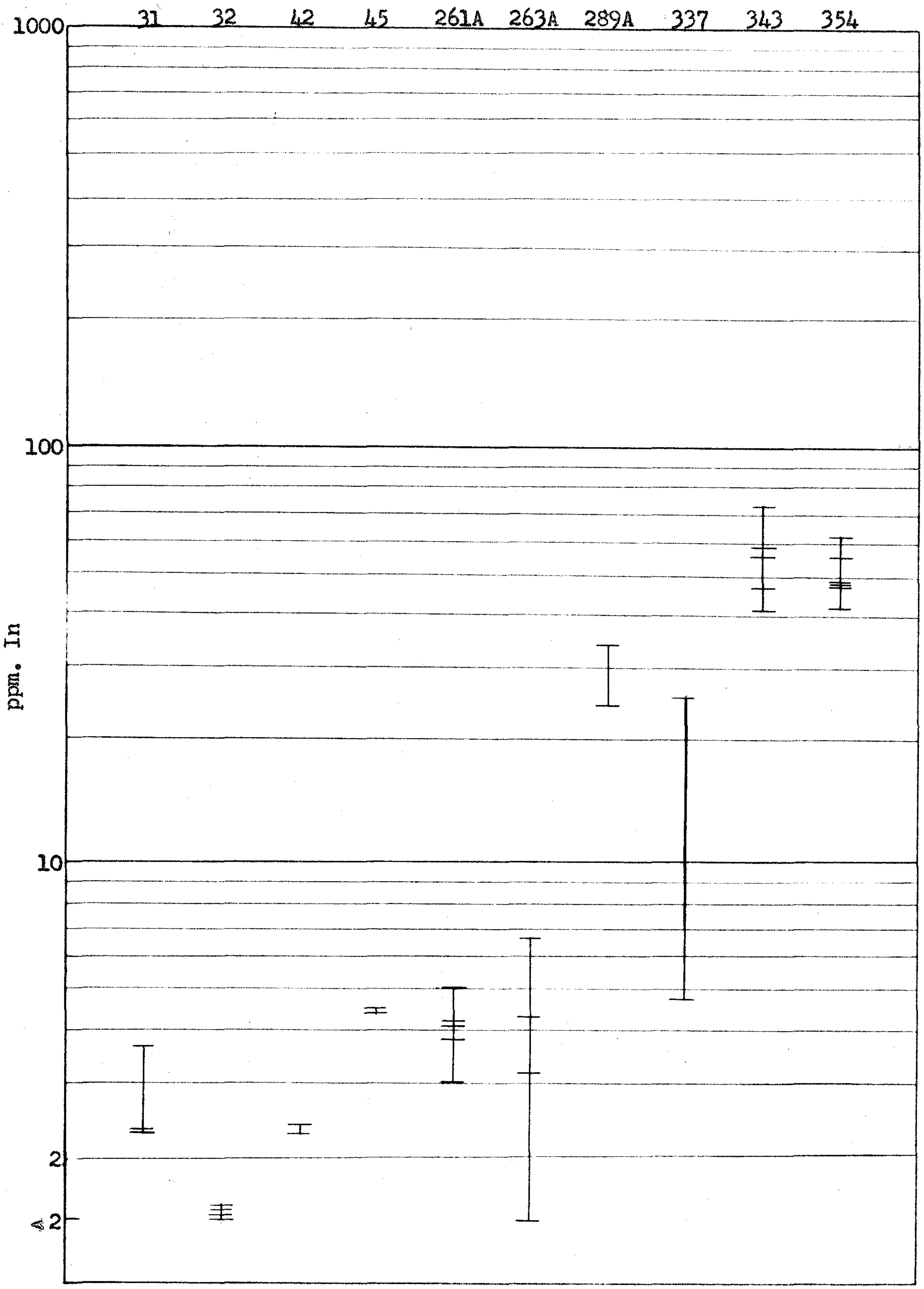


Figure 42. Variation of indium content within polished sections of chalcopyrite, Central mining district, New Mexico.

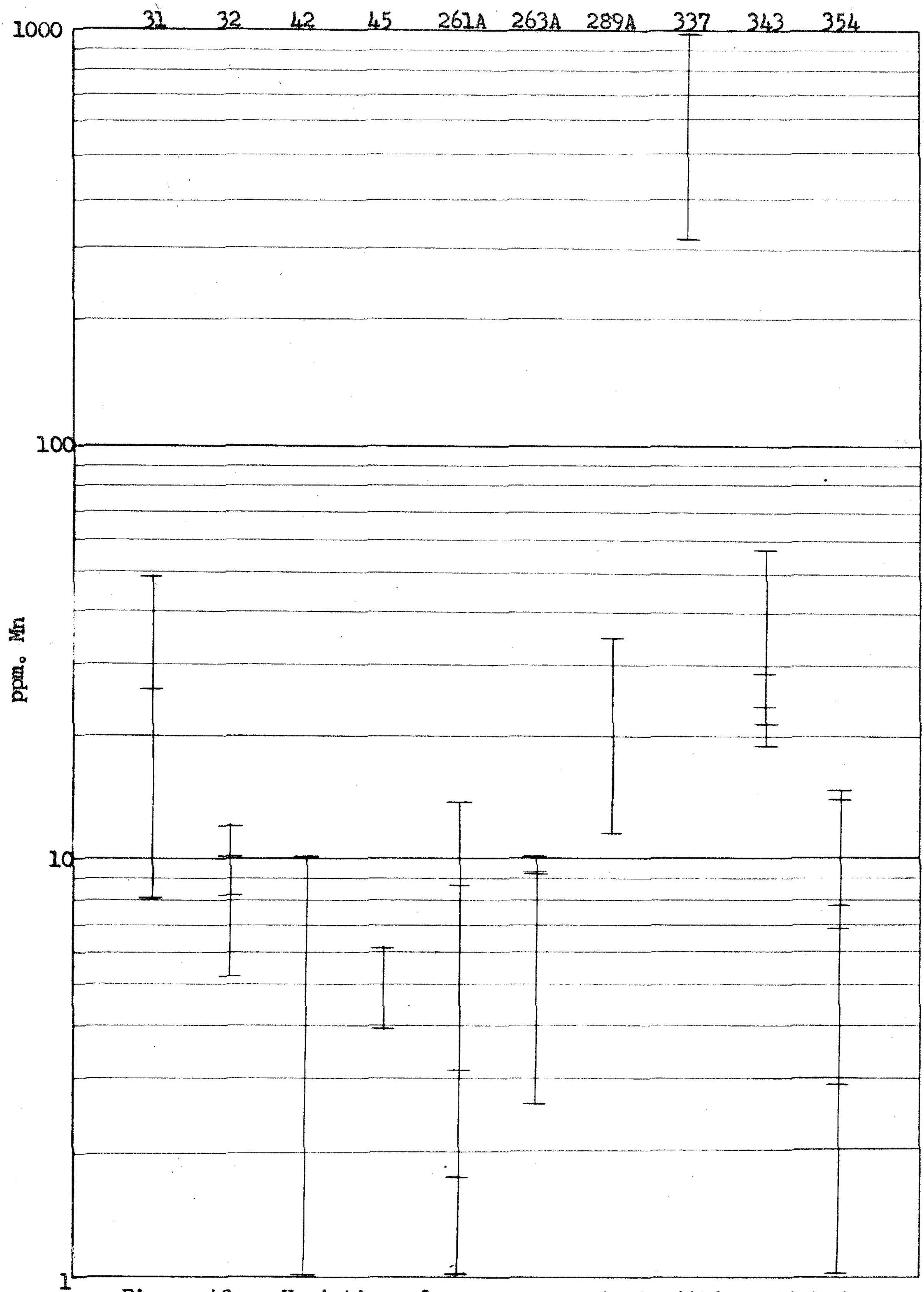


Figure 43. Variation of manganese content within polished sections of chalcopyrite, Central mining district, New Mexico.

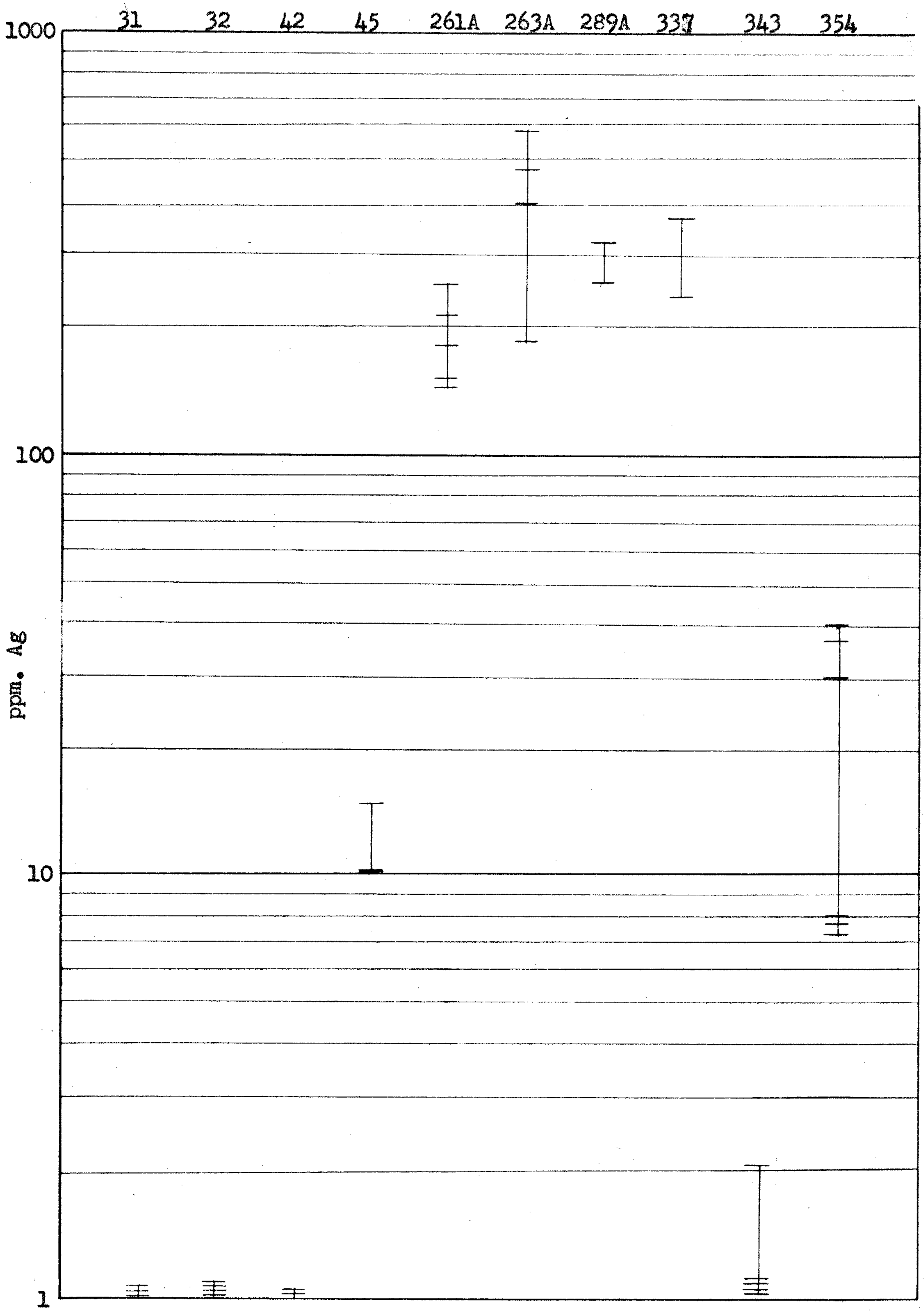


Figure 44. Variation of silver content within polished sections of chalcopyrite, Central mining district, New Mexico.

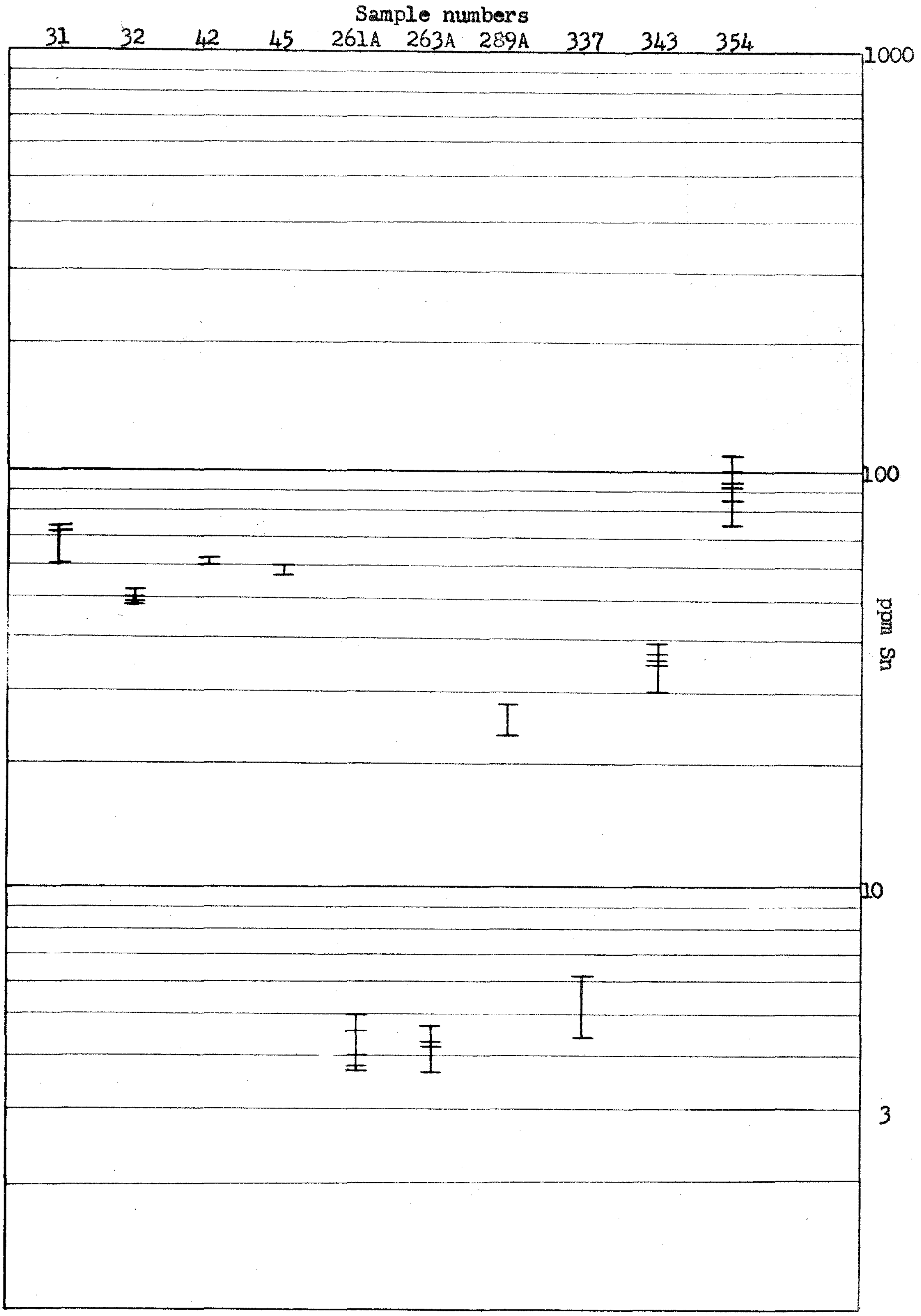


Figure 45. Variation of tin content within polished sections of chalcopyrite, Central mining district, New Mexico.

elements, it seems probable that small variations in the content of some trace elements do occur within the chalcopyrite itself.

Analyses of similar suites of sphalerite samples from single polished sections have been plotted in figures 46 to 50. CEN-193-3, 229-1 and 538A-3 were drilled from sphalerite rich in chalcopyrite blebs whereas the remaining samples drilled from these specimens contained little or no chalcopyrite.

The variability in cadmium, cobalt, and nickel is about equal to the analytical error. Several specimens (CEN-267, 538,and possibly 266) exhibit differences in manganese content greater than the analytical error. In CEN-267 the differences correlate with differences in the iron content.

The elements silver and bismuth show variations within one specimen that are much larger than the analytical error. In the case of silver, the largest variations occur in the suites mentioned above as containing chalcopyrite blebs. In all three of these suites the highest concentration of silver occurs in the sample of sphalerite with chalcopyrite blebs. A similar correlation can be made for the bismuth contents of the three specimens and for the indium contents of two of the three. It seems probable that the correlation results either from higher concentrations of silver, bismuth, indium and copper in the ore fluids during the later stages of sphalerite deposition, or, if the chalcopyrite was deposited by replacement of the sphalerite, from the higher concentrations of silver, bismuth, and indium in the fluid from which the chalcopyrite was deposited. In specimen CEN-241 a large variation in bismuth content is observed which may result from varying abundance of chalcopyrite blebs or from the presence of varying amounts of galena in the samples. Variability of silver, bismuth, and indium in most of the other specimens equals or barely exceeds the analytical error.

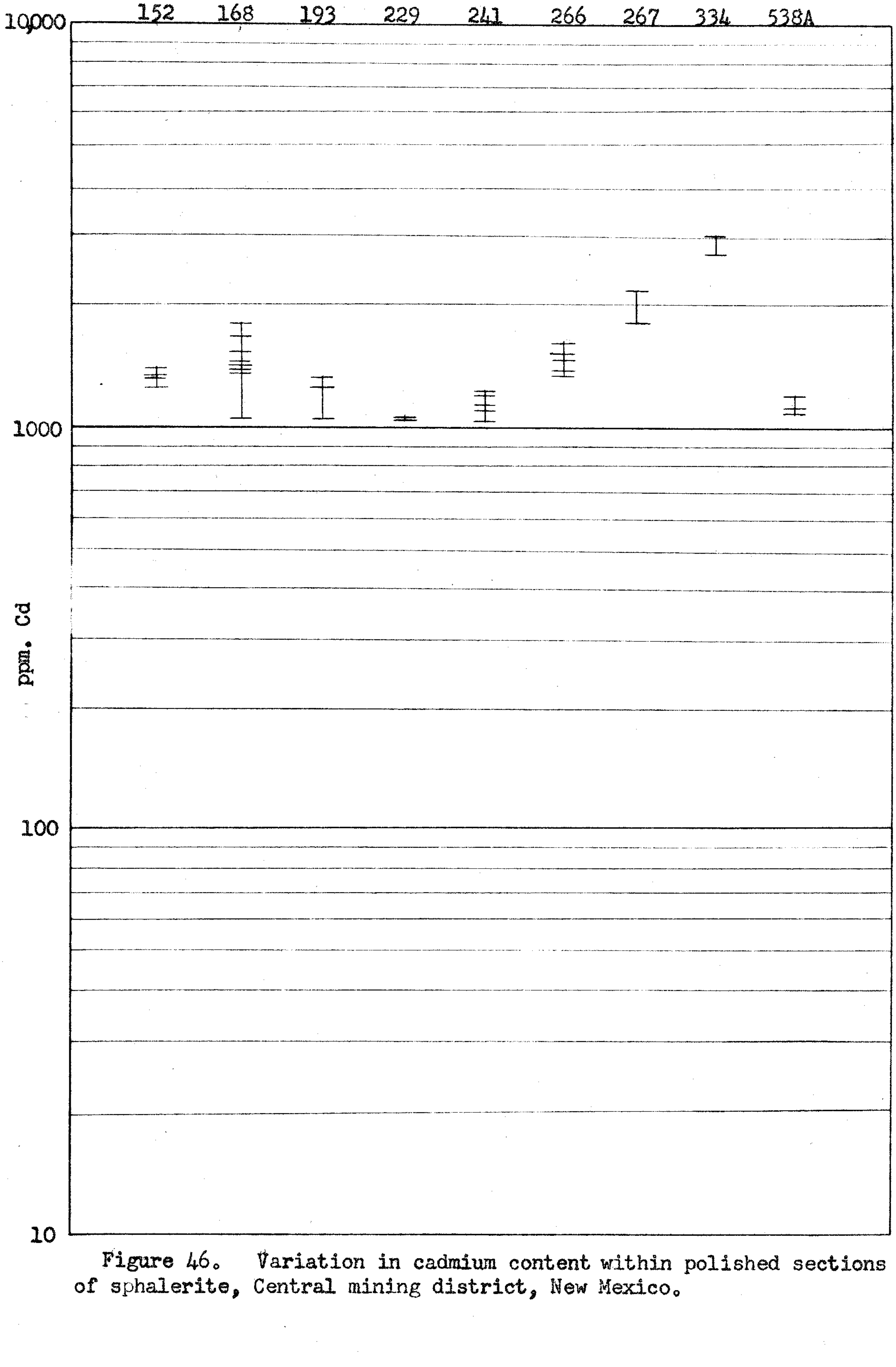


Figure 46. Variation in cadmium content within polished sections of sphalerite, Central mining district, New Mexico.

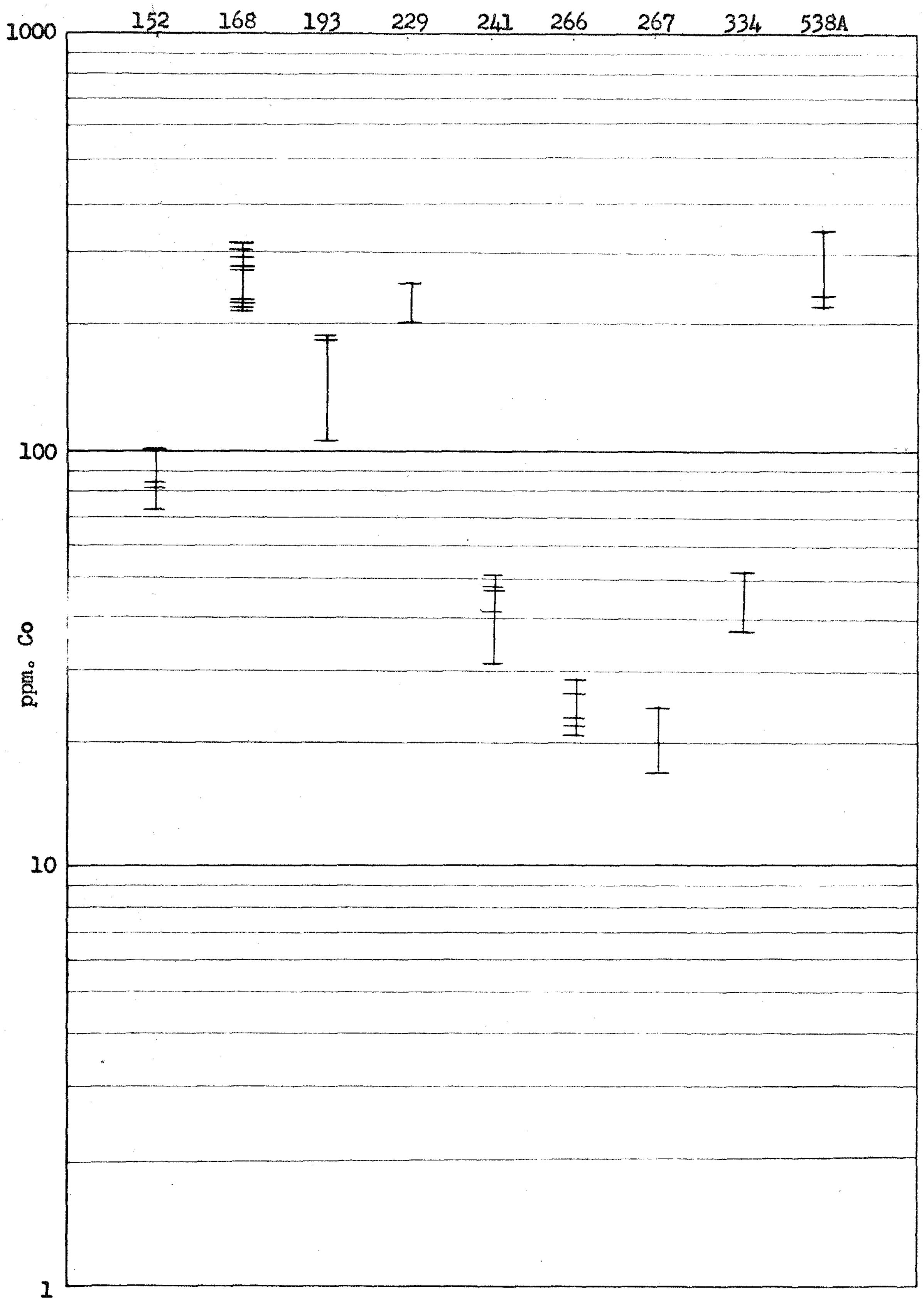


Figure 47. Variation in cobalt content within polished sections of sphalerite, Central mining district, New Mexico.

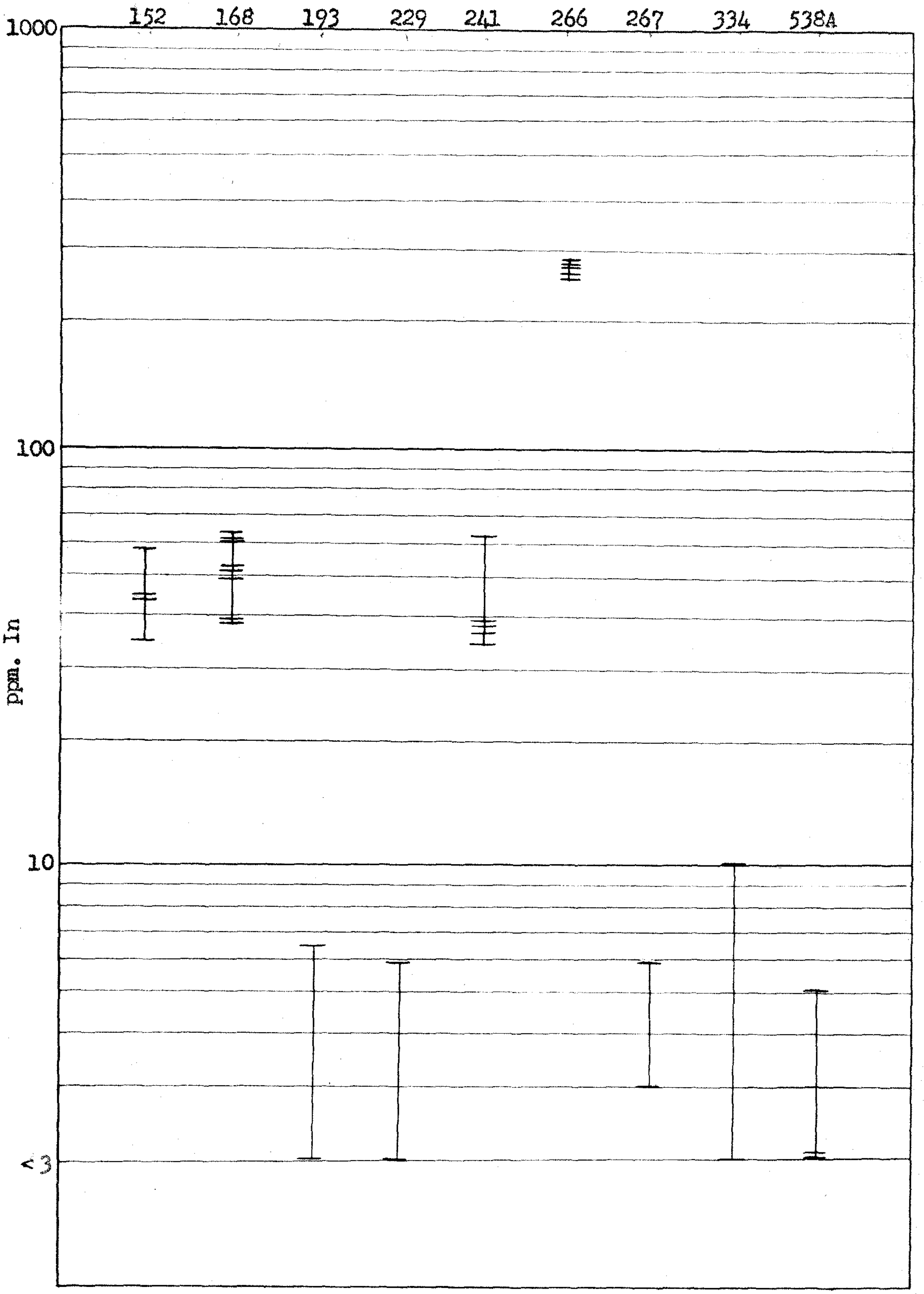


Figure 48. Variation of indium content within polished sections of sphalerite, Central mining district, New Mexico.

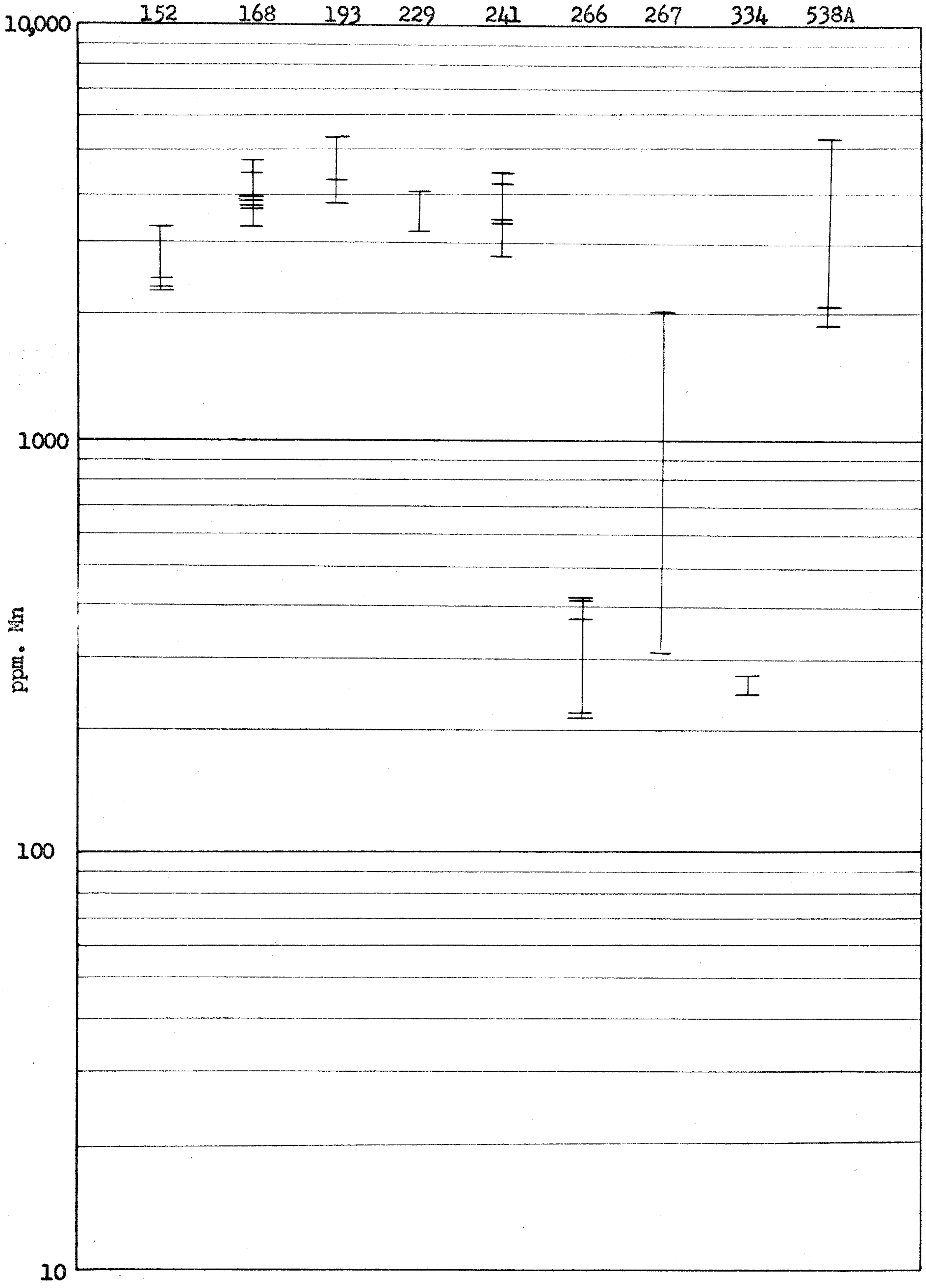


Figure 49. Variation in manganese content within polished sections of sphalerite, Central mining district, New Mexico.

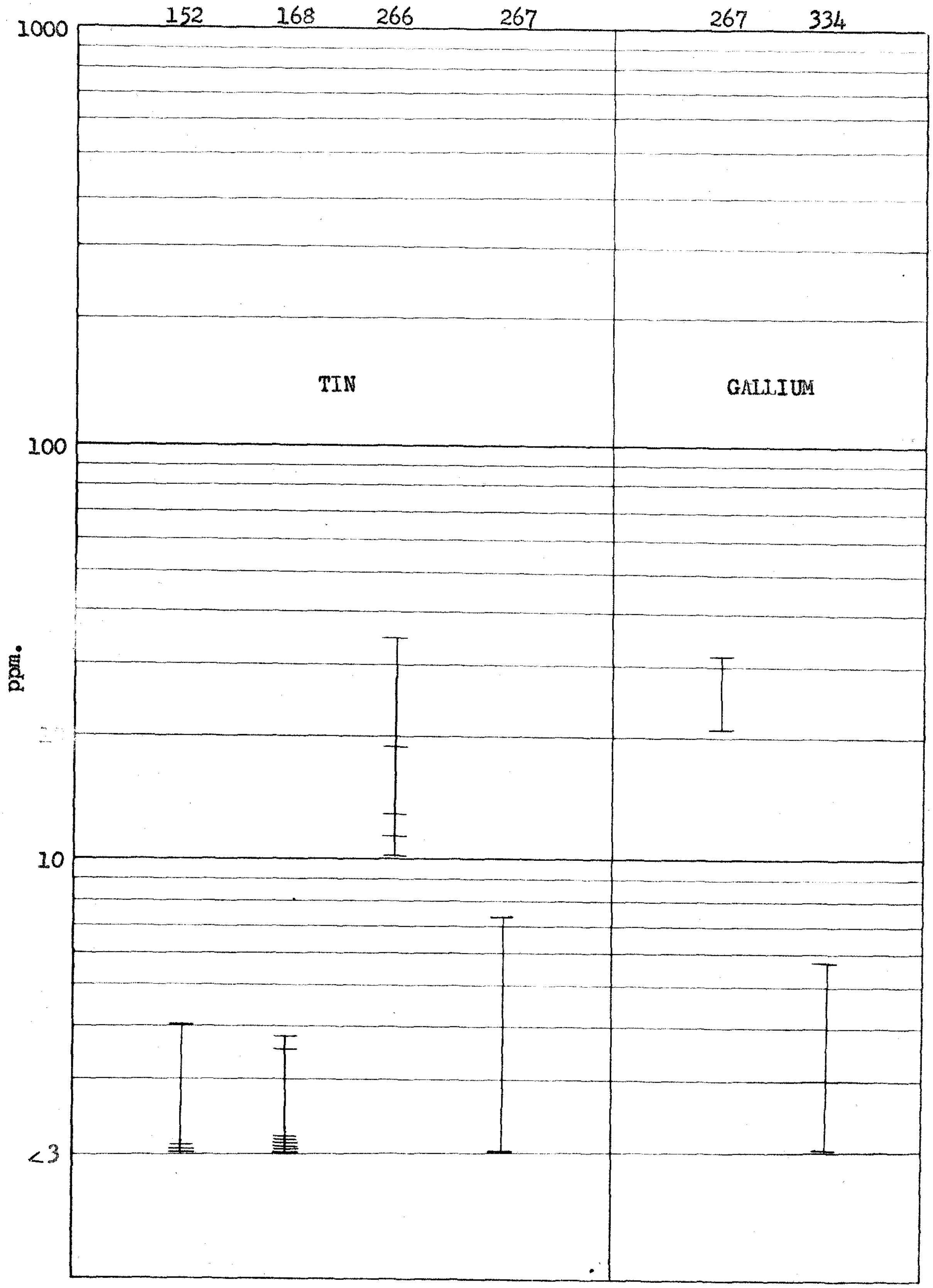


Figure 50. Variation in tin and gallium content within polished sections of sphalerite, Central mining district, New Mexico.

The general picture of trace element variability within polished sections of sphalerite from the Central mining district is that concentrations of cadmium, cobalt and nickel are essentially constant but that concentrations of silver, bismuth, and indium may show distinct variations, especially in sphalerite containing chalcopyrite blebs. However, because the above conclusion is based on relatively few samples and because sample preparation problems restrict the specimens used in this test to relatively pure sphalerite which might show less variability than lower grade ore, the picture may not be complete.

Figures 51 to 53 show variations within polished sections of sphalerite specimens from Bingham. Five of these specimens are banded veins (BIN-580, 586, 589, 595, and 596), one is a banded replacement of limestone (BIN-732), and the remainder are relatively massive replacement ores.

Cadmium shows relatively small variations on the logarithmic scale used, but differences of 2000 ppm. do exist. Variations in manganese content are larger than those of cadmium both in ppm. and in log ppm. Distinct variations in gallium exist, but these are in general smaller than the variations in indium and tin. In the case of indium and tin, a large variation in one of these elements does not necessarily seem to be accompanied by large variations in any other element. Thus the physical or chemical variables causing the differences must be specific in their action, and are probably not simple variations in temperature.

Except for indium in BIN-671, the variations in the relatively massive replacement specimens are in general small compared to the variations in the banded veins. This difference may be the result of the possibility for rapid flow of ore fluid and therefore for rapid changes in

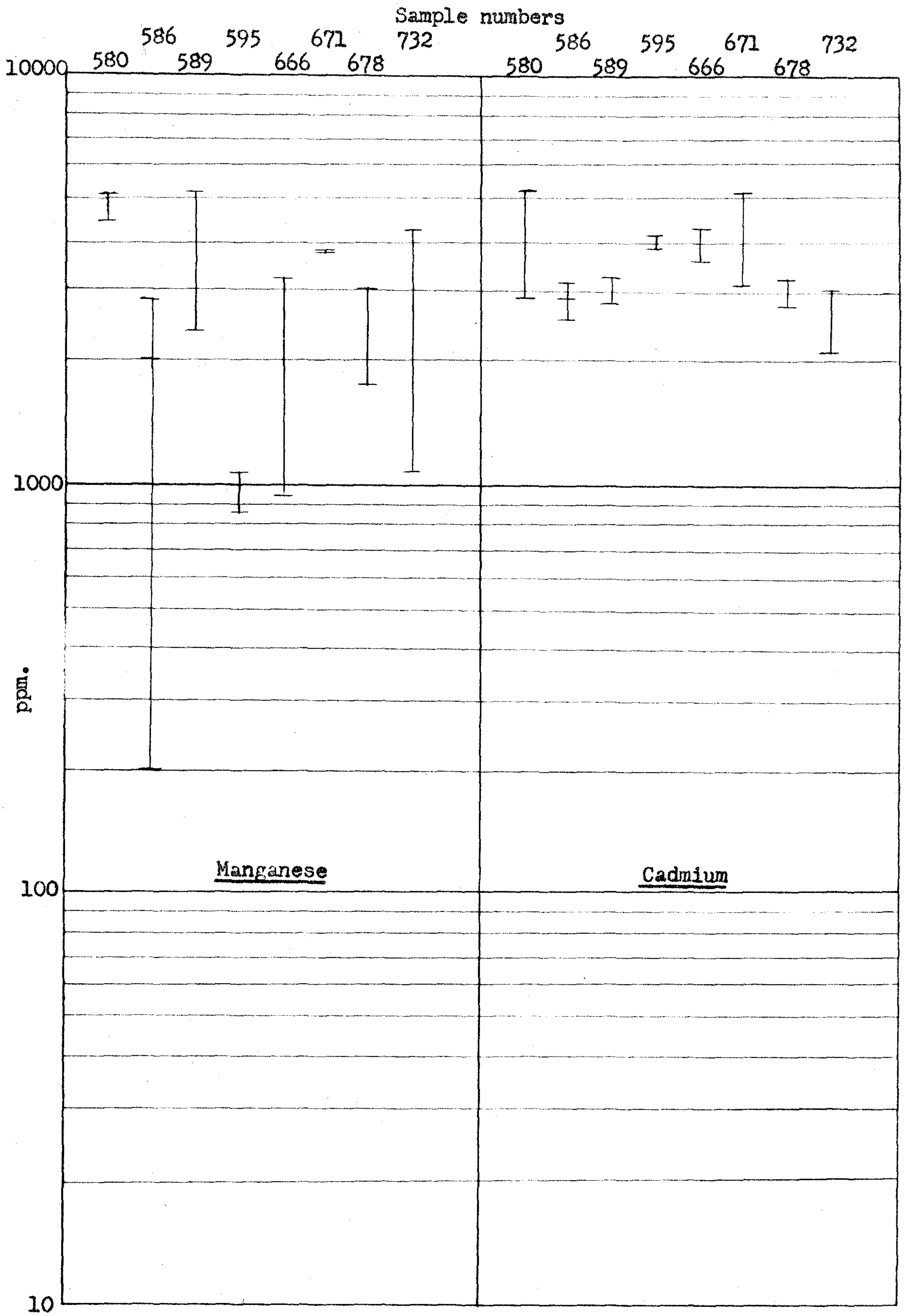


Figure 51. Variation of manganese and cadmium content within polished sections of sphalerite, Bingham mining district, Utah.

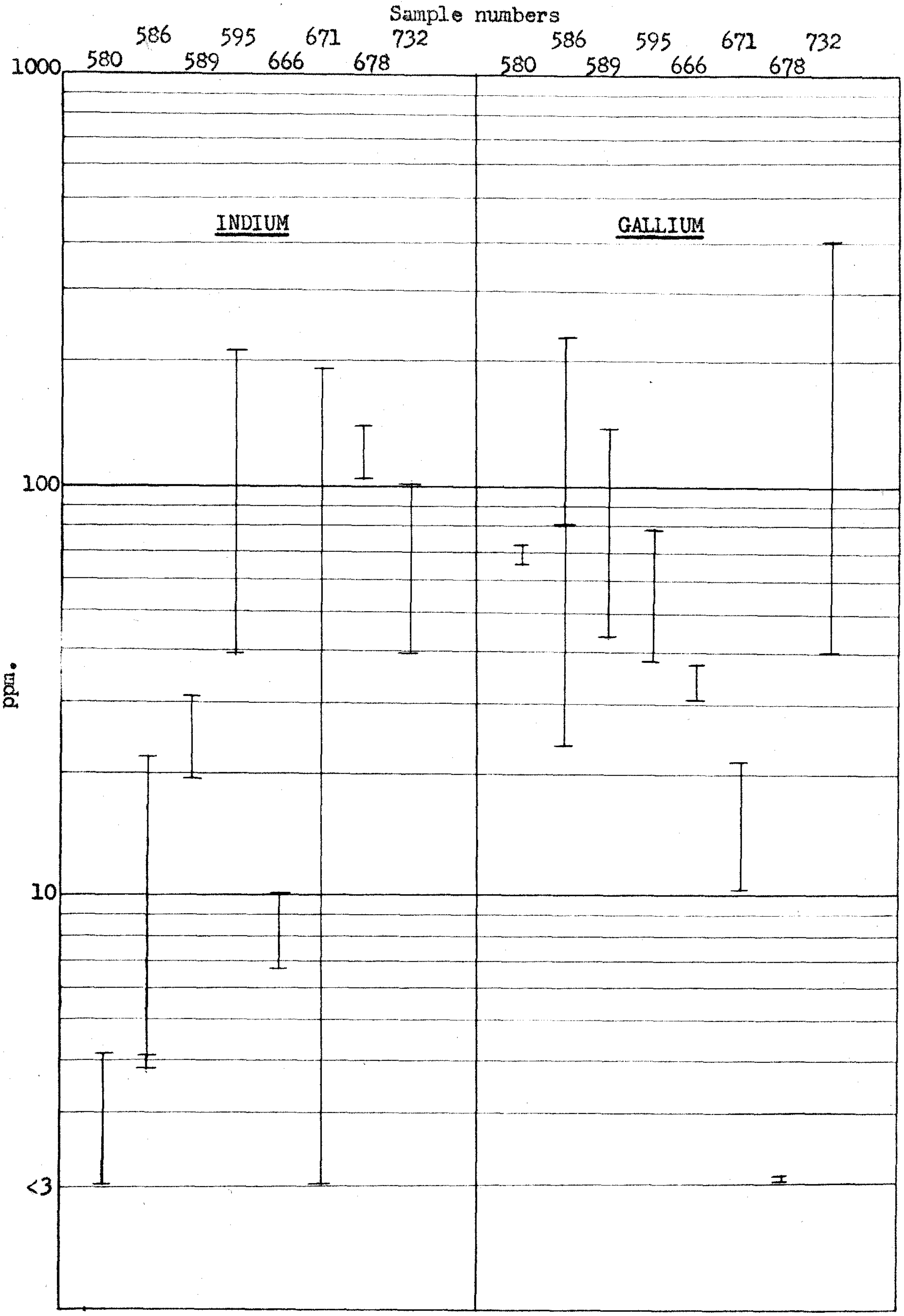


Figure 52. Variation of indium and gallium content within polished sections of sphalerite from Bingham mining district, Utah.

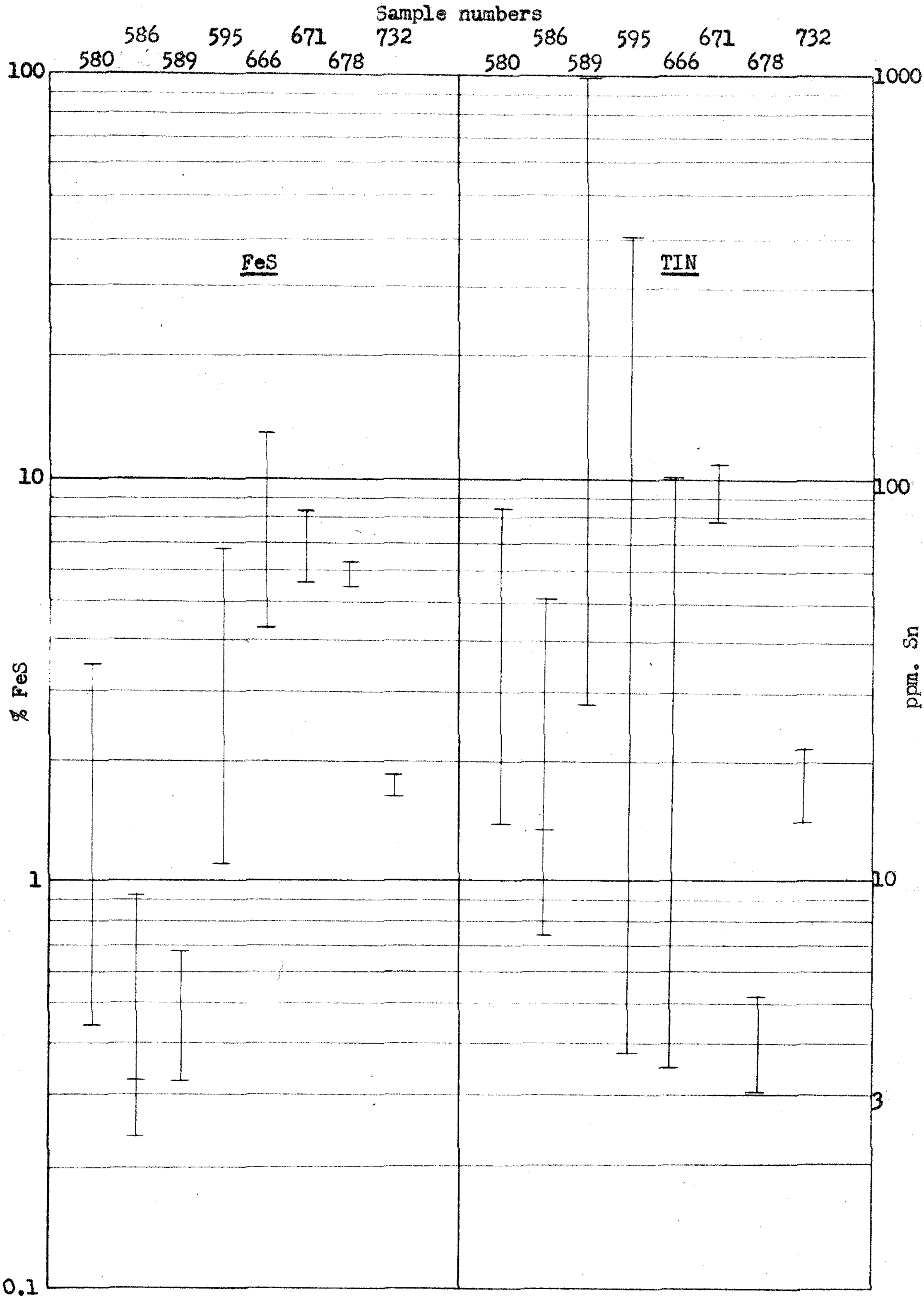


Figure 53. Trace element variations within polished sections of sphalerite from the Bingham mining district, Utah.

character of the ore fluid in a relatively open vein in contrast to the slower movement of the material permeating the rock in the process of forming the replacement type of ore.

Figure 54 shows the concentrations of trace elements in a series of samples from a horizontal diamond drill core through an ore body at Hanover. A dike and fissure occur along one side of the ore body and limestone on the other. Gangue minerals in the specimens include garnet in CEN-538A, hedenbergite in all but 533, ankerite in 533, and coarse pyrite in 535. Significant variations occur for all the elements shown. The low indium and cobalt values at the margins of the ore body, especially on the limestone side, are believed to be characteristic of many of the ore bodies in the mine for reasons which will be discussed later. However, additional work is needed to verify this point in detail.

Figure 55a shows trace element variations in sphalerite samples from a high-grade ore body exposed in the Buckhorn Gulch quarry of the Hanover mine. The five samples were taken from an area about 25 feet in diameter. The variations in manganese and cobalt are larger than the variations found within most single polished sections of similar ore, whereas the variations in cadmium, indium and bismuth are about the same magnitude as those in single polished sections.

It is clear from these two examples, which are believed to be typical of the ore bodies at Hanover, that appreciable variations of every element present in the sphalerite except cadmium may occur within ore bodies. Whereas a single analysis may represent a polished section of the ore from Hanover relatively well, a single analysis for most elements is not necessarily representative of an ore body. The same conclusion appears to hold for the more massive replacement type of ore bodies at Bingham, but for banded

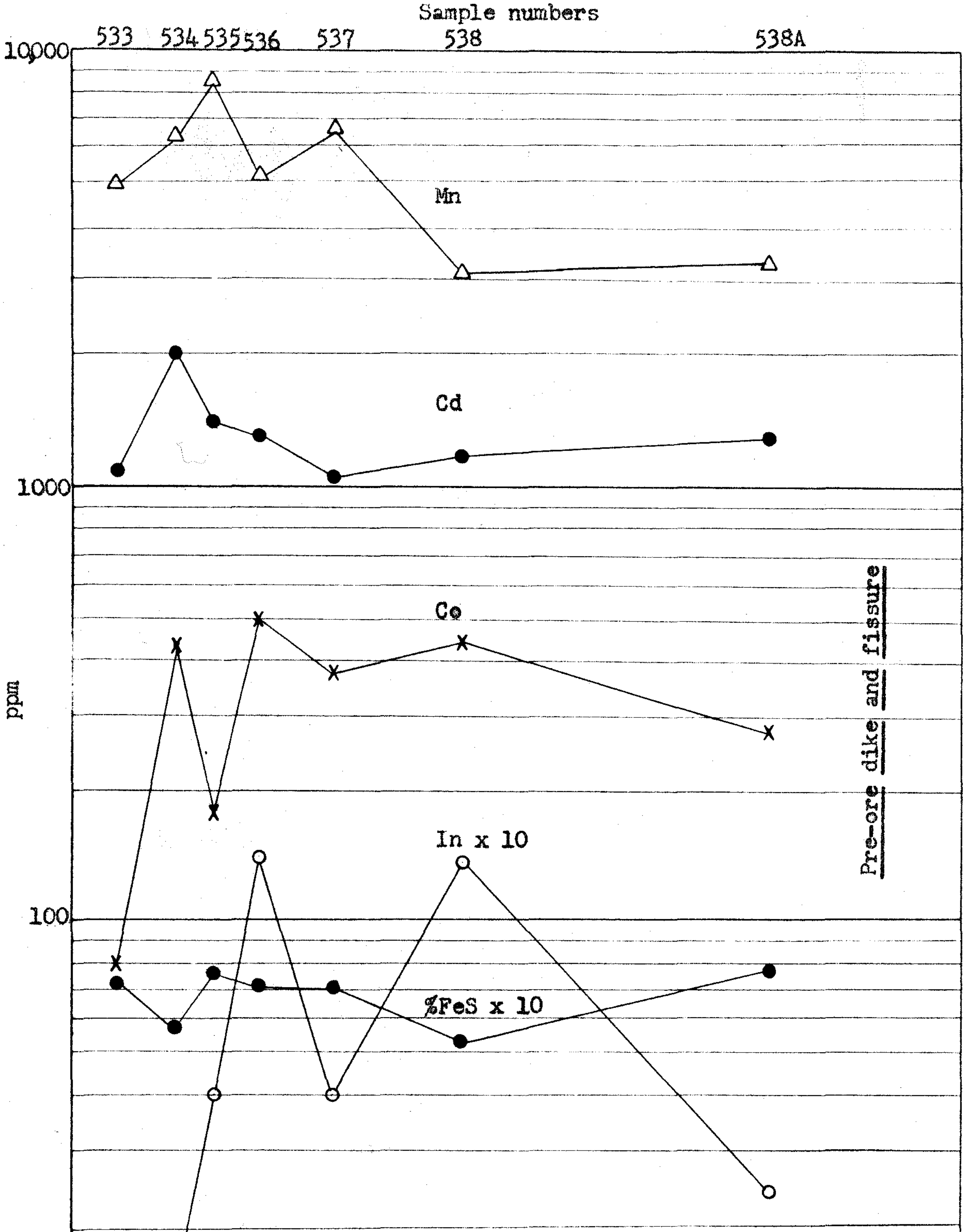


Figure 54. Variation of trace element content of sphalerite from a horizontal diamond drill hole through an ore body at Hanover, New Mexico.

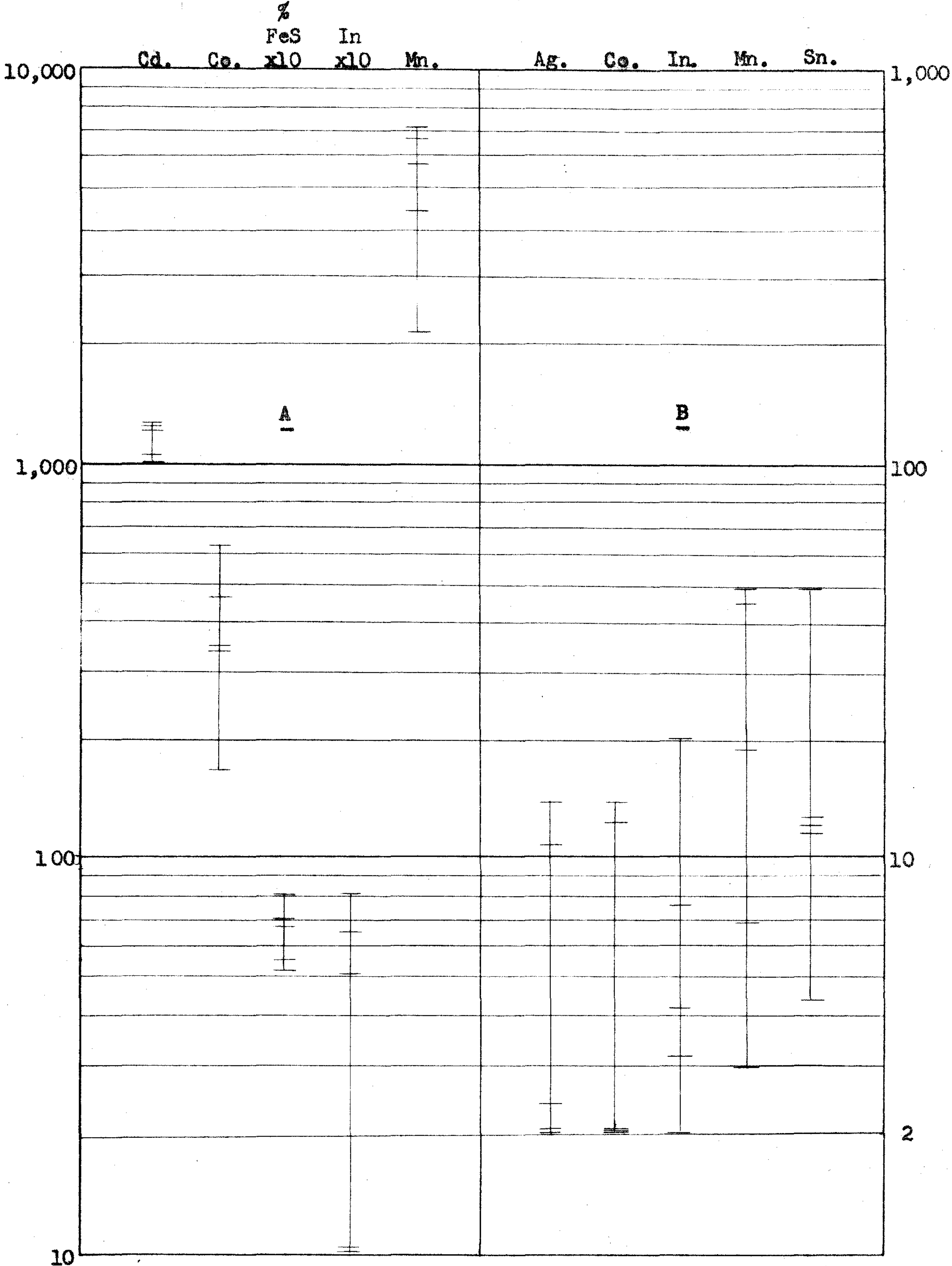


Fig. 55. A: Trace element variations in 5 sphalerite specimens from a 20' x 20' face in the Buckhorn Gulch quarry, Hanover mine.

B: Trace element variations in 5 chalcopyrite specimens from DDH-1263, Chino Mine.

veins at Bingham large variations may occur within single polished sections.

Also shown in figure 55 are the trace element contents of five chalcopyrite samples from diamond drill hole 1263 at the Chino mine. The samples are separated by distances of up to 263' in the core. The figure clearly shows that significant differences in the trace element content of the chalcopyrite occur in this distance. Thus, conclusions similar to those expressed above for sphalerite appear to hold also for chalcopyrite.

## TRACE ELEMENTS IN CHALCOPYRITE FROM THE CENTRAL MINING DISTRICT

Data on trace elements in chalcopyrite are listed in table 8. Several maps (plates 3-8) have also been prepared to show the geographic variations in trace element content of chalcopyrite from the Central mining district. A number of samples analyzed by Burnham are included on these maps. Inspection of the maps suggests that for many elements the samples can be divided into several geographically and geologically defined groups within which the variability is appreciably smaller than for the district as a whole. Five such groups have been set up. In addition to being shown on the maps, the groups are also compared in figures 56 to 58.

Group I consists of chalcopyrite from the porphyry copper at Santa Rita, and from the immediately adjacent tactite zone. The group is distinguished by moderate tin content and low indium and silver contents. In addition, molybdenum, cobalt, and nickel average higher than for the other groups.

Group II includes all chalcopyrite from within and adjoining the northern two-thirds of the Hanover-Fierro stock and from the area to the north of this stock, except the chalcopyrite from the Continental and Pearson mines along the Barringer fault west of Fierro. Group II is distinguished by moderate to high concentrations of both tin and indium.

Group III consists of chalcopyrite from the Continental and Pearson mines, where chalcopyrite is associated with sphalerite in tactite. The group is distinguished by moderate to high concentrations of cobalt and nickel.

Groups IV and V consist of chalcopyrite from the zinc and lead-zinc ores in the area near Hanover and to the southeast, south, and southwest.

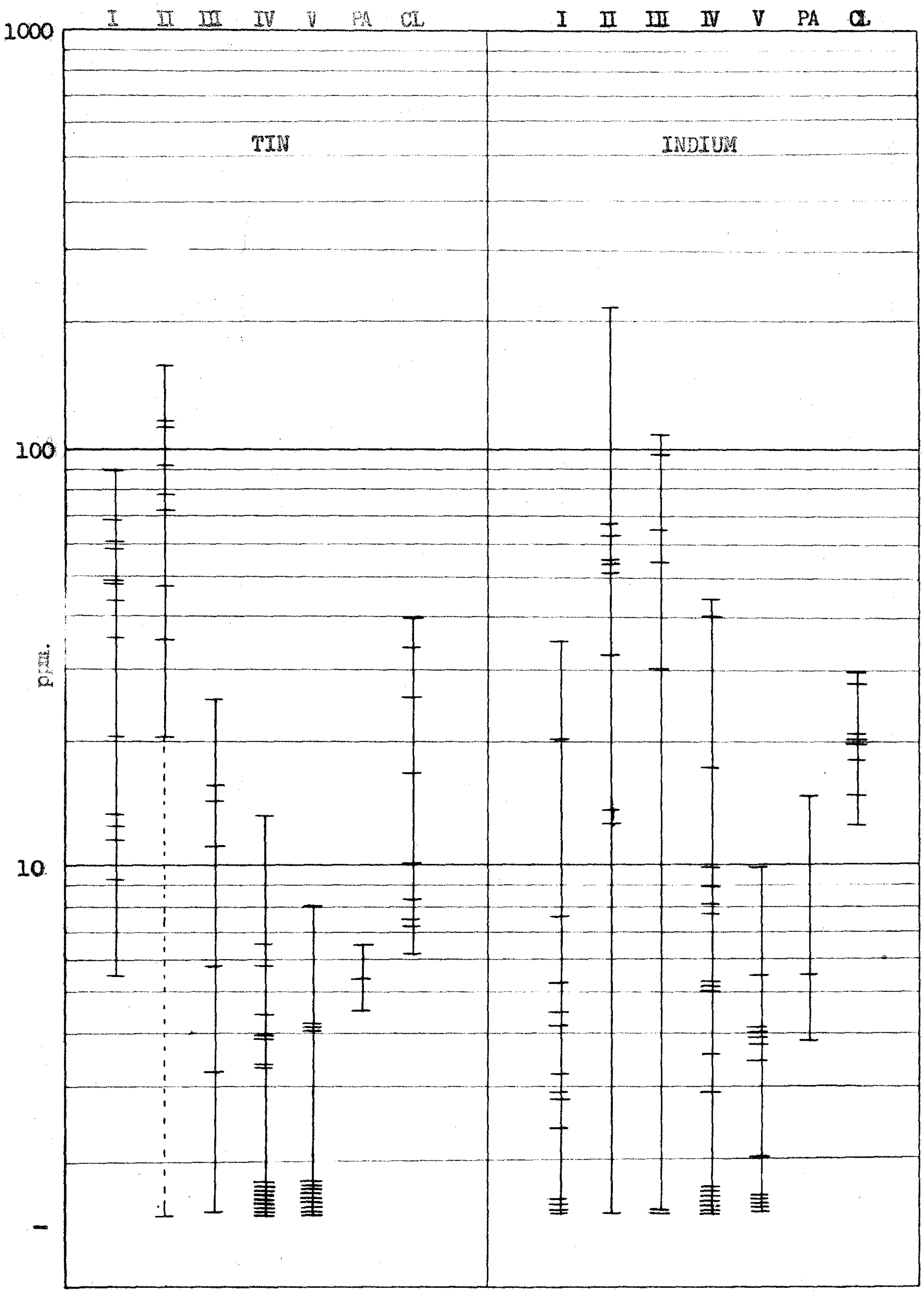


Figure 56. Tin and indium content of chalcopyrite classified according to sample group. I through V from the Central mining district, PA from Pinos Altos, and CL from the Cleveland mine.

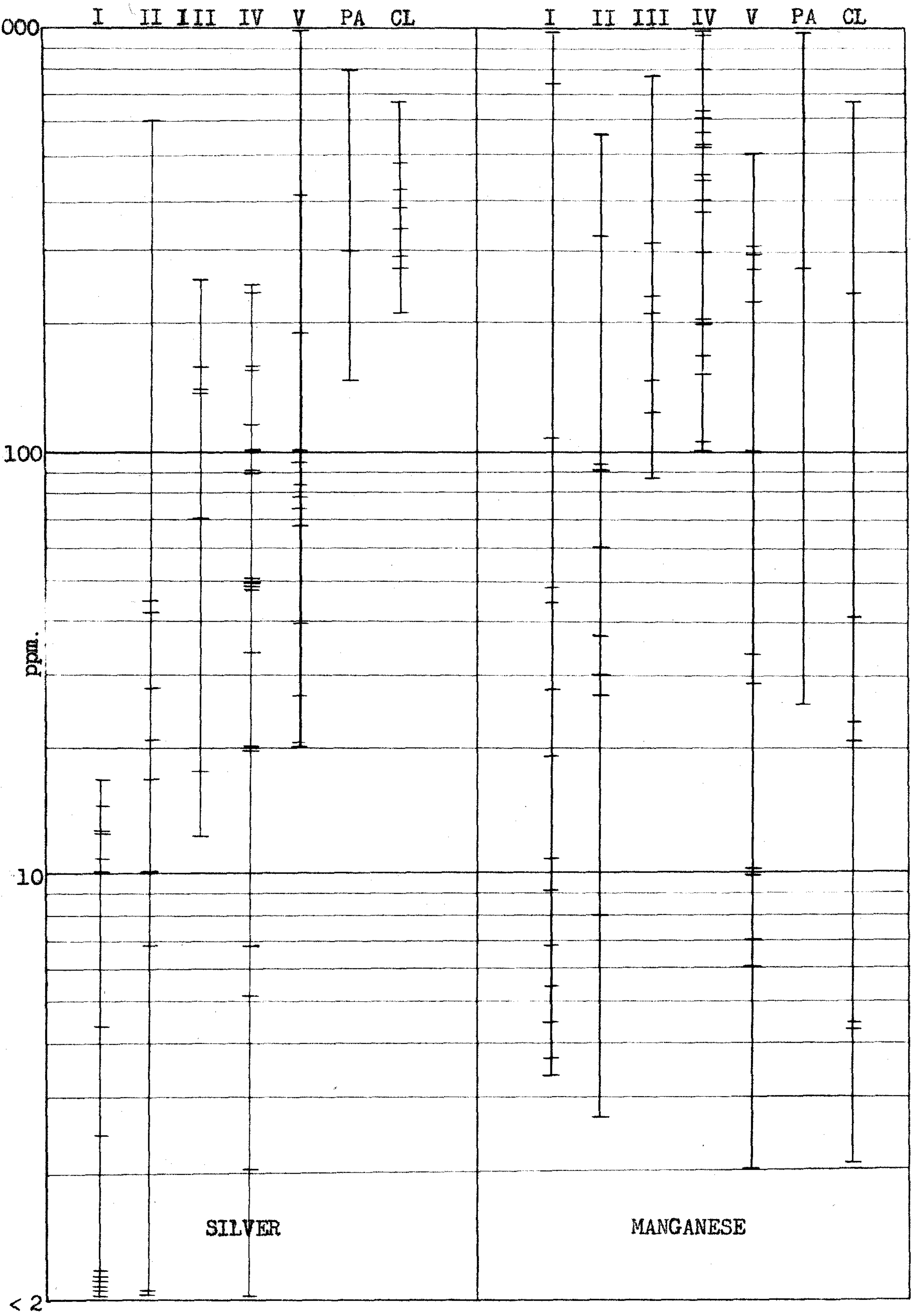


Figure 57. Silver and manganese content of chalcopyrite classified according to sample group. I through V from the Central mining district, PA from the Pinos Altos district, and CL from the Cleveland mine.

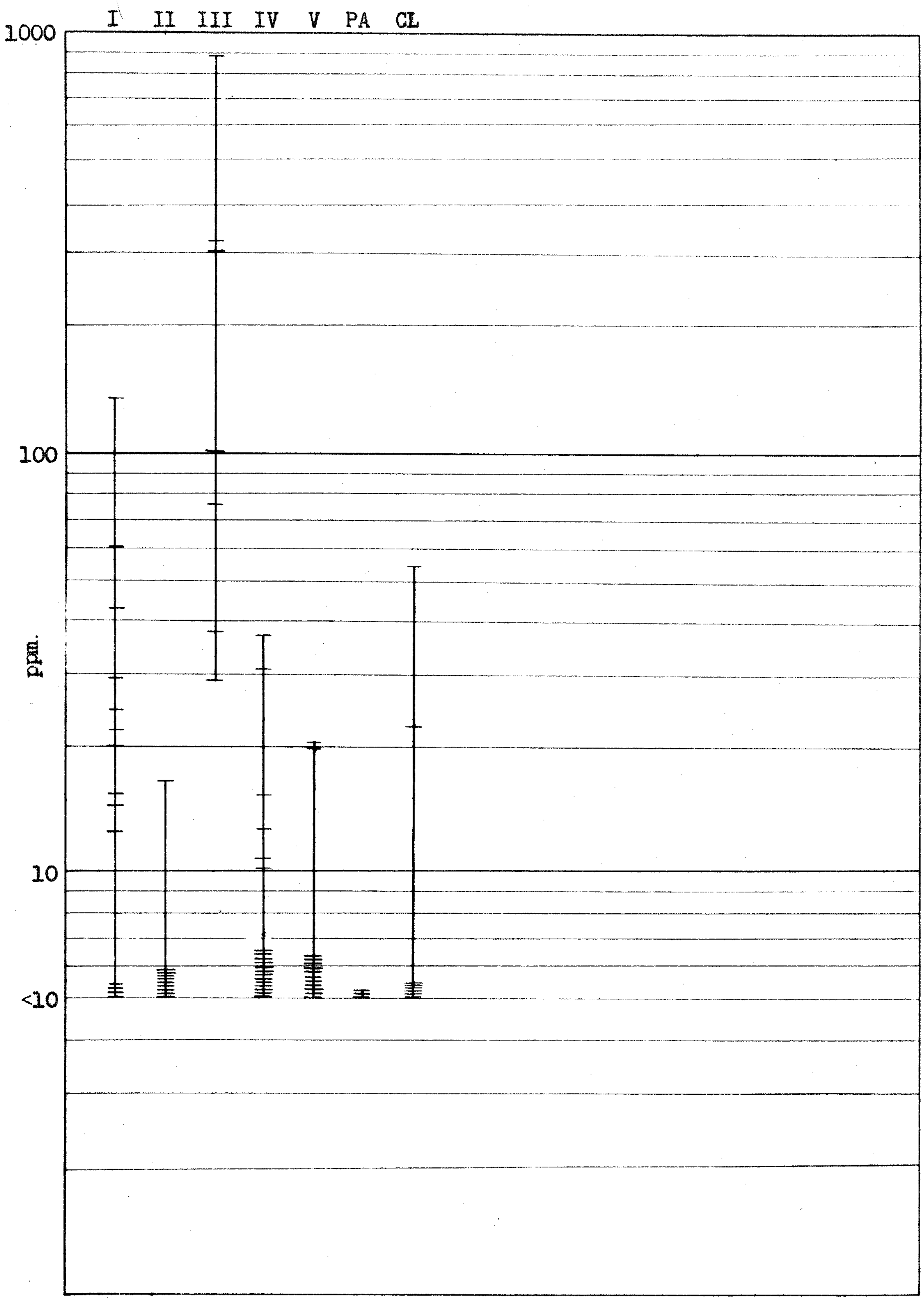


Figure 58. Cobalt content of chalcopyrite classified according to sample group. I through V from the Central mining district, PA from the Pinos Altos district, and CL from the Cleveland mine.

These samples are characterized by low contents of tin and indium. On the basis of possible differences in the manganese and silver concentrations, samples from the Groundhog mine have been designated as group V, and the samples from near Hanover as group IV. The distinction between groups IV and V is more doubtful than the others, and may actually represent a gradual change similar to that postulated for the trace element content of sphalerite in the following section.

A series of statistical tests have been made to verify the existence of the five groups. The principal test used has been the H test (Kruskal and Wallis, 1952). The H test is a nonparametric test using ranking, and is similar to the F test in application (Dixon and Massey, 1951, pp. 121-127). However, being nonparametric, no assumption of normal distribution is required, and the test is believed by Kruskal and Wallis to be relatively insensitive to differences in the variance of the groups being compared. The latter property is especially useful because tests showed that the variance is not homogeneous for one element, and may not be for another.

For the elements tin, indium, cobalt, nickel, silver, and manganese, the following null hypothesis has been tested: The data represent random samples from a single population (rather from two or more populations). A level of significance of 0.5% has been used. Ties have been handled by the mean value method, and the correction for ties has been applied as given by Kruskal and Wallis (1952).

The values of H found from the data are listed in table 12, along with the critical value (14.86) for a $\chi^2$ approximation of H. All calculated values of H are found to be significantly greater than the critical value, indicating that the null hypothesis of a single population can be rejected for all the elements. Use of the F test led to similar conclusions, but was less convincing because of the lack of homogeneity of variance for two elements. An additional advantage of the H test is that analyses less than the detection limit are more easily handled.

Additional tests have been made for differences in silver and manganese content of groups IV and V. Using a t test, the hypothesis of equal means was accepted for silver at the 5% level of significance, but was rejected for manganese at the 1% level of significance. Because of an apparent inequality of variance for manganese, the test was repeated using the nonparametric U test (Hoel, 1954, p. 291), and the hypothesis of equal means was again rejected. Thus, the two groups are concluded to differ in manganese content, but not in silver content.

Table 12

Results of H tests on chalcopyrite groups, Central mining district, N. M.

| Element | H |
|---|---|
| Cobalt | 29.87 |
| Indium | 18.66 |
| Manganese | 22.31 |
| Nickel | 27.96 |
| Silver | 23.47 |
| Tin | 39.25 |

Critical value, 0.5% significance level, for a $\chi^2$ approximation of $H = 14.86$.

Therefore, the hypothesis of a single population can be rejected for all six elements.

In summary, then, the statistical procedures discussed above give results that are consistent with the distinctions drawn between the groups.

The large values of H in table 12 as well as the graphical representations (figures 56 to 58) leave little question that the differences between the groups are real, if the analyzed samples can be assumed to be representative of the groups.

While it is possible that the samples collected are not fully representative of the population delineated on the maps and indicated by the mine or locality names, it seems certain that a grouping of the kind discussed does exist. For instance, the group from Chino may be weighted too heavily by specimens from the northern end of the deposit, but even if this is so, some kind of grouping is possible which includes only samples from the North Pit area, or only those in the contact zone, or some similar division of the samples. Undoubtedly, exceptions to the suggested grouping occur, but the writer believes a grouping exists, and would be modified only in detail by additional work.

The statistical procedures do not give any information on the character of the change from one group to a geographically adjacent one. It is possible that samples with intermediate values occur near the boundary between two groups, or, on the other hand, that samples belong to either one group or the other. This question is particularly interesting with respect to the changes between group I and samples from the Oswaldo #2 mine just to the north, because it is possible that two separate mineralizations are represented. Also, a gradational change might exist for manganese between groups IV and V as previously mentioned.

It is obvious that within the groups some samples deviate widely from the group average. In some cases, particularly for silver, manganese, lead, molybdenum, cadmium, and possibly cobalt and bismuth, the anomalously high concentrations may be the result of contamination by other minerals containing the element in relative abundance. However, a low but definite content of all the elements mentioned above is believed to occur in the chalcopyrite itself, because these elements are found in samples free of microscopically visible impurities containing the elements in question, and because consistent relationships of the elements are found in some of the groups.

Other anomalous concentrations are probably the result of local peculiarities in the processes of mineral deposition. In some cases, correlations with geologic and mineralogic factors can be discerned. For instance, the manganese concentrations at the Groundhog mine seem to fall into two groups. Samples SR-15, CEN-269, 271, and 275 have high contents of manganese, and are all replacements of Carboniferous limestone in the deeper levels of the mine. Although their exact position within the mine is unknown, samples G-3, 4, 6, and 11 were collected about 1930, when the exposed ore consisted of veins and fissure fillings in the Cretaceous sediments and later igneous rocks in the upper levels of the mine. Specimen CEN-6 is believed to have come from the upper workings also. Specimens CEN-261 and 263 are open space fillings from the lower levels. Low manganese concentrations are found in CEN-6, 261A, 263A and G-3, 4, and 6, and the difference in concentration between these samples and those from the limestone replacement ore may result from the difference in wall-rock, or from the chemical and physical conditions under which deposition took place. Another possibility is that the two groups of manganese values correlate with the two generations of chalcopyrite found by Lasky (1936).

On the maps (plates 3-8), and plots (figures 56 to 58), the analyses of chalcopyrite samples from the Cleveland mine and the Pinos Altos district are also shown. The variability exhibited for these two groups of samples is smaller for most elements than for the five groups in the Central mining district proper. In the case of the Cleveland mine this small variability is believed to result from a simple history of ore deposition (i.e., a single surge of ore fluid) within the relatively small area of the mine. The most distinctive characteristic of the two groups is a consistently high content of silver, along with moderate contents of tin and indium.

# TRACE ELEMENTS IN SPHALERITE FROM THE CENTRAL MINING DISTRICT

## TRACE ELEMENTS IN SPHALERITE FROM THE CENTRAL MINING DISTRICT

Plates 10-14 show the distribution of trace elements in sphalerite samples from the Central mining district, and the data are listed in table 9.

Cadmium concentration in sphalerite from the district is essentially uniform except for the three samples from the Copper Flats area, two from the Barringer fault area and possibly a few samples with concentrations of about 2000 ppm. The variability among the remainder of the samples is about equal to the analytical error. The samples from Copper Flats and the Barringer fault area form a geographic and trace element group or groups separate from the rest of the district. The cadmium content of the main group of sphalerites is relatively low compared to sphalerites analyzed by other workers, and the cadmium content of the samples from Copper Flats is lower still. In the sphalerite from the Cleveland mine and the Pinos Altos area, cadmium content shows a consistent value about twice as great as that in the Central mining district samples.

It appears from the data of this report, as well as from data of previous workers, that the ratio of cadmium to zinc is less sensitive to variations in the mineralization process than ratios of other elements, and thus the cadmium content of sphalerite may be determined to a large extent by the cadmium/zinc ratio in the source of the ore fluid. Thus the sphalerite in the area studied might be divided into three groups related to three sources (magmas?) in the Hanover, Copper Flats, and Pinos Altos areas.

The cobalt content of sphalerite from the district is definitely not uniform. A range of cobalt content from less than 10 to 1000 ppm. has been found in the samples analyzed. Inspection of the values suggests that low cobalt contents are more prevalent in the area of the Groundhog and Bullfrog mines than in the vicinity of Hanover. Figure 59 is an attempt to show this relationship by plotting the cobalt content against distance from the outcrop of the Hanover-Fierro or Santa Rita stock, whichever is the closer. The samples from Copper Flats have been left out of this and most subsequent discussion on the basis of their distinctive cadmium content. It is obvious that the zonal relationship is far from perfect, but there does seem to be a correlation. A statistical test also indicates a correlation. In figure 60 are shown histograms of the cobalt content of all samples within 2000' and of all samples between 9000 and 12,000 feet of the nearest stock (the latter group is essentially equivalent to the Groundhog mine). The difference between the histograms appears to be significant. It seems probable that this zonal variation is related to the similar variation in the lead/zinc and silver/zinc ratios discussed in the section on production.

It is clear that while a zonal variation is present, other factors must also be involved in determining the cobalt content. Examination of the large collection of samples from the Hanover mine suggests several characteristics which correlate in a general way with cobalt content. Eleven of the 55 specimens analyzed from the mine contain 100 ppm. or less cobalt. Some characteristics of these eleven specimens are listed in table 13. Six of the eleven specimens are distinctly vuggy, whereas none of the other 44 specimens is observed to show this property. A carbonate mineral is present in every one of the eleven, but carbonates (other than small late veinlets) were noted in only 8 of the remaining 44 specimens and only one of these 8 contains more than 5% carbonate. Several of these

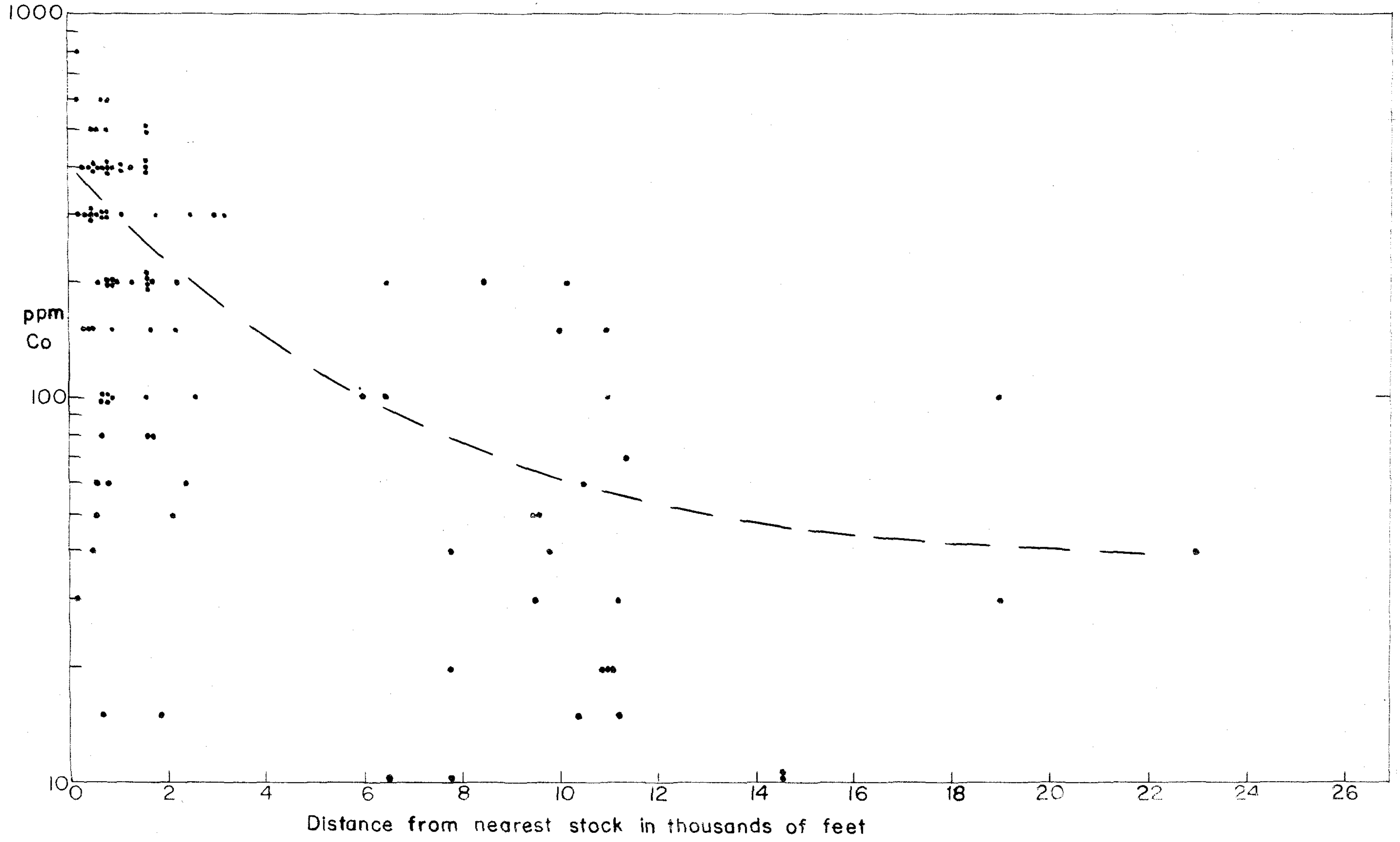


Figure 59. Zonal change in cobalt content of sphalerite, Central mining district, N.M.

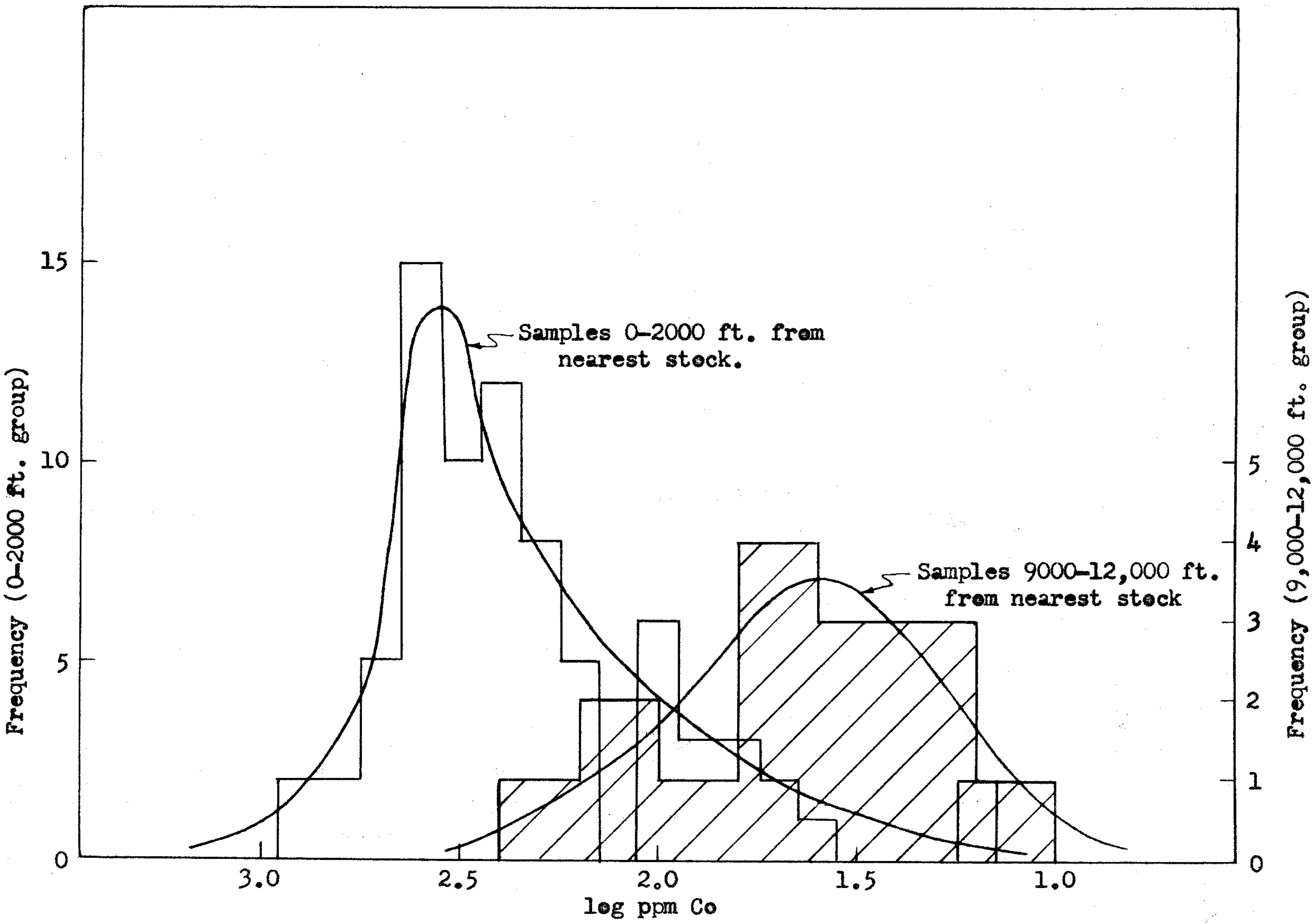


Figure 60. Histograms and frequency plots of cobalt content of sphalerite samples 0-2000 ft. from nearest stock, and 9,000-12,000 ft. from nearest stock, showing the difference in the average values. Central mining district, New Mexico.

Table 13

Mineralogy of low cobalt sphalerite specimens, Hanover mine

| Sample | Vugginess | Carbonate mineral | Est. % carbonate | Chalcopyrite blebs | Est. % galena |
|---|---|---|---|---|---|
| CEN-186 | yes | calcite | 30 | abundant | 5 |
| CEN-188 | yes | dolomite, calcite | 30 | abundant | trace |
| CEN-195 | no | calcite? | trace | moderate | none |
| CEN-204 | no | calcite | 5 | abundant | 5 |
| CEN-209 | yes | ankerite | 50 | abundant | trace |
| CEN-213A | no | calcite | 15 | rare | trace |
| CEN-216 | yes | ankerite | 30 | abundant | 5 |
| CEN-218 | yes | ankerite | 20 | abundant | 2 |
| CEN-227 | no | calcite | 20 | abundant | trace |
| CEN-531A | yes | calcite | 5 | abundant | 10 |
| CEN-533 | no | ankerite | 10 | abundant | none |

8 carbonate-bearing specimens contain less than 200 ppm. cobalt and are thus lower in cobalt content than the average for the mine. In the low cobalt specimens bearing calcite, the calcite is typically intergrown with the sphalerite in grain sizes of 1-2 mm. In four of the low-cobalt specimens the carbonate present is ankerite ($N_o$ about 1.70) and in one specimen dolomite was found. In two of the low-cobalt specimens as well as several specimens which were not analyzed, the ankerite occurs as light-colored fine-grained pseudomorphs of the hedenbergite prisms.

Another correlation is evident on inspection of the polished sections of the specimens. Figure 61 is a plot of the cobalt content versus the estimated abundance of chalcopyrite blebs in the sphalerite. In general, the samples of lower cobalt content tend to have more abundant chalcopyrite blebs. It might be concluded that this correlation results from disturbance of the internal standardization procedure by the added copper content. Comparisons of the intensity of the copper line used as an internal standard show no correlation of intensity with the abundance of chalcopyrite blebs, and in addition, calculation of the effect of even ten percent chalcopyrite in the sample shows that such an effect would be minor compared to the observed differences in concentration.

Other minerals which tend to be associated with the low cobalt group of sphalerites in comparison to the remaining sphalerites are pyrite in coarse cubes, galena, and euhedral quartz lining vugs. Two of the samples contain chlorite, which was not identified in any of the other samples.

The consistent presence of a carbonate mineral with the low cobalt samples suggested that the cobalt might have been deposited in the carbonate mineral rather than in the sphalerite, because cobalt-bearing calcites and cobalt carbonates (sphaerocobaltite) are known.

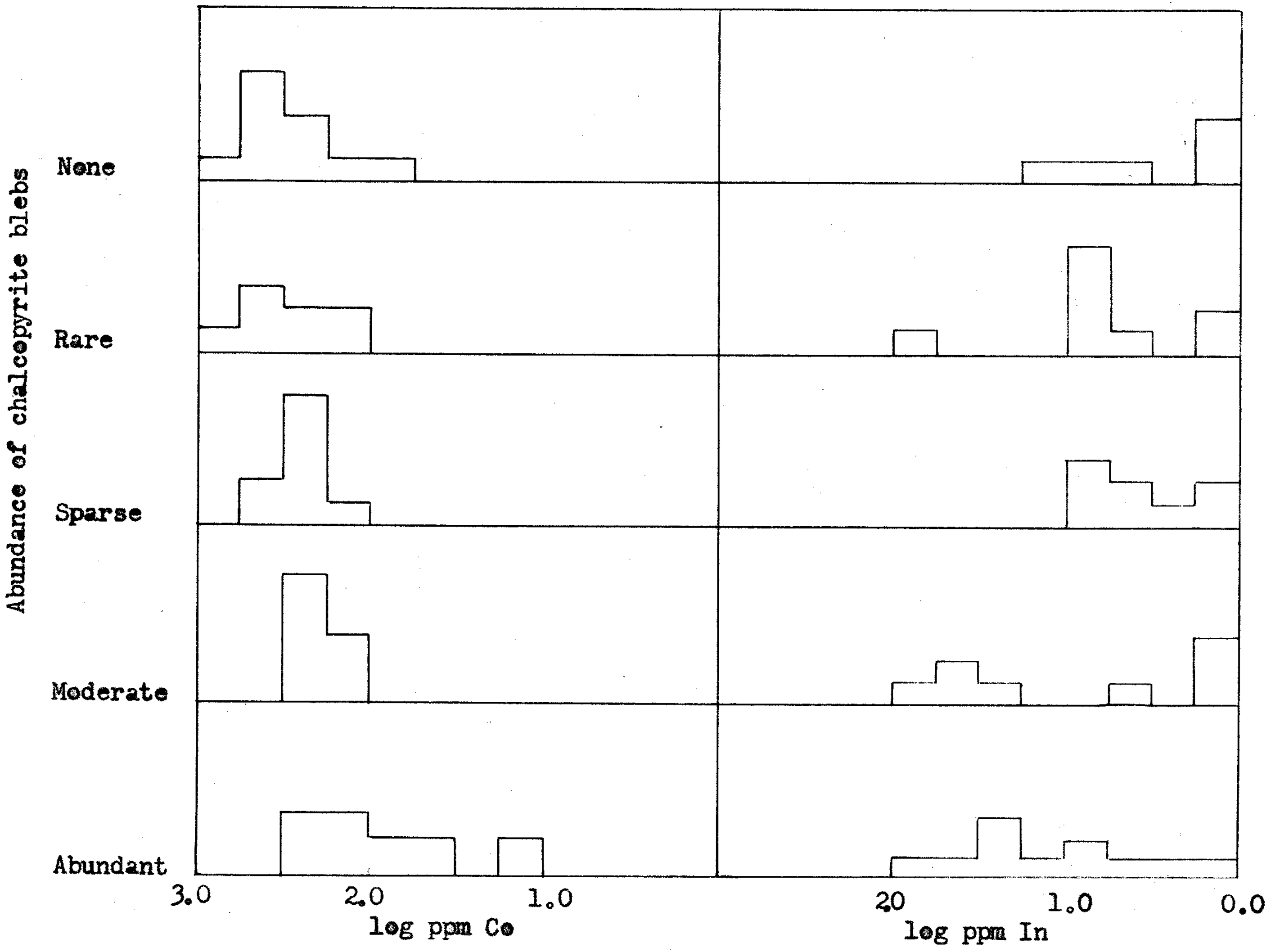


Figure 61. Histograms of Co & In content of sphalerite from the Hanover mine, Central mining district, New Mexico, for differing abundance of chalcopyrite blebs, showing an increase of cobalt and indium content with increasing abundance of chalcopyrite blebs.

Spectrographic analyses of calcite (table 17) from two of the specimens bearing low-cobalt sphalerite show about 3 ppm. cobalt, which is entirely inadequate to account for the lack of cobalt in the sphalerite. Similar conclusions can be reached for pyrite.

In the discussion of paragenesis at the Hanover mine it was concluded that at least some of the chalcopyrite was deposited later than sphalerite, and that galena generally replaced sphalerite. The association of the low cobalt sphalerite with these minerals suggests deposition late in the mineralization process. Schmitt (1939) reports that galena tends to occur as a "leady jacket" enveloping many of the sphalerite ore bodies in the mine. Miners and geologists at Hanover report that carbonate in the ore is more common on the limestone side of ore bodies than on the stock or dike side. Specimens CEN-188 and 533 were observed to occur near the contact of the ore with limestone. The mineralogical zoning away from the stock, coupled with the information on sequence of deposition, suggests that ore deposited late in the mineralization sequence was in general deposited at greater distances from the contact or the main fissures than the ore deposited early in the mineralization. Thus the available evidence indicates that the low-cobalt sphalerite probably was deposited later than the high-cobalt sphalerite.

The deposition of the low-cobalt sphalerite may represent an introduction of ore-forming constituents completely separate from the main zinc mineralization, or merely a late phase of the main mineralization. The writer favors the latter alternative because of the occurrence of exceptions to some of the characteristics discussed above, and because of the lack of observations suggesting deposition of any minerals in a break between two stages of sphalerite deposition. The single crystals analyzed by the writer and by Burnham show that there was not a steady decrease in the amount of cobalt deposited in successively later sphalerite, but they do show that appreciable changes of cobalt content with time did occur, and from the evidence presented above, it is believed that sphalerite of low cobalt content was generally deposited later than the sphalerite of relatively high cobalt content.

It might be concluded that the low-cobalt sphalerite and the associated minerals were deposited contemporaneously with the more abundant type of zinc ore, and that declining temperature or "intensity" of mineralization away from the source fissures determined the characteristics of the ore, as has been proposed by Sales and Meyer (1948) for Butte. However, this theory does not satisfactorily explain the position of altered hedenbergite and carbonate minerals near the outer margins of ore bodies with fresh hedenbergite closer to the "source." According to Sales and Meyer, this spatial distribution would indicate that the carbonate alteration formed under conditions of lower temperature or intensity of mineralization than the pyroxene, but the age relations indicate the reverse. Thus the simple process proposed for Butte does not seem to apply, although more complicated modifications of it might be fitted to the facts. In any case, consideration of the time variable seems necessary on the basis of the phenomena described.

The correlation of low cobalt content with vugginess, calcite, chalcopyrite blebs, and other features discussed above can be extended with few exceptions to the samples at the Pewabic, Oswaldo #1, Oswaldo #2, and Kearney mines. At the Groundhog mine, none of the correlations could be found; the relationship, if any, between chalcopyrite blebs and cobalt content is the reverse of that found at Hanover. It seems possible that the low cobalt content of the sphalerite from the southern and southwestern part of the district results from deposition mainly during the later stages of mineralization in the Hanover area, although other explanations, such as a temperature gradient, are possible for the district-wide zoning of cobalt content.

In the Cleveland mine area the cobalt content of sphalerite varies appreciably with no obvious correlation to geologic features. Smaller variations are found for the samples from the Pinos Altos area.

The range of indium concentrations in sphalerite from the Central mining district is even larger than the range for cobalt--from less than 3 to 1200 ppm. However, no definite district-wide variation can be discerned in the data (figure 62). Within the group of samples from the Hanover mine however, there does appear to be a relation between abundance of chalcopyrite blebs and indium content, as shown in figure 61. Sphalerite with high indium content is likely to have relatively abundant chalcopyrite blebs. It will be recalled that a similar relation to chalcopyrite blebs was noted for indium, silver, and bismuth in the discussion of variation within single polished sections. These three elements appear to increase with increasing abundance of chalcopyrite blebs, in contrast to the inverse relationship just discussed for cobalt. Some or all of the variations in silver and bismuth may be the result of galena or other impurities in the samples, but the concentrations of indium are too large to be accounted for by the presence of any known mineral, and the decrease in cobalt content with increasing abundance of chalcopyrite blebs and galena is not explainable by such a hypothesis.

Concentrations of manganese within the district also show an appreciable variation. A plot of manganese content against distance from the

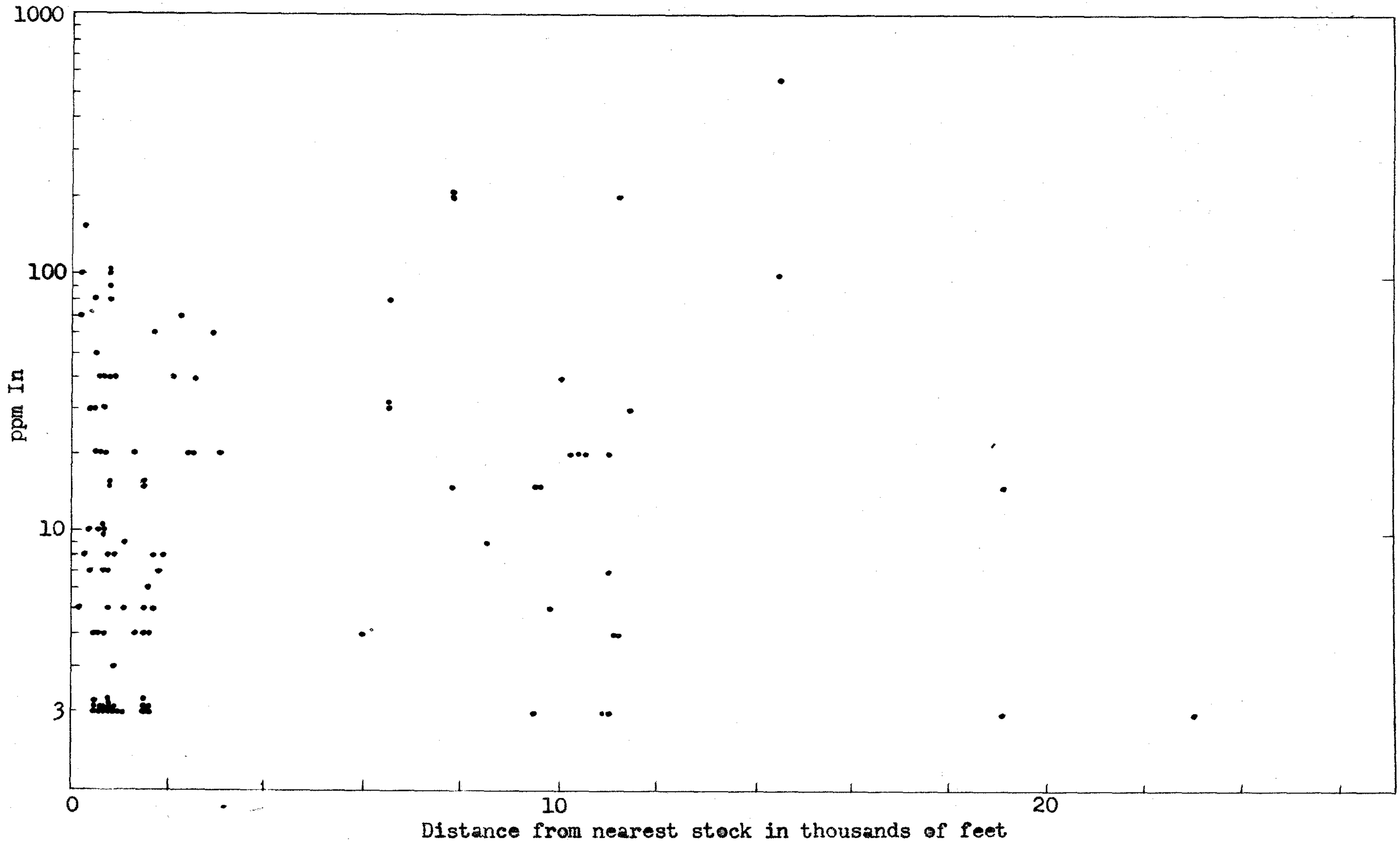


Figure 62 . Variation in indium content of sphalerite with varying distance from nearest stock. No definite trend is evident. Central mining district, New Mexico.

nearest stock is shown in figure 63. A relation similar to the one found for cobalt appears to exist, although again there is a large amount of variability within mines. A plot of manganese content of the sphalerites from the Hanover mine against abundance of chalcopyrite blebs did not show any definite correlation.

Figure 64 shows the relations of gallium content of sphalerite to distance from the nearest stock. Detectable concentrations of gallium are more frequent in the mines at greater distances from the stocks. A similar though still less definite relation appears to exist for tin and perhaps germanium but for these two elements the number of samples containing detectable amounts of the elements is even smaller than for gallium.

The concentrations of silver and bismuth vary widely even in small areas, but the general correlation of high concentrations of these two elements with the presence of lead suggests that they are usually present in inclusions of galena. The analyses of galena (table 17) indicate that galena from the Central mining district may contain large amounts of silver and bismuth. Silver and bismuth minerals, such as argentite and cosalite, may also occur. However, the consistent presence of at least 1-2 ppm. of these elements in the samples suggests that a small amount is probably present in uncontaminated sphalerite. Most of the samples containing appreciable lead are from polished sections in which galena was found. Concentrations of lead greater than 30 ppm. in uncontaminated sphalerite seem unlikely.

At Hanover, high indium and low cobalt content are more prevalent in sphalerite from the area south of the stock than from the area to the east and west. This may be the result of a biased sampling procedure, but it seems more likely that a real difference in the character of the minerali-

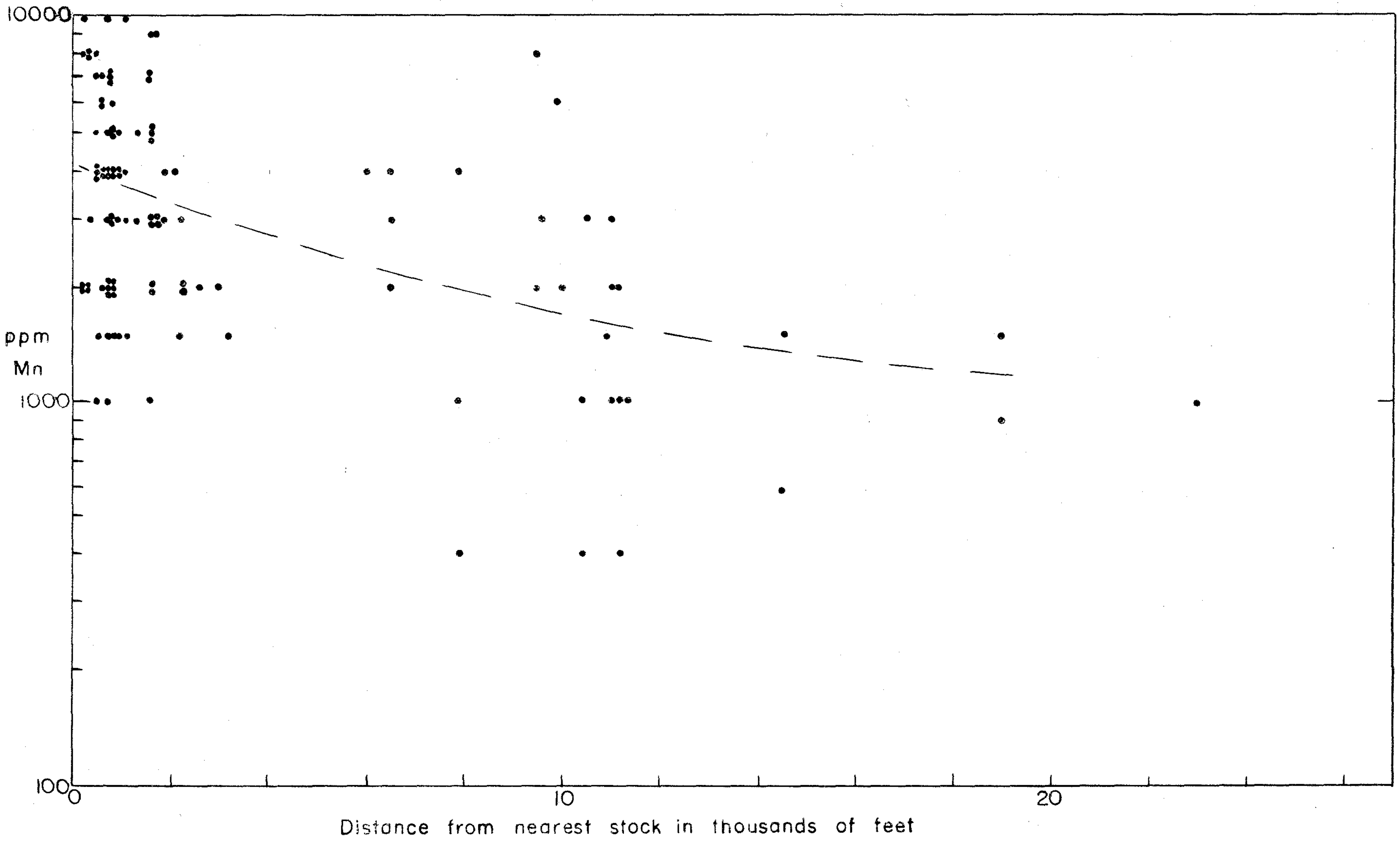


Figure 63. Zonal change in manganese content of sphalerite, Central mining district, N.M.

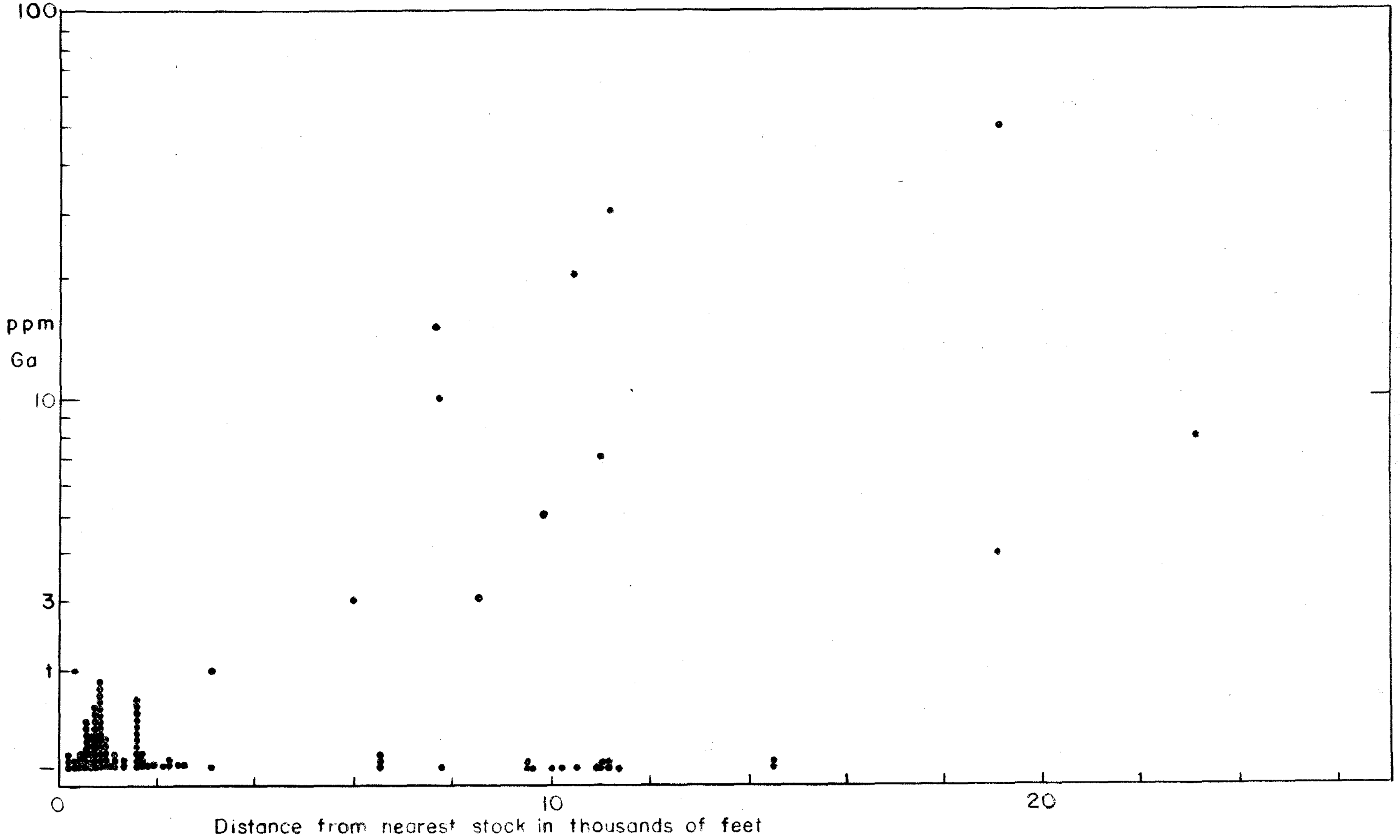


Figure 64. Zonal change in gallium content of sphalerite, Central Mining District, N.M.

zation exists, possibly because of slight differences in age of the ores in the two areas.

Nickel is found in most of the samples but difficulties in the quantitative evaluation of nickel in concentrations near the detection limit make the significance of any variations doubtful. Molybdenum is present in a number of samples but may occur as inclusions of molybdenite. In CEN-208, the initial analysis gave 2000 ppm. molybdenum, but an analysis of a new sample showed only 15 ppm. No molybdenite could be found in the polished section, but it is nevertheless presumed to be the cause of the anomaly.

Figure 65 is a plot of the iron content of sphalerite against distance from the nearest stock. A relation of the type already found for cobalt and manganese appears to be present, but is not as well developed as for those elements. As will be further discussed later, the writer believes that to a large degree the iron content of sphalerite is determined by the same factor determining trace element contents, namely the concentration (or more precisely, the chemical potential) of the component in the fluid from which the sphalerite was deposited.

A variety of other scatter diagrams have been plotted in an attempt to find correlations between two elements or between an element and a mineralogical or textural characteristic, without finding anything of recognizable significance. These plots included %FeS versus indium, manganese and cobalt, and indium versus cobalt and manganese. All of these plots might be expected to show some relationship because the variates showed similar trends when plotted against position or abundance of chalcopyrite blebs. That none of these plots shows any correlation probably results from the relatively poor correlations found in the original

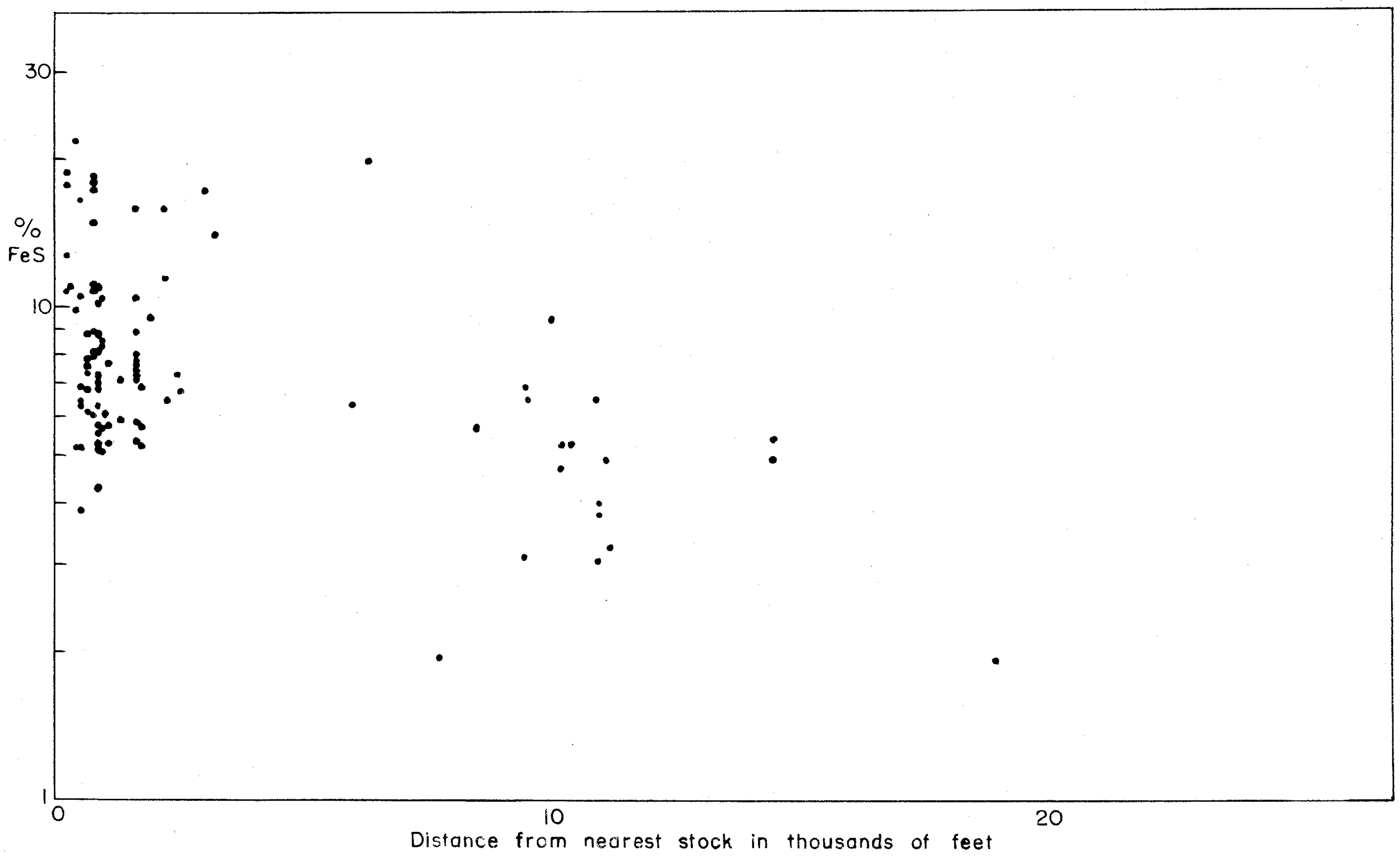


Figure 65. Zonal change in iron content of sphalerite, Central mining district, N. M.

plots, in addition to the characteristic of independent variations of different elements noted in the discussion of the single crystal analyses, and thus gives additional support to the conclusion that changes of a single variable, such as temperature, do not explain the variations.

Samples from the Cleveland mine and the Pinos Altos area appear to show somewhat smaller variations of indium content than the samples from the Central mining district. The more consistent presence of gallium in both groups and the consistently high concentrations of manganese at the Cleveland mine are also worthy of note.

In summary it can be said that the cadmium content is essentially constant within the ores of the district, but that sphalerite from the Copper Flats area, the Pinos Altos area, and probably the Barringer Fault area contains distinctly different amounts of cadmium. On the other hand, concentrations of cobalt, indium, manganese, and other elements vary greatly within the district and within a single mine. Cobalt, manganese, gallium, iron, and probably other elements show a lateral zoning away from the granodiorite stocks. Relationships found in the large suite of samples from the Hanover mine and in studies of single crystals and polished sections are interpreted to show that the concentrations of many trace elements vary with time of deposition of the sphalerite, and that factors in addition to temperature are involved in causing the variations.

## TRACE ELEMENTS IN CHALCOPYRITE FROM THE BINGHAM MINING DISTRICT

Analyses of chalcopyrite samples from Bingham are found in table 10 and the geographic distribution of the trace elements is shown in plates 16 to 20.

Burnham (1955) found that the tin content of chalcopyrite was generally relatively uniform throughout a district. Figure 66 is a histogram of the logarithm of the tin content of samples from the district. The histogram shows a sharply defined peak but has a long tail toward low concentrations. The tin content ranges from less than 3 to 900 ppm., but 80% of the values fall between 30 and 300 ppm. Thus, Burnham's conclusion is relatively well substantiated by the data from Bingham.

Consistent relationships of tin content to geologic, geographic or mineralogic factors are not well developed. No difference appears to exist between the tin content of the chalcopyrite in the peripheral copper-lead-zinc mineralization and chalcopyrite in the Utah Copper stock. There is, however, a suggestion that chalcopyrite replacing silicated limestones within the pit has lower than average tin content. All three samples of this type (BIN-504, 506, and 543) contain less than 100 ppm. tin. There is also a suggestion that disseminated chalcopyrite contains on the average slightly less tin than chalcopyrite in quartz veins, because seven out of eight samples consisting partly or wholly of disseminated chalcopyrite (BIN-507, 523R, 525, 527, 534, 537, 563, 568) contain less than 150 ppm. tin, and the eighth contains 200 ppm. Also both disseminated and vein chalcopyrite from BIN-523 were analyzed, and the sample of disseminated chalcopyrite has a much lower tin content.

On the basis of the above differences, it seems possible that the re-

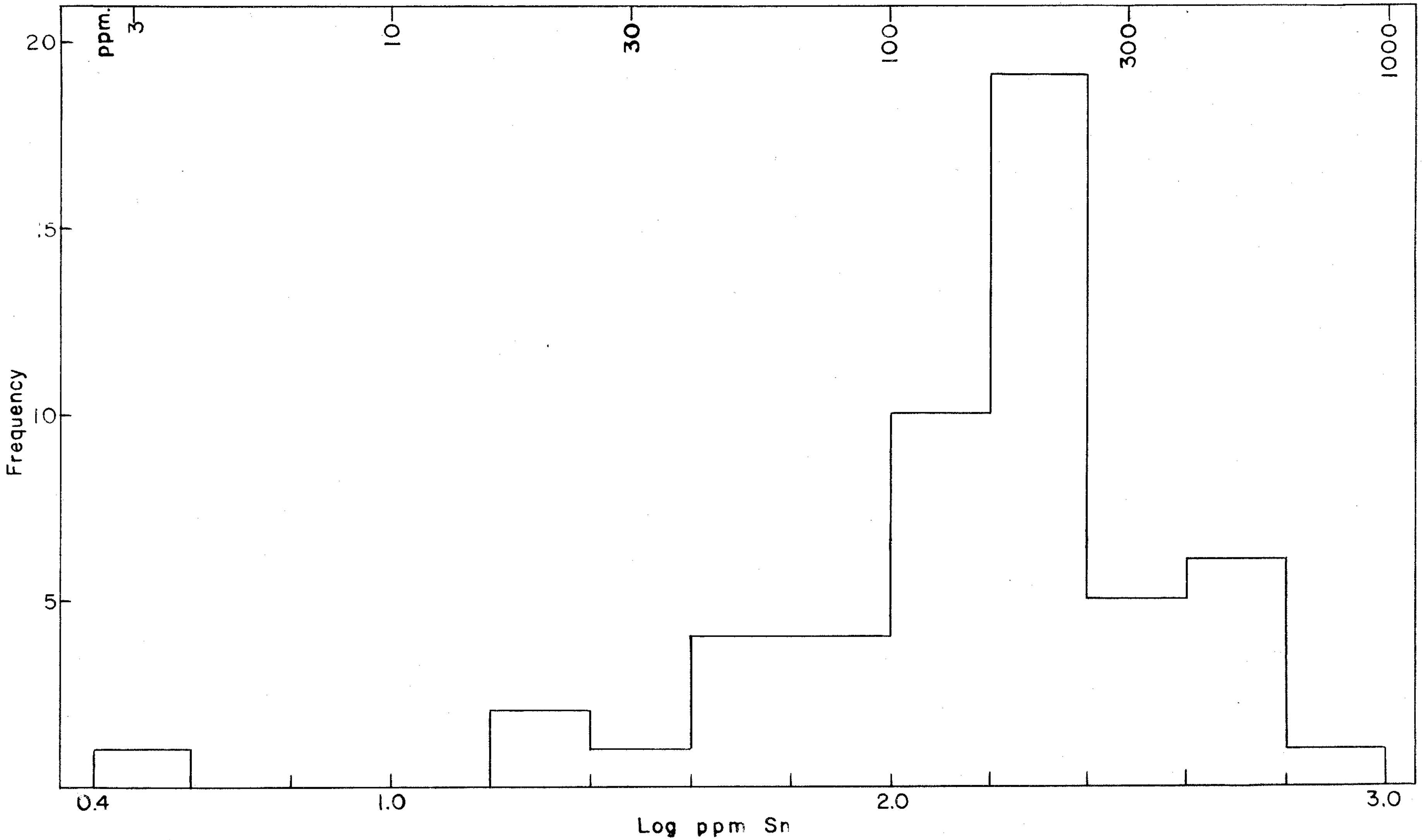


Figure 66. Tin content of chalcopyrite, Bingham district, Utah.

placement process which formed the disseminations and the limestone replacements resulted in chalcopyrite of lower tin content than the open space filling process which formed the veins. A possible explanation of the difference is that some tin which in the veins would enter chalcopyrite has instead entered biotite or other micas in the rock. Micas are known to contain significant amounts of tin in other localities (Ahrens and Liebenberg, 1950). In an attempt to test this hypothesis, two biotite-rich rocks from specimens containing low-tin chalcopyrite were analyzed spectrographically for tin. The tin content of both samples was less than the detection limit of 10-15 ppm. Thus either the hypothesis is incorrect or the large amount of biotite relative to chalcopyrite in the rock allows a large depletion of tin in chalcopyrite by adding only a few ppm. tin to the biotite. Estimates of mineral abundance indicate that the latter alternative may be the case.

In contrast to the tin content, the indium content of chalcopyrite from the Utah Copper stock is distinctly different from chalcopyrite of the peripheral copper-lead-zinc ores. Chalcopyrite from the mines south and west of the pit contains moderate to large amounts of indium but only a few specimens from the pit contain amounts greater than the detection limit. However, the variability in both groups is large. Although additional analyses would be desirable to establish the difference more conclusively, the available analyses seem representative enough to conclude that some difference does exist.

Bornite, chalcocite or digenite is present in eleven out of fifteen chalcopyrite samples from the pit containing detectable amounts of indium, whereas only four specimens contain bornite but no indium in the chalcopyrite.

The distribution of manganese is similar to that of indium. Except for the three samples from the Highland limestone in the U. S. mine, specimens from the underground mines south and southwest of the Utah Copper stock all contain large amounts of manganese, whereas samples from the stock itself all have very low manganese contents. In addition, all three of the chalcopyrite samples from silicated limestone in the pit contain 10 ppm. or more manganese, and one of the two remaining samples with ten or more ppm. manganese is from a quartzite. Thus high manganese concentrations are apparently characteristic of chalcopyrite from outside the Utah Copper stock. The similarity of the distribution of indium and manganese lends additional support to the distinction between the peripheral and central groups of ores.

The content of silver in chalcopyrite varies widely. All chalcopyrite from the peripheral deposits contains appreciable amounts of silver, but many specimens from the Utah Copper ore contain less than 1 ppm., suggesting similarities to the distribution of indium and manganese. However, the significance of this similarity is somewhat doubtful because the possibility of contamination from silver-bearing minerals in the peripheral ores cannot be denied.

Within the pit a correlation of high silver content with the presence of bornite, chalcocite or digenite in the specimens appears to exist. According to Hunt and Peacock (1948) the silver content of the ore is a few hundredths of an ounce per ton, which is equivalent to 30 to 200 ppm. silver in the chalcopyrite. The average of the analyzed samples falls near the lower end of this range. If most of the silver in the ore is present in chalcopyrite, which seems possible, some variability in the silver content of different lots of ore might be expected.

Bismuth concentrations are also erratic, but are similar to indium and silver in showing a correlation with the presence of bornite, chalcocite or digenite in the specimens. An analysis of a bornite concentrate (BIN-525B) shows relatively high concentrations of bismuth and silver, but not indium. Some of the bismuth and silver found in the chalcopyrite samples may thus occur in other copper sulfide minerals present as impurities, but the lack of impurities in many of the samples containing these elements makes it seem unlikely that they are the only source of the silver and bismuth. It is probable that the presence of bornite, chalcocite, or digenite is indicative of certain physical or chemical conditions which also result in the fixation of these elements by chalcopyrite.

Nickel concentrations also show considerable variability, but chalcopyrite from the peripheral deposits south and west of the Utah Copper stock consistently contains only traces of nickel in contrast to the large range of values in samples from the stock. In a few samples the nickel may occur in impurities such as pyrite, but this is not believed to be generally true.

The cobalt content of the specimens is in general low, and many of the higher values may result from the presence of cobalt-bearing pyrite in the samples.

Germanium in significant amounts was found in only one specimen, BIN-567. The chalcopyrite in this specimen occurs in botryoidal form coating the walls of a fissure. A polished section shows small amounts of bornite, chalcocite, and possibly other minerals intergrown with the chalcopyrite in thin layers. Marcasite is a prominent constituent of the specimen. The appearance and mineralogy suggest that the chalcopyrite is supergene. It is interesting that the concentrations of most other trace elements are also relatively high in this sample.

Molybdenum is present in almost every sample but probably occurs mainly as molybdenite. The concentration in the chalcopyrite lattice probably does not exceed a few tens of ppm.

Arsenic was detected in several samples. The presence of enargite in the Utah Copper deposit and enargite and tetrahedrite-tennantite in the peripheral deposits suggests that impurities are responsible. The small amounts of cadmium in several samples doubtless result from contamination by sphalerite.

In the case of lead, concentrations in the thousands of ppm. are almost certainly due to the presence of galena in the samples because galena was observed in most of them. However, at lower concentrations, the lead may be present in the chalcopyrite crystal lattice.

In summary, the most interesting features of the chalcopyrite samples from the district are: 1. The concentrations of manganese and indium are higher and nickel lower in chalcopyrite from the peripheral deposits on the south and west sides of the district than in the Utah Copper stock.
2. Within the stock, tin, silver, bismuth, indium, and possibly nickel tend to be higher in samples containing bornite, chalcocite or digenite.
3. The tin content appears to be somewhat lower in samples of disseminated chalcopyrite than in chalcopyrite from quartz veins.

## TRACE ELEMENTS IN SPHALERITE FROM THE BINGHAM MINING DISTRICT

Analyses of sphalerite samples from Bingham are found in table 11. Most of the sphalerite samples are from the U. S. section; a few are from the Lark section.

One of the more notable features of the data is the great variability in concentration of most of the elements. Many elements range in concentration over a factor of a hundred or more. Cadmium exhibits the smallest variability (on a logarithmic scale), followed by manganese. Tin and indium show very large ranges of concentration in the samples.

Despite the great amount of variability in the Bingham samples, there are several consistent differences from the Central mining district samples. Gallium and tin are present in moderate amounts in almost every sample from the Bingham district but were found only rarely in samples from the Central mining district. On the other hand, cobalt was found in almost every sample from the Central mining district in concentrations averaging hundreds of ppm., whereas in the samples from the Bingham district it is barely detectable. Distinct differences in the average cadmium content also exist. These kinds of differences were concluded by Burnham (1955) to be generally true of mining districts, and the large number of samples utilized in this study is believed to confirm Burnham's conclusion.

Figure 67 shows the gallium content of sphalerite from the Bingham district. The samples have been classified according to the structural unit from which the sample was collected. A gallium content of 20 - 30 ppm. separates the samples into two groups. Samples from the Galena fissure, the Holden fissure, the East fissures, and the Lark and the

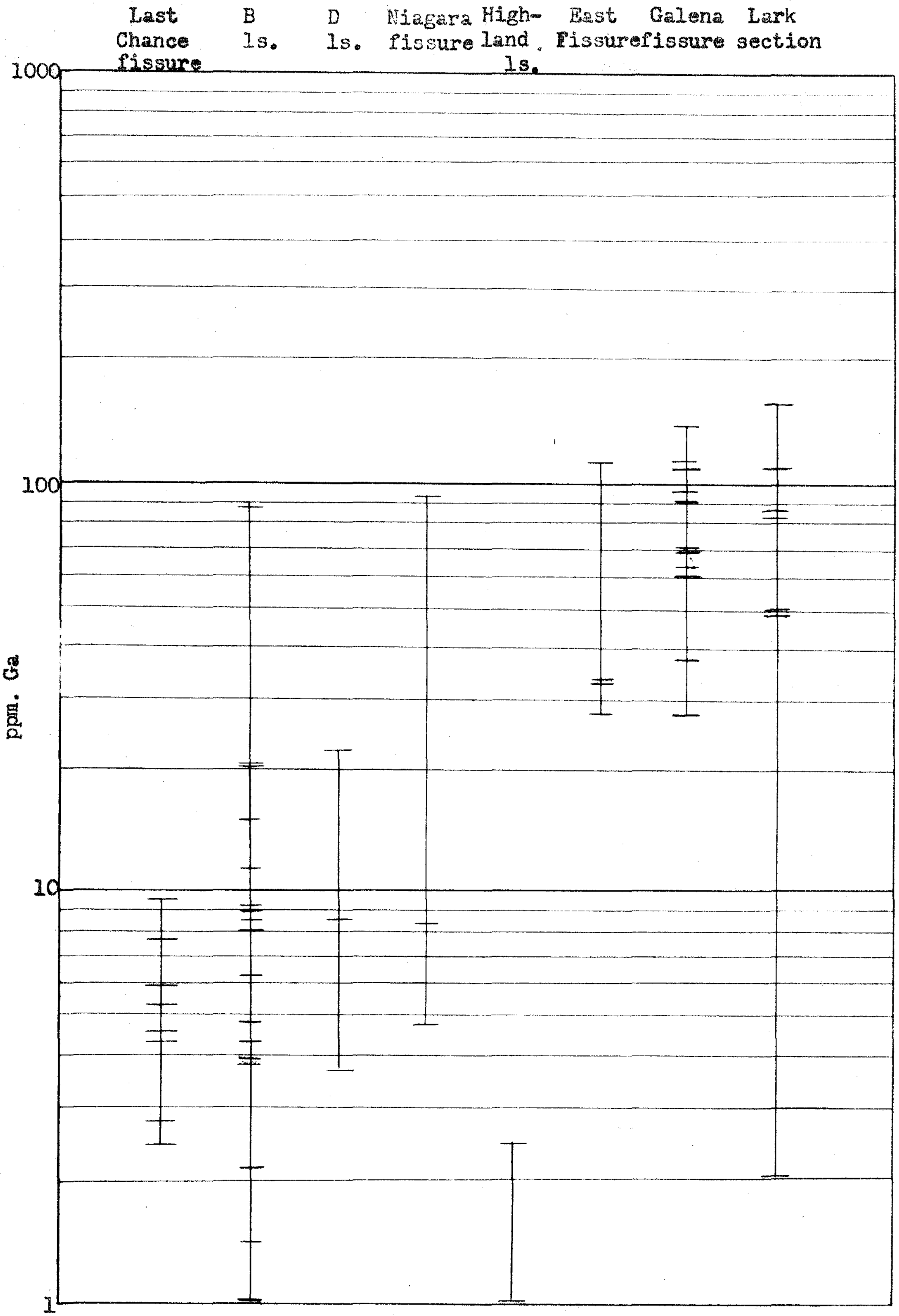


Figure 67. Gallium content of sphalerite from the Bingham mining district, Utah, classified according to structural unit.

Commercial limestones form a group with high gallium content. Samples from the B limestone, the D limestone, the Last Chance fissure, and the Niagara fissure form a group with low gallium content. A few exceptions to the grouping exist, but several of the exceptions show other anomalous features.

The significance of the groups is emphasized by a similar grouping in the FeS content of the sphalerites (figure 68). The samples again fall into two groups with almost the same members in each group. The samples from the Galena fissure, the Holden fissure, the Highland limestone, the Lark vein, and the Commercial limestone make up the low group, and samples from the B limestone, the D limestone, the Last Chance fissure, the Niagara fissure and the East fissures make up the high group. The East fissures samples represent the only definite change in the twofold grouping. The two Highland limestone samples were not placed in the gallium grouping.

The distribution of germanium appears to show a grouping similar to gallium with higher germanium concentrations in the high-gallium, low-iron group, but because most germanium concentrations fall below the limits of detection the grouping is not as clear.

Figure 69 is a plot of gallium content against iron content showing the two groups. A feature of some interest in this plot is the fact that within the high-iron low-gallium group, especially in those samples from the B limestone, there appears to be a correlation of gallium with iron. The significance of this relation is not clear. Apparently within this group there is a close relation between gallium content and iron content, but the effect is the reverse of the gallium-iron relations which define the two groups.

Consideration of the tin content brings out no grouping of the

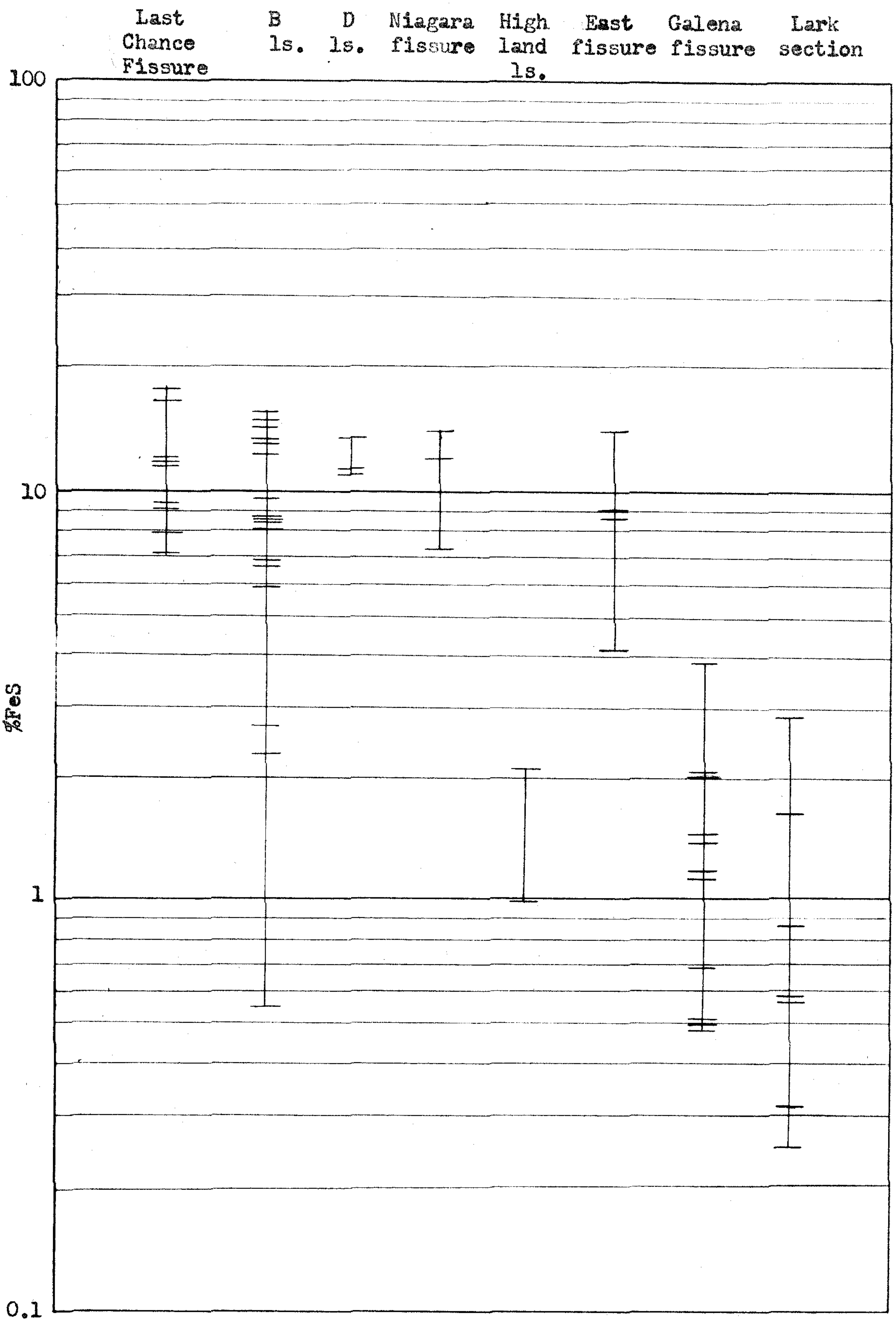


Figure 68. Iron content of sphalerite from the Bingham mining district, Utah, classified according to structural unit.

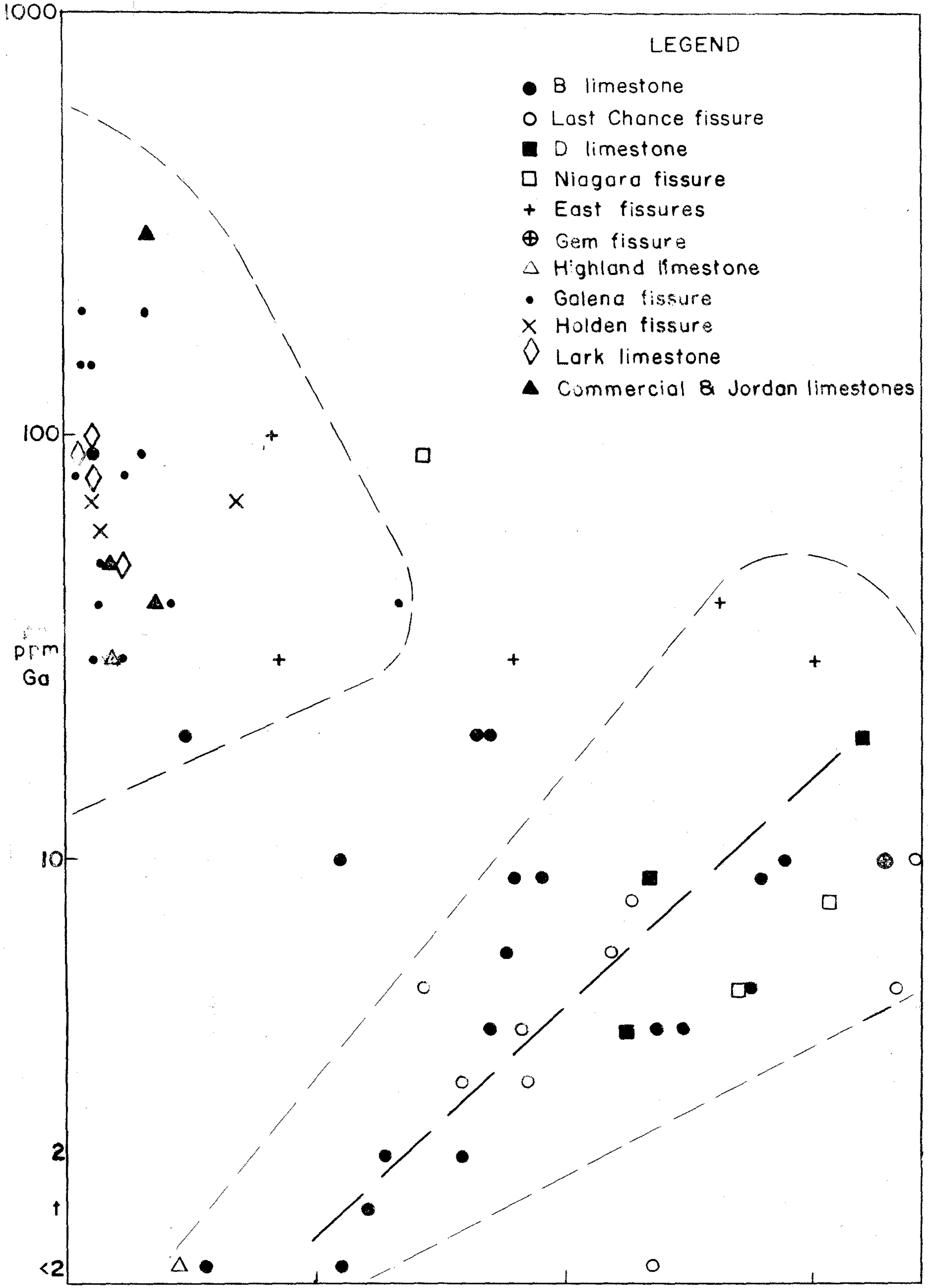


Figure 69. Plot of gallium vs. iron content of sphalerite from Bingham, Utah, showing the two groups of samples.

samples according to structure. However, in figure 70, a plot of tin content against FeS content, the two groups (as defined by iron content) again appear, along with an additional feature. In the high-iron group, tin content tends to decrease with increasing iron content. In contrast, most of the samples from the Galena fissure fall close to a line along which tin content increases as iron increases. A number of samples from other structures fall close to the same line. Although several samples fall well off the line, the relationship appears too good to occur by chance. Thus not only are two groups of samples defined by the gallium, tin, and iron concentrations, but within the groups the relations of tin and iron to gallium are opposite in character.

In addition to the grouping and relations between elements discussed above, tin, iron, and gallium appear to show vertical or lateral zoning or both within the U. S. section. Figure 71 shows the tin content of sphalerite from the B limestone plotted against elevation in the mine. There is a good deal of dispersion in the relationship, but there is a statistical trend toward lower tin content at lower levels in the mine. A rank correlation test (Kendall, 1955, pp. 8 - 60) gives a Spearman rank correlation coefficient of 0.70. The critical value for the 2% level of significance is 0.58. Therefore, the null hypothesis of independence of the two variables can be rejected (i.e., the probability that the observed correlation is due to chance is less than 2%). Here again, additional samples would add to the certainty of the correlation, but the writer knows of no likely reason for the present suite of samples to be biased. However, although there is a definite statistical correlation of the tin content and level in the mine, the samples do not fall very close to a straight

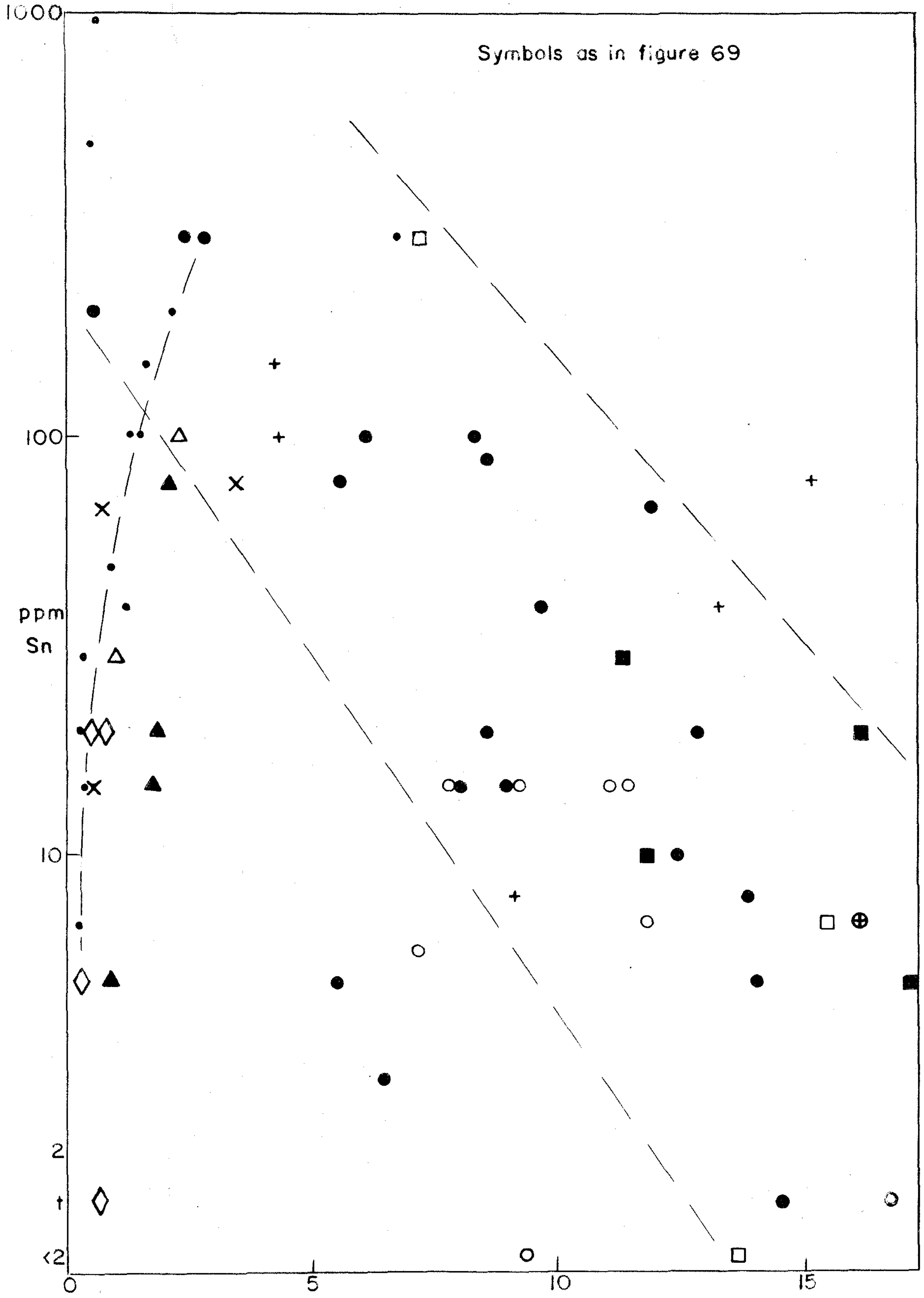


Figure 70. Plot of tin vs. iron content of sphalerite from Bingham Utah, showing the correlations within the high-iron and Galena fissure groups.

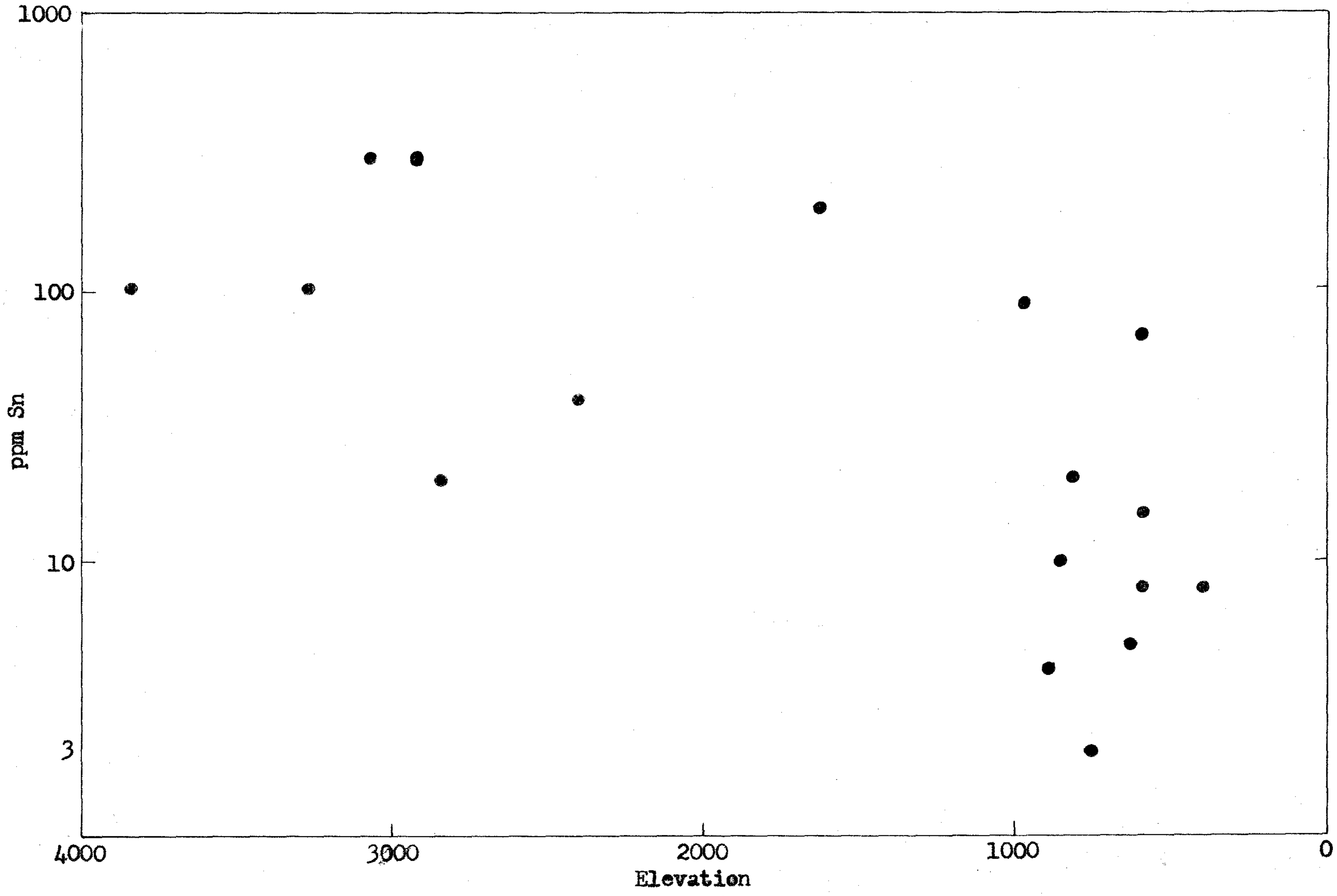


Figure 71. Plot of tin content of sphalerite from the B limestone, U.S. mine, Bingham district, Utah, against elevation in mine,(relative to arbitrary datum) showing a decrease in tin content at depth.

line and certainly the relation of tin content with depth only partly explains the variations of tin content in the samples.

Figure 72 is a plot of iron content of sphalerite from the B limestone against depth. A decrease of iron content at higher levels in the mine is suggested, but again the relation shows a great deal of scatter.

Because the B limestone dips to the north toward the Utah Copper stock, it might be argued that a lateral rather than a vertical zoning is represented. However, because the dip of the B limestone is nearly vertical in the deeper levels, the maximum separation of the samples in a direction perpendicular to the strike of the beds is about 1500 feet, and for 15 of the 17 samples it is about half of this amount. The range in depth is over 3000 feet, and it therefore seems reasonable to regard the changes in tin content as primarily a function of depth, and only secondarily a function of horizontal position. No consistent changes along the strike can be detected.

Attempts to correlate indium content with position or with other elements have led to no significant relationships. In the case of gallium, however, the pattern of the values suggests a lateral change (figure 73). Samples from nearest the Utah Copper stock generally contain gallium concentrations of 10 ppm. or less, whereas the more distant samples in the Galena and East fissures contain larger amounts. No regular changes of gallium content with depth in the B limestone or other structures can be found, and it therefore seems proper to regard the variation in gallium content as a lateral rather than a vertical change. The interpretation of this change as zoning depends on the significance of the two-fold grouping discussed previously.

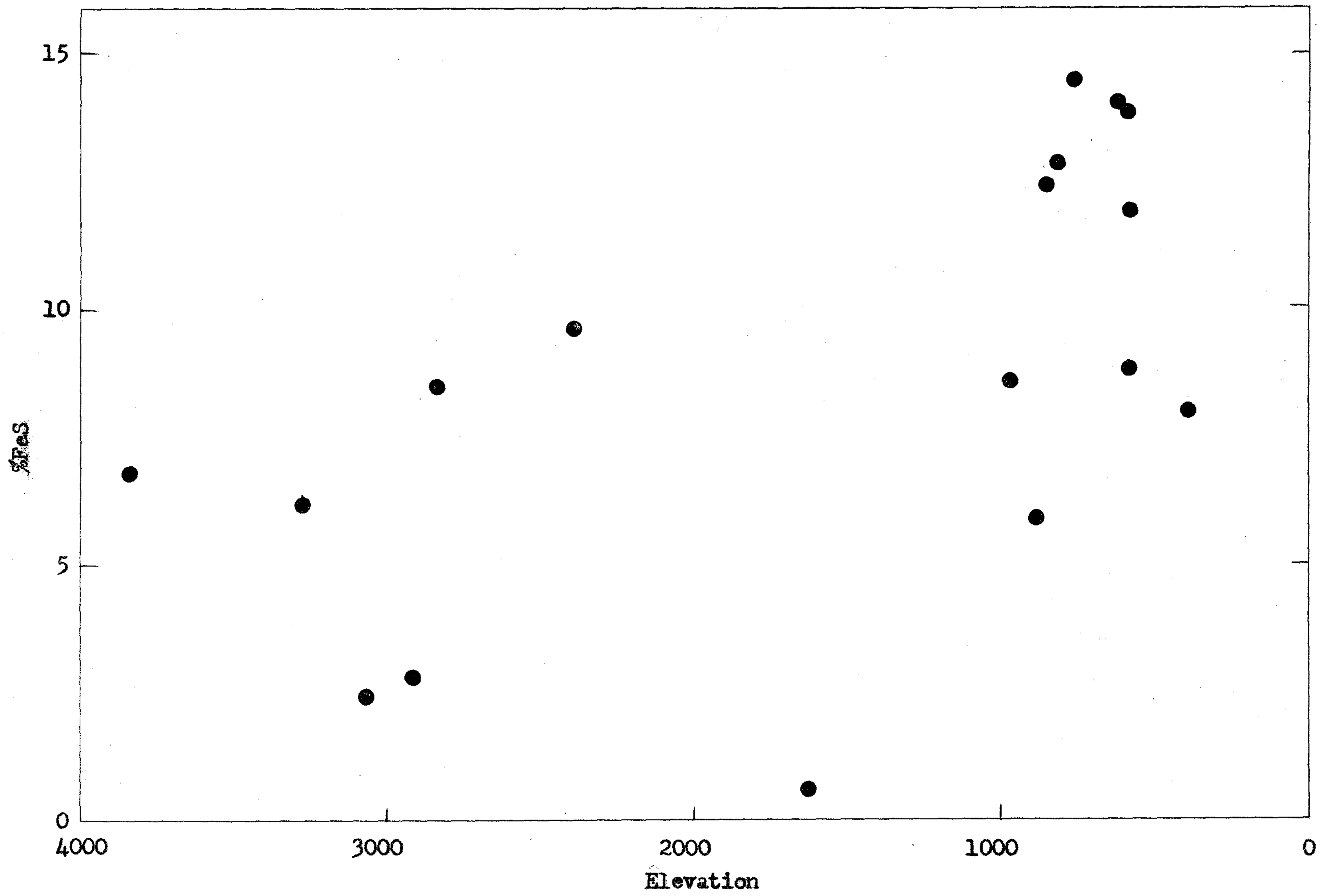


Figure 72. Plot of FeS content of sphalerite from the B limestone, U.S. mine, Bingham mining district, Utah, against elevation in the mine (relative to arbitrary datum), showing an increase in FeS content at depth.

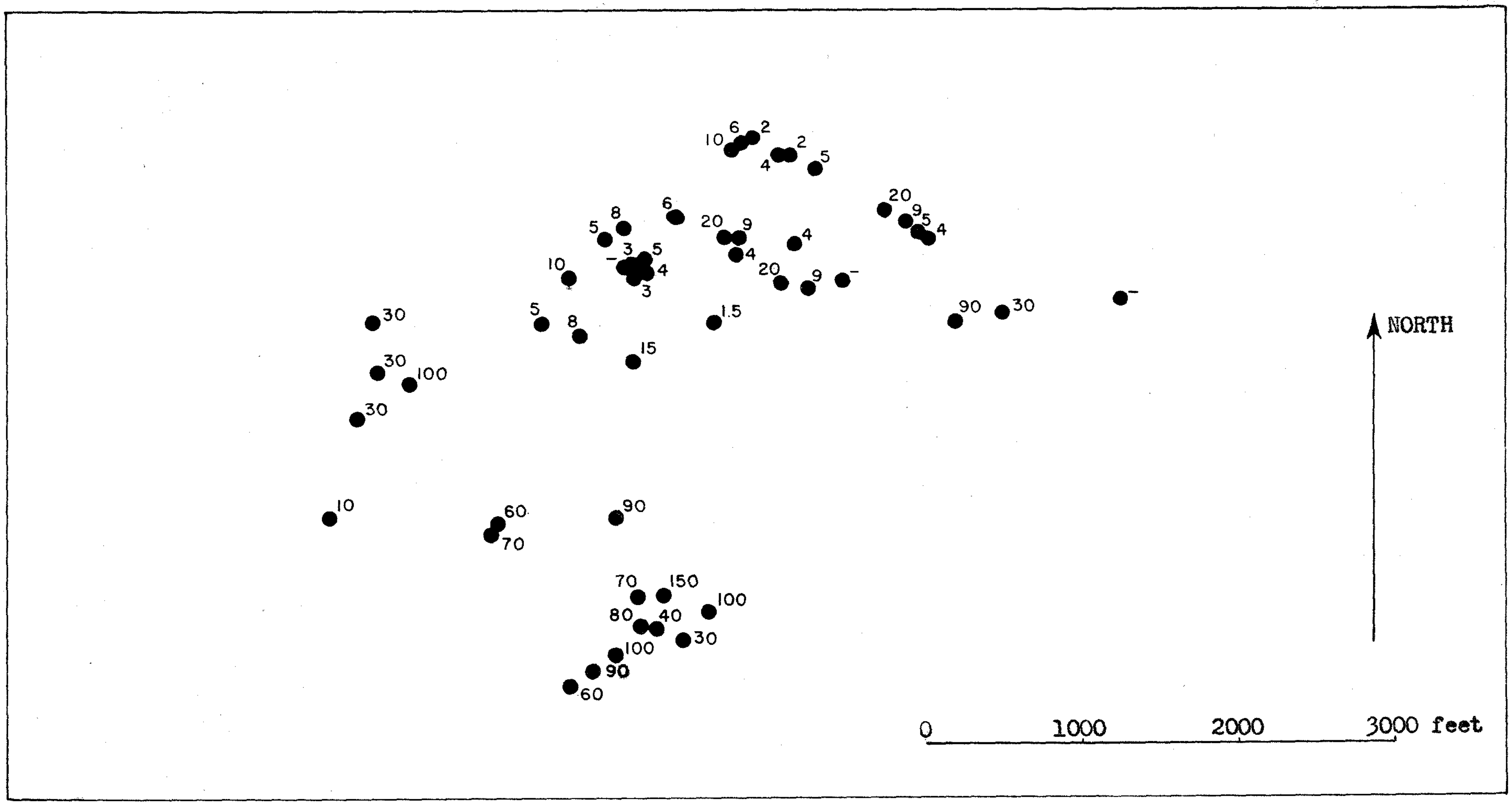


Figure 73. Map showing the change in gallium content of sphalerite away from the Utah Copper stock (located near the north edge of the map). Concentrations in ppm. U.S. section, Bingham mining district, Utah.

Fryklund and Fletcher (1956) found a correlation between manganese content and iron content of sphalerite from the Star mine in the Coeur d'Alene district. No such correlation exists for the samples from the Bingham district. In fact, the highest manganese concentrations occur in sphalerite of very low iron content.

Contamination by other minerals is doubtless the most important factor in determining the concentrations of lead, antimony, arsenic, and possibly silver. For lead (and possibly silver) the consistent presence of about 100 ppm. suggests that some lead may be present in the sphalerite crystal lattice or that galena occurs in extremely small inclusions in all of the sphalerite analyzed.

The specimens from the Lark mine are too few to draw any conclusions. The analyzed samples do appear to be similar in appearance to the much larger collection from the mine, obtained mainly from the Lark vein. The color of the sphalerite in all the specimens is relatively light, suggesting that they belong to the group low in iron, and by inference relatively high in gallium. This inference is in agreement with the few analyzed samples.

## THE OCCURRENCE OF TRACE ELEMENTS IN SULFIDES

Before discussing the data further, it seems worthwhile to examine the mode of occurrence of trace elements in sulfide minerals. The mode of occurrence of trace elements in minerals has been classified by Haberlandt (1952) in the following manner:

1. Substitution of the element for major constituents of the crystal or for vacancies in the crystal lattice.
2. Occurrence in flaws in the crystal lattice.
3. Incorporation by adsorptive processes during growth.
4. Occurrence as trace minerals.

In considering the substitution of trace elements in crystal lattices of sulfide minerals it is important to realize that the bonding in these minerals is covalent to an important degree. Moreover, metallic and ionic bonding are also important in some sulfides. Thus the substitution of one element for another in a sulfide crystal may involve the formation of directed bonds or bond orbitals, the filling of Brillouin zones, and other considerations, in addition to the effects of size and charge which are so important in the formation of ionic crystals.

The simplest type of incorporation of a minor element in a crystal lattice is the direct substitution of the element for a major constituent of the structure. Simple substitution is probably the most common mode of occurrence of the trace elements discussed in this study. Almost certainly it is the mode of occurrence of Cd and Mn in sphalerite, and of Ni and Co in pyrite, pyrrhotite, and chalcopyrite. In such cases a partial or complete solid solution between the simple end members would be shown by a phase diagram. The phase diagram in its simplest form would be similar to that worked out by Kullerud (1953) for the FeS-ZnS system, although the limits of solid solution might be much smaller. If solid solution was not complete, the amount of solid solution would in general be expected to increase with increasing temperature. Relatively sharp breaks in the composition of the saturated solid solution might occur at temperatures of polymorphic transitions, or ordering phenomena. The latter might be important in the case of chalcopyrite, which is known to be disordered with respect to copper and iron at high temperatures, and ordered at low temperatures. Supersaturated solid solutions of this type are also possible (Kroger, 1940).

In ionic crystals the coupled substitution of two elements is necessary if the major constituent being replaced has a different charge from the element being added. Although balance of charge in crystals with covalent or metallic bonding may be more complicated, coupled solid solution probably also occurs in sulfide minerals. The presence of Bi in galena has been explained as partial solid solution between galena and matildite ($AgBiS_2$).

Another pertinent feature of some sulfides is the omission of some atoms from positions in the structure to form defect structures. Pyrrhotite, which has some vacant Fe positions in the lattice, is the best known example. Chalcopyrite is also known to be non-stochiometric (Geophysical Lab Annual Report, 1956). Buerger (1934) has proposed that marcasite and wurtzite are defect structures. It seems probable that other sulfide minerals have defect structures to an extent that is important in the incorporation of trace elements in the lattices. The presence of trivalent indium and gallium in sphalerite, or silver and bismuth in galena might be explained in this way without postulating a coupled substitution. No definite evidence for such effects is known other than the lack of consistent relations between two elements which would be required for coupled substitution, but the significance of defect structures does seem to have been ignored in the past as a possible explanation of certain substitutions in sulfide minerals.

Another type of solid solution which may be important for some trace elements is interstitial solid solution, as suggested by Goldschmidt (1954) and Burnham (1955). The minor element in this state occurs in the interstices between the normal lattice positions.

The behavior of trace elements residing in flaws in the crystal structure rather than substituting for major constituents might be expected to differ appreciably from the categories previously discussed. The common occurrence of mosaic structure, dislocations, and the like suggests that significant amounts of an element might be expected to occur in such sites. An element might come to occupy a position in such a flaw by capture during the growth of the crystal, by later addition to the crystal, or by some more complicated process.

Occurrences of elements as trace minerals can be divided into several categories. The trace mineral may have formed as a result of exsolution, in which case it originally existed in one of the categories discussed above. The trace mineral might also occur as inclusionsof material older than the host mineral, the same age, or younger. In the last case the inclusion might originate by replacement of the host, or by filling an open space in the host. Occurrences as a trace mineral would grade downward in size to the condition of the trace element present in flaws in the structure. Occurrences of microscopically visible inclusions would be noted in the polished section procedure used in this study, but if the inclusions were submicroscopic the mode of occurrence of the trace elements would be difficult to distinguish from occurrence in the lattice or other sites discussed above. Inclusions of minerals other than the common sulfides were rarely observed in the present study; hence it seems unlikely that an element like gallium or indium occurs as microscopically visible impurities.

Adsorption is a process which may result in the incorporation of trace elements in a crystal growing from a fluid phase. Aspects of this process have been discussed by Haberlandt (1952) and Devore (1955). Crystal surfaces have properties not shared with the interior of the crystal, and these properties may result in the attraction and adherence of atoms or ions which may not normally fit into the solid crystal lattice. Highly charged or highly polarizing atoms might especially fall into this category. If growth of the crystal was relatively rapid, these adsorbed units might be covered over and remain in the crystal. Adsorption might be an important factor leading to the presence of trace elements in greater than equilibrium amounts residing in lattice positions, otherwise vacant positions in defect structures, or flaws.

## CAUSES FOR VARIATION OF TRACE ELEMENT CONTENT IN HYDROTHERMAL MINERALS

In the preceding pages the causes for a few of the variations in trace element content have been discussed, but the majority of the variations have been left unexplained. This section will discuss the possible causes of variation from a more theoretical viewpoint and attempt to reach some conclusions regarding the causes of the variations discussed in the preceding sections.

Let us first of all discuss a few aspects of the process by which the ores in question have formed. Many, perhaps most aspects of the hydrothermal process, especially the chemical features, are poorly understood, and present concepts may well turn out to be incorrect. However, on one important aspect of the process a definite statement does seem possible. The formation of replacement ore bodies like those near Hanover, New Mexico, or the peripheral copper-lead-zinc ores at Bingham must be regarded as taking place in an open system. In any epigenetic ore deposit, material (the heavy metals and other constituents) has moved into the area of the ore body from some other area. But more significantly, in replacement deposits it is also necessary that much of the replaced material leave the site of ore deposition. For instance, from a study of the geology and chemistry of the Pewabic mine, Schmitt (1939) concluded that large tonnages of iron, silica, zinc, and sulfur had been added to the block of ground containing the ore, and that approximately equal tonnages of calcium and carbon dioxide had left the block. In addition, the preservation in the ore of structural and textural features of the host rock (see for example Hunt 1924, p. 872) indicates that the processes of addition and removal of material took place at the same time. In deposits filling open spaces, such as veins, the strong leaching of bases from igneous rock bordering veins also indicates removal of material, but here the time relations are not so clear. In any case, the process of forming a hydrothermal ore deposit cannot be understood on the basis of processes taking place in a closed system, as can the crystallization of a magma, but must be regarded as a process of simultaneous addition and removal of material. During the period of ore deposition, then, the writer believes that material is continuously entering and leaving the area of the ore body.

It also seems clear that changes take place with time in the composition of the material (the ore fluid) entering the system. The system in this case can be thought of as the volume occupied by an ore body or a mine. For instance, at Hanover, the minerals were shown to have been deposited in a sequence with garnet and magnetite early and sulfides late, with a sequence also existing within the sulfides. The textures and zonal relations as discussed in the section on geology and on sphalerite from the Central mining district leave no doubt in the writer's mind that the age relations mainly resulted from changes in the composition of the hydrothermal fluid with time. The sequence of minerals suggests falling temperatures with time, and does not seem consistent with the interpretation proposed for Butte by Sales and Meyer (1948). If concentrations of the major constituents of the hydrothermal fluid change with time, undoubtedly the minor constituents show similar changes. In addition, the lack of correlation between various trace elements in sphalerite at Hanover indicates that factors other than temperature have caused variations in trace element content of sulfides. Variations in the trace element content of the hydrothermal fluid seem a very likely explanation. Thus in explaining the trace element content of hydrothermal minerals, attention must be given to the possibility of changes in the composition of the hydrothermal fluid in addition to differences in temperature, pressure, and wall rock composition at the site of deposition. This point of view has not been taken in most previous studies of trace elements in sulfides.

Before considering in more detail the effects of various factors on the concentration of trace elements in hydrothermal minerals it is worth while considering the possible sources of the trace elements. We will assume that the hydrothermal fluid originates from a source at some depth--a magma, region of granitization or some other site of "mobilization" of elements. The bulk of the heavy metal content in the fluid presumably is derived from this source, and it is logical to assume that much of the chalcophile trace element content is derived from the same deep source. As the fluid moves upward, a second possible source of trace elements is encountered in the form of the wall rocks. Significant quantities of the trace elements in question might conceivably be derived from the wall rocks by leaching and other alteration processes. This leaching might occur within the present zone of mining, or well below it, nearer the source. During the stage in which this process is in operation, the major constituents of the hydrothermal minerals are still in the fluid phase, and have not yet begun to form crystals.

After the hydrothermal fluid reaches the site of deposition two additional processes may provide trace elements for a particular mineral. The mineral may acquire some constituents from wallrock minerals or earlier hydrothermal minerals by partially or completely replacing them, or trace elements may be acquired from the other minerals by diffusion and other equilibration processes between stable solid phases during or after crystallization of the host mineral. Another possibility is the incorporation of trace elements from hydrothermal fluids passing through the area after growth of the host mineral has ceased.

For all the above processes only two real sources of the trace elements exist; the deep-seated source of the heavy metals represented by the ore; and the rock minerals at the site of deposition and along the pathway from the deep-seated source to the site of deposition. However, several possible variations of the process of adding these trace elements to the host mineral have been mentioned above.

From the relatively common occurrence of zoned and inhomogeneous sphalerite specimens, such as the single crystal analyzed from Hanover, it seems probable that the present composition of a sphalerite sample depends largely on the composition of the material originally deposited from the fluids. Redistribution by diffusion through the solid crystal, at least at low and moderate hydrothermal temperatures, has usually been of secondary importance. For chalcopyrite and other minerals the evidence is less clear, but probably the same conclusion applies. To the extent that this is true, the measured trace element concentrations represent the concentration at the time of deposition rather than at the time of some later equilibration process under differing conditions.

Let us next consider the effect of various factors on the trace element content of a growing crystal. If the process of growth proceeds slowly enough and the trace element is forming a solid solution, the concentration of the trace element in the surface layer of the crystal will be equivalent to that produced by an equilibrium between the crystal and the fluid. The independent variables of the system will be the temperature, pressure, and composition.

The quantity of the trace element present in the fluid is clearly one of the more important factors in determining the amount of the element present in the crystal. Because the hydrothermal environment is an open system, the composition of the system is most conveniently expressed in terms of concentration or some other intensive variable, such as chemical potential. If none of the element is present in the fluid, there will be none in the crystal (unless the hydrothermal mineral is replacing a mineral containing the element). If other factors remain constant, increasing concentrations of the trace element in the fluid will result in increased concentrations of the element in the crystal, up to the limit of solid solution. However, complex formation and other interactions between constituents may reduce the effective concentration of a trace element well below its total concentration in the fluid. Or, in the case of elements having several possible valences, such as copper, tin, and bismuth, the oxidation potential of the system may be important. Thus the concentration variable is better expressed in terms of activity or chemical potential than in terms of the total concentration of the element. The most obvious cause of changes in concentration of the fluid would be changes originating in the deep-seated source, but changes in the effectiveness of leaching trace elements from the wallrocks or in the complexing properties of the fluid might also be significant.

Previous workers have emphasized temperature as a control on the trace element content of sulfides. However, without specific experimental data little can be said except that an effect of some sort would be expected from temperature variations. In general, an increase in temperature increases the possible amount of solid solution of a trace element in the crystal, so that if the concentration of a trace element in the crystal is the saturation value, then a change to a higher temperature will allow an additional amount of the element to enter the crystal, and a decrease in temperature will decrease the amount of the element present in the mineral (at equilibrium). However, if the mineral is saturated, further addition of the element to the system will also result in the formation of a new phase containing the element. Phases containing significant amounts of the trace elements considered in this work are relatively rare, and it therefore seems probable that saturation values are rarely reached for the elements in question. Silver, arsenic, antimony and bismuth are possible exceptions.

The direction of the effect produced by changing the temperature of a system containing a fluid in equilibrium with a solid unsaturated in the trace element cannot be predicted, but in general there will be a change in the equilibrium concentrations. For instance, work by Eugster (1955) on the distribution of cesium between vapor and sanidine showed the distribution coefficient $F = \frac{\mathrm{Cs/K(sanidine)}}{\mathrm{Cs/K(vapor)}}$ changed from 0.48 at 500° C. to 1.20 at 800° C. The Cs/K ratio in the sanidine ranged from 0.002 to 0.01. Cesium enters the sanidine lattice more readily at high temperatures. On the other hand, studies by Gordon and Rowley (1957) and Salutsky, Stites and Martin (1953) show that radium enters the lattice of barium sulfate and barium chromate as compared to water, more readily at low temperatures. Changes in the distribution coefficient with temperature might be the result of formation or breakdown of complexes in the fluid phase as well as changes in the chemical potential of the trace element in the crystal with temperature. However, the experiments referred to above show that an equilibrium concentration of the trace element can be attained even in the part per million range of concentration, and that the distribution coefficient between the solid and fluid phase is, in general, a function of temperature.

Pressure changes should have an insignificant effect on the equilibrium distribution coefficient between the solid and fluid phases. Eugster (1955) reports no detectable change in the distribution coefficients for a pressure change of 1000 bars. The effect of pressure is proportional to the difference in partial molar volumes of the major and trace elements in the two phases, and this difference will generally be very small. A possible exception is a system containing both a liquid and a gas along with the solid. If one of the elements of the crystal is present in solution as a complex with a constituent of the gas phase, a change of pressure might force more of the volatile constituent into the liquid phase, thereby decreasing the activity of the element.

In the above discussion of the importance of various factors in determining the trace element content of a mineral, the most important variables were shown to be the temperature and the composition of the system. The discussion assumed equilibrium between the fluid and a thin surface layer of the growing crystal. It is probable that such an equilibrium does not always occur. For instance, the case of single crystals with differing concentrations of trace elements in different face loci (Frondel, Newhouse, and Jarrell, 1942) clearly does not represent such a simple equilibrium. Nor would equilibrium considerations apply to trace elements present in imperfections in the crystal lattice.

The adsorption process discussed previously is similar in character and effects to the equilibrium mentioned above between the fluid and a thin surface layer of the crystal. However, the two cases differ because the trace element content of the crystal would not change in any amount of time in the equilibrium case, whereas covered-over adsorbed trace elements, if present in greater than equilibrium amounts, would eventually be ejected if any migration of ions was possible. The content of adsorbed trace elements would be expected to be relatively small for minerals crystallized at high temperatures because of the decreased effectiveness of surface forces and the increased mobility of trapped atoms at high temperatures. Such a decrease in amount of the adsorbed constituent with increasing temperature is characteristic of adsorbtion. The charge of the trace element might also have an important bearing on the amount of adsorbtion, more highly charged ions being more likely to be adsorbed.

Diffusion of the major and trace elements through the fluid to the crystal surface is another process which might result in lack of equilibrium between crystal and fluid if crystallization was proceeding rapidly. Or if the trace elements were being captured in imperfections in the crystal, changes in the rate of crystal growth might give rise to differences in perfection of the crystal lattice which would in turn correlate with variations in trace element content. Other non-equilibrium processes can be imagined but the above examples suggest the kinds of effects which might result.

Having established some general background on the subject of causes for trace element variation in hydrothermal minerals, let us now examine the observed variations. The origin of the five groups of chalcopyrite samples in the Central mining district has so far not been explained; neither have the similar groupings defined by the indium and manganese content of chalcopyrite at Bingham, the cadmium content of sphalerite in the Central mining district, and the gallium and iron contents of sphalerite from Bingham. The following hypotheses might account for the observed differences:

1. The hydrothermal fluid from which the chalcopyrite of the different sample groups of the Central mining district was formed differed in composition when it reached the site of deposition. Such differences might

have originated at the source of the fluid or during its migration to the site of deposition.

2. The differences between the groups were determined by differences in temperature at the site of deposition.

3. The differences between the groups were determined by differences in the host rock at the site of deposition, either by differences in the trace element content of the host, or differences in the chemical effect of the host rock on the fluid.

More complicated alternatives exist but they involve considerations similar to the possibilities listed above.

It seems very unlikely that the difference between groups are the result of differences in host rocks. For instance, of the groups in the Central mining district, all the samples in group III, and most of the samples in groups IV and V and three samples from group II occur in carbonate host rocks, and it seems unlikely that the various carbonate rocks differ to a significant extent in content of Co, Ni, Sn, and In. In addition, group III contains samples occurring in limestone replacements, veins in granodiorite, veins in quartzite, and veins in diorite, and all (except CEN-17) contain the typical moderate to high concentrations of tin and indium, whereas chalcopyrite from the Santa Rita stock, which is very similar to the Hanover stock in trace element content (see the section on trace elements in rocks), contains little or no indium. In addition, the concentrations of indium in most rocks are well under a ppm. (Shaw 1952) and probably are well under 0.1 ppm. (the crustal abundance according to Shaw) in carbonate rocks. Therefore it also seems unlikely that the differences in indium content at Bingham are related to the host rock. Also, two of the high-indium chalcopyrites from the peripheral mineralization at Bingham were collected from fissures in the Last Chance stock, which is very similar in composition to the Utah Copper stock containing the low-indium chalcopyrite. Although the content of some elements, such as manganese, may be determined in part by the trace element content of the host rock, it seems very improbable that the existence of the groups depends upon the host rock in any way.

It also seems unlikely that the groups owe their characteristics to differences in temperature. Chalcopyrite from limestone replacement deposits of the contact metasomatic type occurs in three of the five groups in the Central mining district, whereas the samples in groups II and IV cover a large area and, in the case of group IV, a variety of geological occurrences. One might reasonably expect differences in the temperature of deposition to have existed within such groups, but if so, the effect was apparently subordinate to some other factor. In general, it is difficult to believe that the temperature of deposition could be so constant within groups of the type found, but yet differ so consistently between groups when the groups give the appearance in their mineralogy and alterations of relatively similar temperatures. None of the groups would be classified as epithermal, and probably all represent moderate to high hydrothermal temperatures. In addition, the independent variation of tin, indium, cobalt, and other elements as indicated by the single crystal studies and the lack of correlations at the Hanover mine cannot be the result of change in a single variable such as temperature. Therefore temperature does not seem to be the controlling variable for the origin of all the groups. It is possible that the differences between groups IV and V are the result of temperature. The differences between these two groups are similar to the zonal differences found in the trace element content of sphalerite from the district. This zonal relation will be discussed later. It is also very possible that differences in temperature are responsible for some of the variability within the sample groups.

Having disposed of hypotheses 2 and 3 as the major cause of the grouping observed in the Central mining district, there remains hypothesis 1. Unfortunately we know relatively little about the processes of origin of hydrothermal fluids, and knowing so little, there is no way of denying the possibility that relatively large variations in the trace element content of the hydrothermal fluid can occur. But if, for instance, the hydrothermal fluid is derived from a magma at some depth below the present surface, it seems possible that fluids of slightly different composition might be produced from this magma at slightly different times and places. The partition of elements between a magma and a hydrothermal fluid might depend on the temperature, pressure, stage of differentiation of the magma, and rate of the separation process, thus allowing an ample number of variables to account for the observed variation. Although the hypothesis of variation at the source of the fluid buries the cause of variation out of our sight and observation and is therefore somewhat unsatisfactory, it seems the most probable reason for the major features of the observed grouping.

Some uncertainty was previously expressed regarding the nature of the boundaries between the groups in the Central mining district. If the groups actually represent separate surges of hydrothermal fluid, there would be no transition from one group to the adjacent one; a sample would belong in either one group or the other. However, it is possible that chalcopyrite from two or more groups is present in one area, thus giving the appearance of a transition. The writer views the groups as having arisen in this manner, with the exception of the distinction between groups IV and V.

These two groups may actually grade from one to the other in the manner depicted on the graphs of cobalt, manganese, iron, and gallium in sphalerite.

The cadmium content of sphalerite is believed to determine groups of sphalerite samples similar to the chalcopyrite groups just discussed. Thus among the sphalerite samples from the Central mining district we can distinguish two or three groups-- the main large group of sphalerite samples from the district; the Copper Flats group and the Barringer fault group. The samples from the Pinos Altos area form a fourth group. There is no reason to suspect that conditions of deposition or wallrock have caused the differences in Cd content. The Copper Flat group occurs in the same lithology as some samples from the Hanover area, and samples from the Hanover area occur in tactite very similar to that at Copper Flats, indicating no particular difference in temperature or other conditions, whereas within the main group a variety of wall-rocks and probably conditions of deposition are represented. It is also significant that the trace element content of both sphalerite and chalcopyrite from the Barringer fault group differs from the same minerals in the Hanover area, and that the age relations of chalcopyrite and sphalerite in the two areas appear to differ.

It is somewhat more difficult to come to a definite conclusion concerning the cause for the zonal relationship found for cobalt, manganese, iron and gallium in sphalerite from the Central mining district. Wallrock control seems very unlikely as a cause because many specimens from both the Groundhog mine and the Hanover mine were collected from the Hanover limestone. A temperature gradient is one possible cause for the zoning. Changes in the composition of the hydrothermal fluid similar to those postulated for chalcopyrite are another possible explanation of the zoning, but in this case the changes in the fluid were gradual rather than discontinuous as in the groupings discussed above. If the variations within the

Hanover mine are the result of temporal changes in the composition of the fluids from which the sphalerite formed (rather than temperature changes with time), then it might be postulated that deposition of the sphalerite in the southwestern part of the district took place at a later time than the main deposition of the sphalerite at Hanover. A gradual change of trace element content of the fluid concurrent with a gradual migration of the area of most intense mineralization would be required by this hypothesis. A number of other possible explanations of the zonal relationship exist, but both temperature and composition changes seem capable of explaining the available facts.

At Bingham the difference between the two gallium-iron groups in sphalerite seems most readily explained by deposition from hydrothermal fluids of different composition, probably derived from different sources or from the same source at different times. The unlike relations of iron to tin and iron to gallium within the two groups constitute the best argument for this point of view. Evidence of a consistent age difference between sphalerite of the two groups would add support to this hypothesis, but so far as the writer knows, such an age difference has not been noticed if it exists.

The cause of the vertical and horizontal zoning is not clear. For the cause of the vertical zoning within the B limestone, a temperature gradient is the most attractive hypothesis. The depth of the ores below the surface at the time of ore deposition is not known, but probably the present surface is between a few thousand and ten thousand feet from the surface at the time of deposition. Therefore the range in depth of 3000 feet represented by the samples is an appreciable fraction of the distance from the location of the ores to the surface at the time the ores were deposited. The temperature at the surface was probably not over $100^{\circ}$ C., whereas the temperature of the ore deposition reached at least 550° C., judging from the iron content of the sphalerite. Thus, a temperature difference of 100-300° C. between the top and bottom of the 3000 foot section represented by the samples seems likely, on the assumption of a uniform temperature gradient with depth. Such a temperature gradient might be adequate to cause the observed variation of tin content and iron content. The possibility of other causes for the zoning cannot be ruled out, however.

The lateral zoning found for gallium is in part the result of the presence of samples from the high gallium group (mainly samples from the Galena fissure) at greater distances from the Utah Copper stock than the low gallium group. However, the samples from the East fissure area contain high gallium and also relatively high iron content, showing similarities to both groups, but fitting into the zonation in gallium content, and suggesting that there is more to the zonation than just the relative position of the two gallium-iron groups. The cause of the lateral zonation at Bingham, as in the Central mining district, remains uncertain.

In the preceding discussion of the causes of variation in trace element content of hydrothermal minerals, an attempt has been made to point out some of the many alternatives. In some cases a relatively definite conclusion could be arrived at, but in other cases several alternatives must be regarded as possible. Variations due to differences in the composition of the hydrothermal fluid seem very probable as a cause for the grouping of chalcopyrite samples observed in the Central mining district. Temperature seems a likely cause for the vertical zoning observed in sphalerite from Bingham. Lateral zonation in both the Central mining district and the Bingham district seems most likely to be the result of either temperature gradients or progressive concurrent changes in the composition of hydrothermal fluids and the site of deposition. Low values of the tin content of chalcopyrite at Bingham may have resulted from fractionation of tin into micas or other sheet structure minerals at the time of deposition. Some variation is the result of small amounts of contaminating minerals in the samples. A number of other processes resulting in variation have been mentioned. It is probably significant that all the correlations found are statistical in nature, that is, the correlations are not very good. This erratic nature of the data indicates that a number of factors have operated to produce the observed trace element content, and that the interpretations of cause which have been made are merely the more important factors, and not the only causes of variation.

## THE SIGNIFICANCE OF IRON CONTENT OF SPHALERITE

Kullerud (1953) published a phase diagram of the system FeS-ZnS and proposed that the amount of iron in sphalerite, under certain assumptions, was a measure of the temperature of deposition of the sphalerite. Part of Kullerud's phase diagram is reproduced in figure 74 with a few corrections. Kullerud calculated the mole percent values incorrectly from the weight percent data. His mole percent values have been recalculated by the writer, and the values below 400°C have been graphically extrapolated from the new mole percent figures by the method originally used by Kullerud. The iron content of the solvus at 138°C (the temperature of a transition point in pyrrhotite) varies several tenths of a percent depending on exactly how the extrapolation is carried out. Because of this uncertainty and because of the dubious nature of the extrapolation method, the results below 500°C are not believed to be highly accurate. The error in Kullerud's mole percent figures was pointed out to the writer by Bruce Doe, and confirmed in a letter from Kullerud to Doe.

The use of the phase diagram as an indication of temperature is dependent on equilibrium between FeS and sphalerite. The composition of the sphalerite in equilibrium with FeS at a certain temperature is given by the position of the solvus for that temperature.

In addition to being dependent on temperature the solvus is also dependent on pressure. Kullerud (1953) derived a pressure correction, but the values were based on the incorrect mole percent figures. A corrected curve for 1000 atm. pressure has also been plotted on figure 74.

Pyrrhotite in nature is normally slightly deficient in iron atoms relative to the composition FeS. Kullerud carried out several experiments

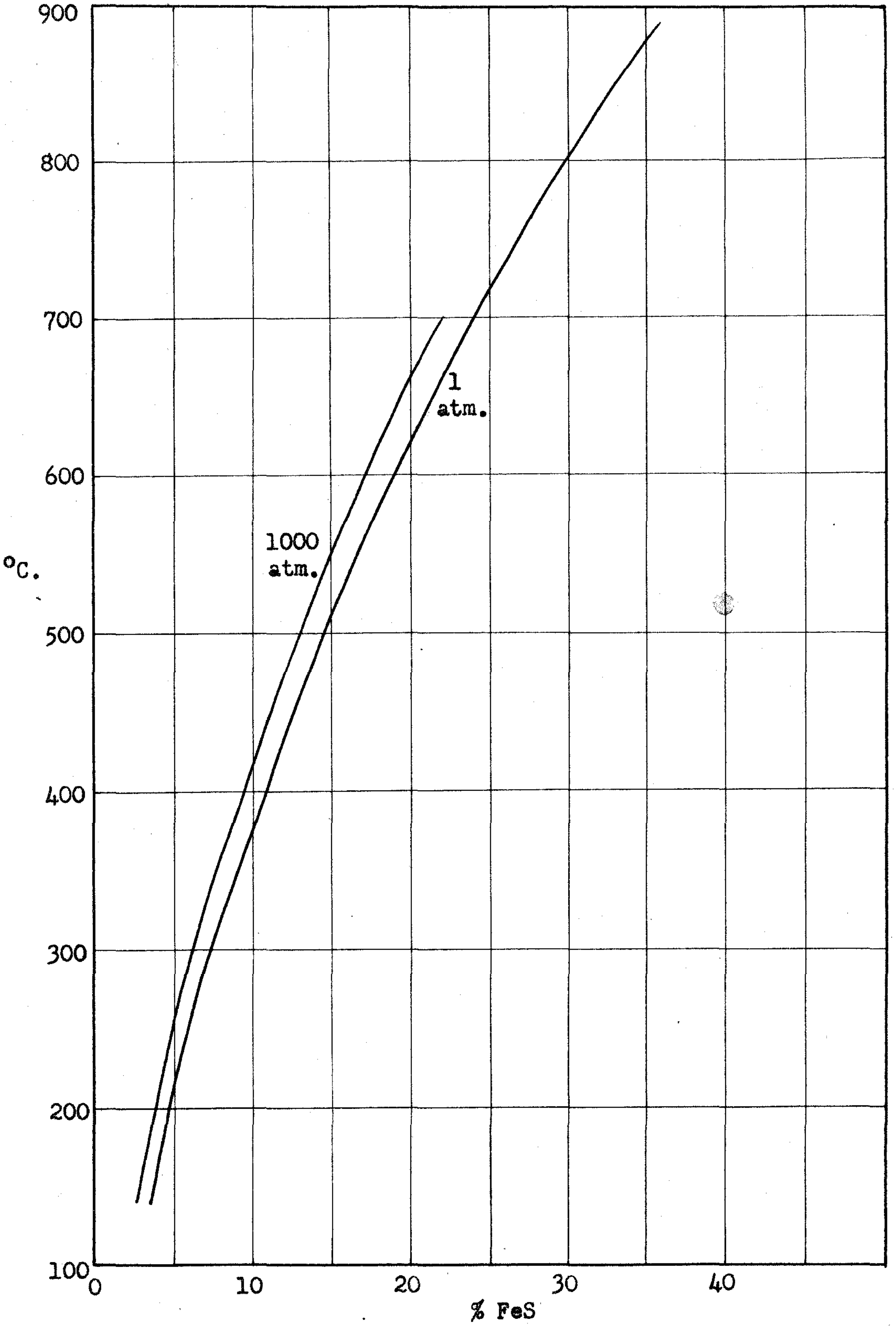


Figure 74. Solvus of the system ZnS-FeS at 1 atm. and 1000 atm. (modified from Kullerud, 1953).

to find out whether the variability in composition of pyrrhotite had any effect on the iron content of coexisting sphalerite and found essentially no effect. The experiments were extended to systems containing enough sulfur to form pyrite. Unfortunately, the compositions investigated are not precisely described by Kullerud. In one experiment the amount of sulfur was "almost enough to form $FeS_2$" and in another it was "more than enough to form $FeS_2$." Figure 75A shows an inferred isothermal section of the system FeS-ZnS-S. The diagram is not intended to be quantitatively correct, but the stability fields should be similar to those shown. When the amount of sulfur was "more than enough to form $FeS_2$ " Kullerud found a relatively large decrease in the iron content of the equilibrium sphalerite. Preliminary reports of more recent work (Barton and Kullerud, 1957) indicate that "temperature estimated using the FeS-ZnS data for sphalerite in equilibrium with pyrite can be as much as 300°C too low." This situation is indicated by the range of tie lines between $FeS_2$ and sphalerite in figure 75A. Because of the lack of exact knowledge of the effect of sulfur pressure and a lack of knowledge of the sulfur pressure in ore deposits, the quantitative use of a sphalerite-pyrite equilibrium as a geological thermometer does not seem justified to the writer. It is true however, that sphalerite in equilibrium with pyrite will never have more iron in solid solution than it would have if in equilibrium with pyrrhotite at the same temperature. In other words, increased sulfur pressures will tend to form increased amounts of pyrite at the expense of the iron content of the sphalerite. Therefore a pyrite-sphalerite equilibrium can give a minimum temperature of deposition. Barton and Kullerud (1957) independently point out the same fact.

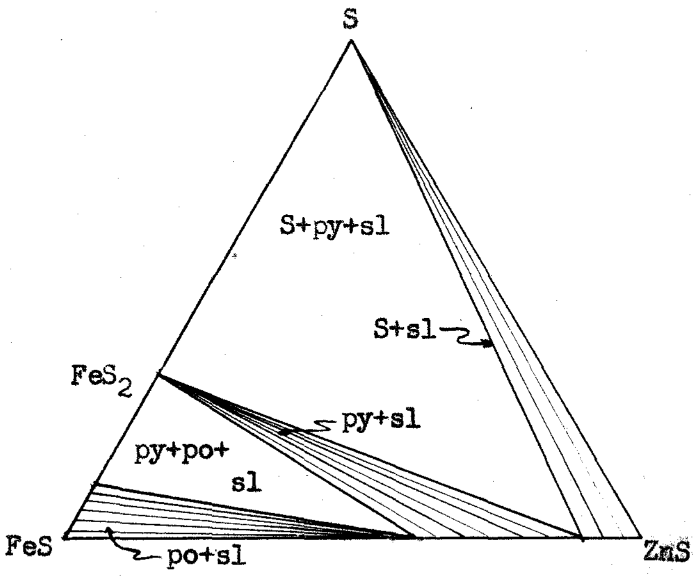


Figure 75A. Hypothetical phase diagram of the system FeS-ZnS-S at an elevated temperature. The diagram is not intended to be quantitatively correct, but shows the stability fields expected. py=pyrite, sl=sphalerite, po=pyrrhotite.

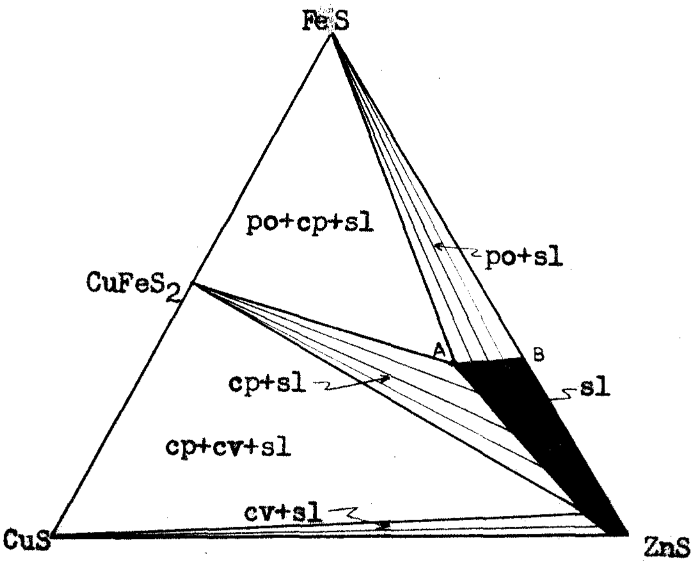


**Figure** 75B. Hypothetical phase diagram of the system FeS-ZnS-CuS at an elevated temperature. The diagram is not quantitatively correct, and ignores copper-iron sulfides other than chalcopyrite and non-stochiometry of chalcopyrite and pyrrhotite, but shows the stability fields expected with sphalerite and chalcopyrite. Sl=sphalerite, po=pyrrohotite, cp=chalcopyrite, cv=covellite.

Solid solution between sphalerite and chalcopyrite is a possible complication which has not previously been discussed. In figure 75B an attempt has been made to show the phase relations in a simplified isothermal section of the system FeS-ZnS-CuS. Possible complications resulting from the non-stochiometry of chalcopyrite, and from bornite and other copper-iron sulfides have been neglected. The relations shown are qualitative, not quantitative. The position of point A is one of the more critical features. If line AB trends toward the CuS corner, then the addition of chalcopyrite or CuS to the system has no effect on the iron content of sphalerite. If the line AB trends toward chalcopyrite, the presence of chalcopyrite in the system would tend to increase the iron content of a sphalerite in equilibrium with pyrrhotite. Most probably the actual relations are intermediate between these two alternatives, but more extreme trends of the line AB are also possible. Exsolution of chalcopyrite is an additional complicating factor.

Equilibrium between sphalerite and pyrrhotite (or possibly pyrite) is necessary for valid measurement of the temperature of deposition by the method. Much evidence shows that ore minerals are in general deposited in a sequence. Therefore, it cannot be assumed that sphalerite and pyrrhotite were deposited simultaneously, or that they are in equilibrium. The writer believes that lack of equilibrium and the lack of criteria for demonstrating equilibrium are among the most important difficulties in the use of the method. In some ore deposits evidence has been found that sphalerite has replaced pyrrhotite. Replacement of pyrite by sphalerite is relatively common. In such cases it is clear that the hydrothermal fluid was not in equilibrium with the iron sulfide mineral, because the iron sulfide mineral was dissolving in either the fluid phase or the sphalerite or both, and was thus unstable. Possibly the process of replacement resulted in an equilibrium sphalerite, but this is only an assumption. It is also possible that the reaction rate was not fast enough to allow equilibrium. Available indications of reaction rates are somewhat contradictory. Kullerud obtained equilibrium at 500°C in about a year, but found difficulty in explaining the lack of exsolution in natural sphalerites of very high iron content such as those at Broken Hill, Australia. The Broken Hill sphalerite shows relatively little exsolved pyrrhotite, yet it seems almost certain that cooling of the ore from the inferred deposition temperature of 620°C (Kullerud, 1953) to 500°C took much more than one year. Exsolution of an appreciable proportion of the iron would be expected under such conditions. Edwards (1947, p. 71), in discussing this problem, suggests that ore fluids may be injected at much higher temperatures than the wall rocks and are therefore chilled or quenched on deposition. It is also possible that diffusion and reaction rates between solid sulfides in nature are not as rapid as those measured in the laboratory, perhaps because the higher confining pressures in nature close cracks and defects in crystals and thus impede diffusion processes.

Consideration of the many factors affecting the iron content of sphalerite leads to the conclusion that most of the important factors cause decreases of iron content from the values given on Kullerud's solvus for 1 atm. pressure. For instance, increased pressures result in a lower iron content. Exsolution of pyrrhotite or equilibrium with pyrite has the same effect. Lack of equilibrium, except the formation of a supersaturated solid solution, results in lower iron content. These factors, plus the lack of criteria for equilibrium, and the difficulty in making pressure corrections lead the writer to believe that the iron content of sphalerite, using Kullerud's solvus, is best interpreted as giving a temperature lower than or equal to, but not exceeding the true temperature of deposition. This hypothesis will be referred to as the "minimum temperature" interpretation.

Unfortunately, several factors exist which might cause the opposite effect on the iron content, and these should be kept in mind. Solid solution of chalcopyrite might increase the iron content above the amount given by Kullerud's solvus. However, if most of the chalcopyrite later exsolved, as seems possible, and if the iron content is measured from the unit cell dimensions by x-ray diffraction, the error is minor. In addition, the total amount of chalcopyrite in solid solution in most sphalerite is probably relatively small.

The formation of a supersaturated solid solution is a second possible cause for exceptions to the minimum temperature interpretation. The formation at room temperature of ZnS supersaturated in cadmium and manganese has been demonstrated by Kroger (1940). If it can be shown that sphalerite has replaced pyrrhotite, the possibility of supersaturated (Zn,Fe)S mixed crystals can be ruled out. Pyrrhotite would be a stable phase under conditions resulting in the formation of a supersaturated sphalerite, whereas the evidence of replacement indicates that pyrrhotite was not a stable phase. The same statement cannot be made concerning the replacement of pyrite by sphalerite, because this reaction might be caused by low sulfur pressure as well as low chemical potential of iron. Unfortunately, textures unmistakably indicating replacement of pyrrhotite by sphalerite seem to be relatively rare, so this criterion may not be very useful. Therefore, the possibility of supersaturated (Fe,Zn)S crystals must be regarded as a possible difficulty in the interpretation of the iron content of sphalerite.

The formation of supersaturated crystals at high temperatures should be less likely than at low temperatures, however. A third possible cause of an incorrect interpretation is the presence of iron bearing minerals in the sample if a chemical method of analysis is used. Measurement of the unit cell dimensions solves this problem.

Some evidence relating to the problems discussed above is found in the natural sphalerites analyzed by the writer.

The sphalerite single crystal from Hanover (CEN-531) contained zones with an FeS content of 12% (425°C) overlying zones with FeS content of 5.4% (230°C). Sharp boundaries separated the layers. Some sphalerite grains from Bingham have similar rims of high iron content covering cores of low iron content. This arrangement of zones indicates either that the time during which the higher temperature was maintained was geologically brief or that the reaction rates found by Kullerud are too fast. Either alternative casts doubt on the importance of reactions between solids in establishing equilibrium.

Fryklund and Fletcher (1956) have published the best discussion of the equilibrium problem known to the writer. They showed that sphalerite near a post-ore dike developed iron-rich rims where in contact with iron minerals (magnetite, pyrite, and siderite), presumably because of the high temperature reached during the intrusion and cooling of the dike. On the other hand, sphalerite in most of the ore shows no such rims. They therefore concluded that equilibrium existed at the time of deposition.

The validity of this argument depends on two factors: the reaction rates at various temperatures, and, because the iron minerals involved are not pyrrhotite, the ease of disposal of reaction products from the vicinity of the sphalerite-iron mineral contact. Reaction rates commonly are an exponential function of temperature, and the rate of reaction might easily be great enough at the 600°C temperature of the dike to cause the rims, but be slow enough to be unnoticeable at the 400°C or less at the time of ore deposition. Relative to the second factor, the addition of iron from pyrite involves the loss of some sulfur from the mineral assemblage. This loss might occur readily under the conditions of the dike intrusion, but might be prevented during the deposition process by the abundance of sulfur in the fluid phase (i.e., high sulfur pressure). Reaction with magnetite or siderite involves similar complications with regard to reaction products.

The writer has been impressed by the large amount of low-iron sphalerite present in many areas in the Bingham district. Veins in the Lark mine, an example of which is shown in figure 35, are particularly good examples. The iron content of sphalerite from the Lark vein is generally less than one percent, yet large shoots of pyrite occur in the structure, and pyrite is relatively common in the ore, sometimes as fine intergrowths with sphalerite. The most obvious color zoning in the sphalerite is related to late veinlets containing chalcopyrite and galena. The color of the sphalerite along these veins is gray, rather than brown, and this gray probably results from solution of chalcopyrite rather than FeS. The following conclusions are possible concerning low-iron sphalerite associated with pyrite in the Lark vein:

1. Deposition temperatures were very low ($\ll$ 138°C). Such a low temperature seems unlikely to the writer.

2. Equilibrium with pyrite rather than pyrrhotite has resulted in a very much smaller iron content than that given by Kullerud's phase diagram for the FeS-ZnS system.

3. Equilibrium between pyrite, sphalerite, and the hydrothermal fluids is achieved very slowly, if at all.

The writer prefers one or both of the last two alternatives as an explanation.

In the Central mining district, sphalerites of extremely low iron content do not occur, and color zoning is relatively rare. Observed instances of color zoning are largely restricted to sphalerite of low iron content with the prominent exception of the single crystal discussed above. The writer ascribes this uniformity of iron content within hand specimens to a greater uniformity of the mineralization process. A uniformity of the mineralization process might be imposed by the mixing resulting from the slow flow or diffusion of material from the main ore channels through fine cracks and pores in previously-formed deposits to the site of deposition. It seems possible that the mineralization process in the sediments at Bingham took place in and near relatively open fissures, thereby allowing variations in the composition of ore fluid along the main ore channels to be more directly reproduced in the deposits. However, equilibrium with iron bearing minerals may be responsible for the uniformity of iron content within specimens at Hanover.

In contrast to the uniformity within hand specimens in the Central District, the iron content of sphalerites from different hand specimens is clearly not the same. In the Hanover and Pewabic mines the iron content ranges from 4.2 to 18.5% FeS. The temperatures represented by these values range from 175 to 600°C. Sphalerite from other mines in the district shows a similar range in iron content. This large variability can be explained by a large range in temperature of deposition, by lack of equilibrium, by the complications resulting from equilibrium with pyrite rather than pyrrhotite, or by some combination of these factors.

If the temperature in the contact zone was in any way controlled by the cooling of the adjacent stock, a considerable time must have elapsed between stock intrusion and ore deposition in order for the temperature to fall to 200°C or less only a few hundred feet from the contact. For this reason, and because of the zoning in the single crystal, the writer prefers to believe that the temperature range of sphalerite deposition was not as large as that obtained from the iron contents quoted above, although a range of several hundred degrees may have existed. Chemical variations in the fluid or lack of equilibrium seem better explanations for much of the variability in iron content.

It is perhaps significant that in all specimens containing pyrrhotite the sphalerite has a relatively high iron content, indicating temperatures in the range 450 - 600°C. While this correlation of pyrrhotite and high-iron sphalerite might be the result of the high temperature necessary to form pyrrhotite at the sulfur pressures prevailing under hydrothermal conditions, it might also result from true equilibrium in contrast to the complications discussed concerning the sphalerite-pyrite equilibrium.

If the iron content of sphalerite is interpreted to give a minimum temperature of deposition, then the sphalerites of highest iron content might be expected to most nearly yield the actual temperature of deposition (if the sphalerite was deposited in a fairly narrow temperature range). On this basis the consistently high iron content of sphalerite at the Cleveland mine, coupled with the association with pyrrhotite, is especially interesting. The composition of this sphalerite ranges from 18 to 24% FeS. Several of the sphalerite samples, especially those of higher iron content, were observed to contain small amounts of pyrrhotite and chalcopyrite. The maximum amount of pyrrhotite and chalcopyrite in the samples is estimated to be 2%. A thin section shows that the sphalerite near these blebs of pyrrhotite or chalcopyrite is lighter in color and therefore has a slightly smaller iron content than the rest of the sphalerite, thus suggesting that all or part of these pyrrhotite and chalcopyrite blebs originated by exsolution. However, even if a correction for these inclusions is made the iron content falls in the range of 18 - 22% FeS. With no pressure correction a temperature of 580 - 640°C is indicated.

It is interesting to compare the deposition temperature of the sphalerite with temperatures indicated by other minerals in the deposit. Chalcopyrite contains "stars" of sphalerite, suggesting exsolution and an origin at or above 550°C (Edwards, 1947, p. 79). Quartz occurs as prisms capped by various pyramids, but no trapezohedral faces could be found, leaving unanswered the question of whether it crystallized as high or low quartz.

As discussed above, textures suggesting exsolution of chalcopyrite from sphalerite can be observed, thus indicating temperatures of 350°C or greater (N. W. Buerger, 1934). Marcasite is relatively abundant in some specimens. According to Allen, Crenshaw, and Johnson (1912) this mineral transforms to pyrite relatively rapidly above about 400°C. Ankerite-quartz intergrowths occur in sphalerite ore and calcite-quartz aggregates occur within a half inch of ore. With a reasonable $CO_2$ pressure, reactions between the carbonates and quartz to produce various silicates might be expected at temperatures of 500-600°C, yet no such silicates were found in a search of a number of thin sections containing these assemblages. To the contrary, a clay mineral, probably an iron-rich montmorillonite, occurs in a few specimens, suggesting a relatively low temperature of deposition.

The presence of marcasite and some of the other less definite indications of relatively low temperature seem most reasonably explained by deposition of the hydrothermal minerals in a sequence accompanied by appreciable changes in temperature. The marcasite probably formed at a late low-temperature stage of deposition. No objection to this hypothesis could be found in a study of the textures. However, the position of the ankerite-quartz intergrowth as a zone an inch or so thick bordering most of the ore suggests that ankerite and quartz formed during or before the deposition of the sphalerite. The calcite-quartz assemblages were almost certainly present when the sphalerite was deposited. This line of reasoning leads to the conclusion that either the temperature found from the sphalerite is incorrect, or that we are incorrect in expecting carbonate-quartz reactions to take place, or that such reactions should have taken place but did not because of slow reaction rates. The second possibility seems most likely to the writer, but the problem needs further study.

The iron content of sphalerite in the Central mining district suggests that temperatures of ore deposition reached at least 550-600°C in the Hanover area, and at least 350°C in the Groundhog mine area. The presence of hedenbergite, garnet, ilvaite, and epidote in the Groundhog ore suggests that temperatures were probably somewhat higher than 350°C during the earlier part of the ore deposition process.

At Bingham, application of the minimum temperature interpretation indicates that temperatures of at least 550°C were reached.

In an additional attempt to check on the validity of the iron content of sphalerite as an index of temperature of deposition, the writer has estimated the iron content of most of the sphalerite samples studied by Burnham (1955) and compared the resulting iron content with the Lindgren temperature classification of the deposit.

The iron content of the samples has been estimated by comparing the color of the powdered sphalerite with the colors of four sphalerites of known iron content. The iron contents of these four sphalerites are as follows:

| Sample Number | %FeS | Color | Index Number |
|---|---|---|---|
| Sphalerite I | 0.3% | White | 1 |
| Sphalerite III | 3.2% | Pale brown | 2 |
| CEN-214 | 8.6% | Medium brown | 3 |
| TS-68 | 18.1% | Dark brown | 4 |

The color of each powdered sphalerite sample was assigned a value on a scale running from 1 to 4, including + and - values. Previous experience has demonstrated that the powder color is a relatively good index of the iron content of most sphalerites. In a few cases powdered sphalerite of low iron content may show a gray color rather than the normal tan and brown shades, and this gray color is believed to result from inclusions of chalcopyrite or galena in the sphalerite. In the present study an attempt was made to allow for the effect of such impurities in the relatively small proportion of cases in which pure powder was not obtained. Powdered sphalerite from samples of high germanium content has a distinct pink tinge (Burnham, 1955), and an attempt was also made to allow for this effect.

Temperature is one of the more important factors in the Lindgren classification of hydrothermal ore deposits. As many as possible of the districts studied by Burnham were classified as epithermal, mesothermal, hypothermal, or pyrometasomatic by reference to Lindgren (1933), to Ore deposits of the Western States (1933), or to various articles in the literature on the districts. Less than half of the districts could be classified in this manner, although no exhaustive study or search of the literature was made in the attempt. For a number of districts there was some question of the correct classification; for instance, several districts contain deposits of both pyrometasomatic and mesothermal types. Samples from such districts were included in both of these groups.

In figure 76 histograms of iron content have been plotted for the four types of deposits. If epithermal deposits formed at temperatures of less than 200°C as suggested by Lindgren (1953), then sphalerite containing over about 5% FeS should not be found in an epithermal deposit. The histograms show that to a large extent this is true. The exceptions are samples from Parral, Mexico (4-, 3, and 3-), Mogollon, New Mexico (3) and Safford, Nevada (3-). All three of these deposits are mentioned in Lindgren (1933) or Ore Deposits of the Western States (1933) as being epithermal deposits, but it is possible that these deposits are incorrectly classified. Clearly sphalerite from epithermal deposits does not tend to have as high an iron content as sphalerites from the other temperature classifications.

In mesothermal and pyrometasomatic deposits, the most notable fact is the large range in iron content. Some of these deposits have sphalerites of high iron content, but a large proportion of the samples from mesothermal and pyrometasomatic deposits have very low iron content. Lack of saturation with iron seems the most probable explanation for this characteristic, but other factors, such as temperature variation during deposition, may be responsible. It is interesting to note that fewer sphalerites from pyrometasomatic deposits than mesothermal deposits have extremely high

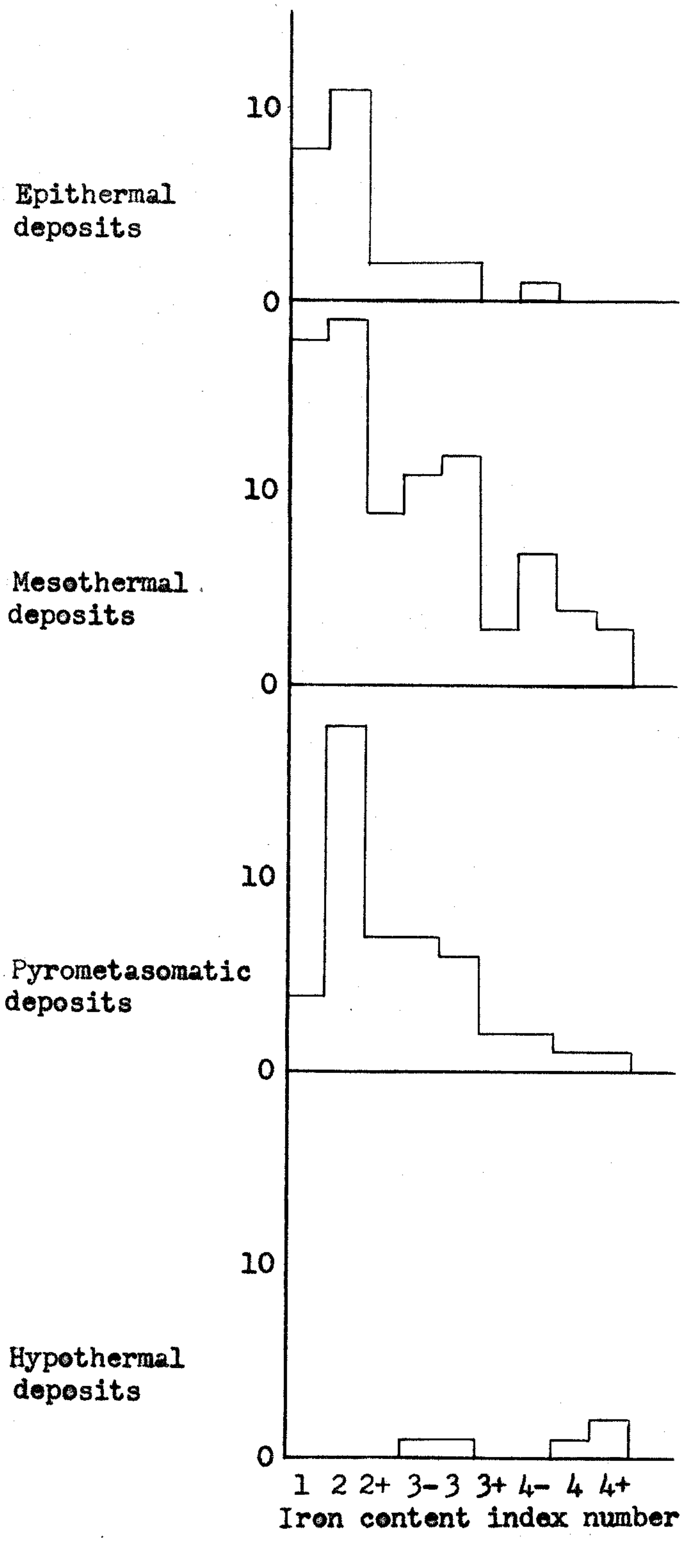


Figure 76. Plots of frequency against iron content of sphalerite (as indicated by powder color) for sphalerites analyzed by Burnham (1955).

iron contents.

According to Lindgren (1933) the upper temperature limit for mesothermal deposits is about 300°C. Therefore the sphalerite from these deposits should not contain more than about 8-10% FeS (about 3 on the scale used here). For a relatively large number of mesothermal sphalerites this is not true, including samples from Leadville, Colorado, Gilman, Colorado, and Ophir, Utah. It seems possible that temperatures higher than 300° have existed during the formation of some deposits of the mesothermal type.

Too few deposits of the hypothermal type are represented to draw any conclusions except to point out that several of the sphalerites do have the high iron content expected for this group.

In summary, the writer feels that the iron content of sphalerite can be used with some assurance to obtain a minimum temperature of deposition of the sphalerite, although many additional field and laboratory checks of the results must be made before this consideration can be regarded as firmly established. Additional work on the equilibrium between pyrite and sphalerite is needed to clarify the phase relations of these two minerals, but the determination of minimum temperatures seems justified at present. Additional work on reaction rates between the solid phases may enable further conclusions to be reached concerning the temperature of deposition.

## COMPARISONS WITH PREVIOUS STUDIES

In this section, an attempt will be made to compare the results of this study with previously-published work of a similar nature, and to examine the conclusions of previous studies in the light of the findings of this study.

One of the purposes of this study was to determine the minimum number of samples necessary to obtain useful average trace element concentrations for a mining district. The approach to this problem has been to find the variability (expressed as standard deviation) of the various trace elements within the Bingham, Central, and Pinos Altos districts, using all the analyzed samples. In addition, standard deviations have been computed from the data of Burnham (1955) and Fryklund and Fletcher (1956).

For the Pinos Altos district, the Coeur d'Alene district (Fryklund and Fletcher 1956), and the district composites from Burnham (1955), the standard deviations of the logarithms of the concentrations have been computed. These values are shown in table 14. For several elements in the column of composites from Burnham, two kinds of values are given. For tin in chalcopyrite, and cadmium and cobalt in sphalerite, Burnham computed the within-district variance for all districts from which he had analyzed two or more samples. (The number of degrees of freedom used by Burnham is incorrect, and the writer has re-computed the standard deviations from the sum of squares values and the correct degrees of freedom.) The remaining values from Burnham represent computations by the writer of the pooled standard deviation for the districts from which Burnham had analyzed five or more chalcopyrite samples (Cedar Valley, Eureka, Jerome, Bunker Hill, and Ajo, Arizona; Lordsburg and Santa Rita-Hanover, New Mexico; Ely, Nevada; Cananea, Sonora; and Ducktown, Tenn.) or four or more samples of sphalerite (Silver Bell and Dragoon, Arizona; Hanover-Fierro and Santa Rita, N. M.; Park City, Utah, and Yellow Pine and Pioche, Nev. ). One of the problems in computing these values was the question of what to do with samples in which the element was not detected. In general, these samples were arbitrarily assigned a value of 1 ppm., but if an element was not detected in an appreciable fraction of the samples from the district, the district was not included in the summation.

For the samples from the Central and Bingham mining districts, the standard deviation has been found graphically by plotting a cumulative distribution curve on special lognormal probability paper (sold by the Codex Book Co., Inc., of Norwood, Mass.) On this paper, a lognormal distribution plots as a straight line. The plots of the trace element data were in general not straight lines, but most of them closely approximated a straight line for much of their length, especially for the central range of values. A straight line was drawn by eye through the points and the standard deviation of the distribution represented by this line was found and entered in table 14, after conversion to a logarithm. This graphical procedure partially eliminated the uncertainties caused by values less than the detection limit. The method is also much less time-consuming than the normal mathematical computations. It is perhaps significant, however, that appreciably more than half of the plotted distributions deviate from being lognormal by having fewer very high values than called for by the lognormal distribution.

It is realized that sampling problems and non-normality may affect

Table 14

Standard deviations of the logs of concentrations for trace elements in sphalerite and chalcopyrite from various districts.

a. Chalcopyrite
Mining District

| | Central | Bingham | Pinos Altos | Composite (Burnham, 1955) |
|---|---|---|---|---|
| Ag | 0.75 | 0.73 | 0.21 | 0.59 |
| Co | 0.88 | 0.65 | ---- | ---- |
| In | 0.83 | 0.98 | 0.27 | 0.44 |
| Mn | 0.77 | 1.7 | 0.83 | 1.11 |
| Ni | ---- | 0.75 | ---- | ---- |
| Sn | 0.78 | 0.32 | 0.30 | 0.53<br>0.59* |

b. Sphalerite

| | Central | Bingham | Pinos Altos | Composite (Burnham, 1955) | Coeur d'Alene |
|---|---|---|---|---|---|
| Cd | 0.08 | 0.09 | 0.07 | 0.15<br>0.14* | 0.33 |
| Co | 0.51 | ---- | 0.52 | 0.55<br>0.64* | 0.35 |
| Ga | ---- | 0.78 | 0.48 | 0.50 | 0.49 |
| Ge | ---- | ---- | ---- | ---- | 0.69 |
| In | 0.75 | 0.68 | 0.55 | 0.74 | ---- |
| Mn | 0.32 | 0.25 | 0.62 | 0.55 | 0.63 |
| Sn | ---- | 0.71 | ---- | ---- | ---- |

*all districts represented by 2 or more samples from Burnham (1955).

the standard deviations given in the table, but the influence of these factors is believed to be relatively minor. The difficulty of sampling the population of chalcopyrite or sphalerite in a district is believed to be the more serious, and if so, the true values of the standard deviations are likely to be slightly larger than the values given, owing to inadequate sampling of values far from the mean. For the purposes at hand, however, the values are believed to be adequate.

Having obtained the standard deviations, the required number of samples necessary for an average of a given accuracy has been found. To do this, it is assumed that the population distribution is adequately represented by a normal or lognormal distribution. If this assumption is valid and it seems a good approximation in this case, then $\sigma_{Av}^2 = \frac{\sigma_p^2}{n}$ where $\sigma_{Av}^2$ is the variance of the average of n samples, and $\sigma_p^2$ is the population variance.

For instance, let us say we wish to find the average content of indium in sphalerite for a number of districts with an accuracy such that we are 95% confident that the average is within a factor of 3.16 ($= \sqrt{10.}$) of the true value. For the lognormal distribution, this is equivalent to saying that $2\sigma_{Av} = 0.5$ ($=$ log 3.16) or $\sigma_{Av} = 0.25$. For indium, the value 0.7 seems a relatively good approximation of $\sigma_p$. Then $n = \frac{\sigma_p^2}{\sigma_{Av}^2} = \frac{0.49}{0.06} \cong 8$. Eight samples would be required for this accuracy. Table 15 gives values of n for other combinations of $\sigma_p$ and confidence interval.

Table 15

Approximate number of samples necessary to obtain with 95% confidence an average lying within a desired concentration interval ($\sigma_{Av}$) for various values of population standard deviation ($\sigma_p$).

| Desired Value of $\sigma_{Av}$ | | Value of $\sigma_p$ | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Conc. Factor | Log | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.7 | 1.0 |
| 2 | 0.30 | 1 | 2 | 4 | 7 | 11 | 22 | 45 |
| 3.16 | 0.50 | 1 | 1 | 2 | 3 | 4 | 8 | 16 |
| 10 | 1.0 | 1 | 1 | 1 | 1 | 1 | 2 | 4 |

Burnham (1955) prepared contoured maps of the average content of certain trace elements for a number of districts. The contour intervals were spaced by a factor of 3.16 in parts per million. Most of the districts were represented by only a few samples. Out of 116 districts, 62 were represented by only one chalcopyrite sample, and 44 out of 109 districts were represented by only one sphalerite sample. On the basis of the above discussion of the number of samples required and the values in table 15, it is seen that one sample from a district is adequate for some elements and two samples from a district are adequate for almost all elements <u>if</u> it is only desired to be within a factor of 10 (two contour intervals on Burnham's maps) of the true value. However, if an accuracy equivalent to one contour interval is desired, from four to eight samples are required from a district. Burnham had this number of samples from less than 10% of the districts. It is concluded from this discussion that the district averages on which Burnham's maps are based are reliable (at a 95% confidence level) to a factor of about 10 for most elements. However, it should be noted that for most elements, the district averages range over a factor of 30 - 1000. Also, the 95% confidence level used in the foregoing discussion is perhaps higher than is required to demonstrate the features shown on the maps.

In addition to the number of specimens collected from a district, statistical theory also requires that the group of specimens be chosen in a manner which will give an unbiased average value. Sampling technique becomes a definite problem in view of the geographic and geological groupings demonstrated in the previous sections. One method of taking a valid sample of the population is to collect samples from the district in a random manner. The difficulties inherent in this procedure have been discussed in the section on sampling and statistics. An alternative technique, especially if only a few samples are to be taken from a district, is to break down the total sample into geologic or geographic sub-populations which can be weighted by size to give the average. For instance, at Bingham, if only one to three chalcopyrite samples were to be taken, one might choose to collect all of the samples from the porphyry copper type of occurrence, because this type of mineralization makes up such a large proportion of the ore in the district. However, even if such a procedure is used, an attempt should be made to select the samples within the chosen sub-population in some unbiased fashion. In a study such as that of Burnham (1955) in which only a few samples are taken from a district, disregard of the possibility of groupings such as those discussed on the preceding pages might easily be responsible for deviations by a factor of 3, and possibly more, from the true population average.

Burnham (1955) showed by a statistical treatment that significant differences do exist between mining districts in the trace element content of chalcopyrite and sphalerite. Although Burnham's sampling from many districts was probably somewhat biased, the statistical possibility of obtaining his results by chance, if all mining districts had the same average trace element content, is so small that the possible influence of the sampling error can be neglected. The differences between the Central, Pinos Altos and Bingham mining districts, found on the basis of many samples in this study, also support the conclusion that differences between mining districts exist. Concentrations of tin in chalcopyrite and cadmium, cobalt, gallium, and tin in sphalerite fall in distinctly different ranges for the three districts.

The interpretation of the causes for these differences between districts is a separate problem. Burnham showed that the district averages for various trace elements could be contoured to show beltlike patterns. The belts for different elements had similar, though not identical, shapes and positions. He also found that the larger mining districts tended to fall into the belts. His discussion of the importance of regional control in determining trace element concentrations rests largely on the consistency of the geographic patterns for various elements and the definity of the patterns as determined by positions and values for the mining districts. It would be desirable to test the lack of random geographic distribution of the district averages by some statistical procedure, but the writer has not been able to discover any satisfactory procedure for accomplishing this. Thus, the validity of the patterns shown on Burnham's maps must be left to the judgment of the reader. However, although it is certainly possible to contour the maps differently in places, the consistent geographic similarities between trace elements, production of metals, and geologic features, such as the margin of the Colorado Plateau, seem to the writer to be convincing evidence for the existence, at least in Arizona, of the belts postulated by Burnham.

The work of Schroll (1955) on the eastern Alps lends additional support to the concept that the trace element content of sulfide minerals fits regional geographical patterns. Schroll studied sphalerite and galena from about 200 localities in the eastern Alps. Maps of his data show belts of high trace element content with roughly east-west trends. The area studied by Schroll is much smaller than that studied by Burnham, but the data are more closely spaced. The number of samples from most localities is small. Instead of attributing the pattern to compositional heterogeneities in the subcrust as Burnham did, Schroll concludes that temperature, as determined by position relative to a central zone of intrusion and metamorphism, was a principal factor in controlling the concentrations of trace elements. Schroll found that concentrations of certain trace elements were highest along the zone of plutonic activity, whereas others were highest along the margin of the area studied. While Burnham did not deny the possible modifying influence of temperature and other environmental factors, he found difficulty in correlating trace element content with temperature. The writer also finds evidence of important variables other than temperature. In addition, Burnham noted that certain ore deposits of pre-Cretaceous age fell into the pattern defined by the more numerous deposits of Cretaceous and Tertiary thus suggesting that the pattern was not determined by an environmental factor, such as temperature, existing for only a limited period of time.

The writer has also attempted to correlate Burnham's trace element data with temperature, but has not had much success, except for the germanium content of sphalerite. High germanium contents appear to correlate relatively well with the presence of features suggesting low temperature of deposition. Similar conclusions have been reached by Brewer, Cox, and Morris (1955). They concluded that germanium occurs in amounts greater than 100 ppm. only in sphalerite of low temperature origin, although it does not occur in all sphalerite of low temperature origin. It seems probable that similar tendencies exist for other trace elements, but that these tendencies are disguised by the effects of other factors.

A number of studies of trace elements in sulfides have demonstrated the existence of groupings and zonal relations similar to those found in the Central and Bingham mining districts. Edwards (1955, 1956) in a study of the iron, manganese and cadmium content of sphalerite from Broken Hill, Australia, found gradual horizontal changes along the length of the several lodes, and also distinct differences in a vertical direction between lodes.

El Shazly, Webb, and Williams (1957) in a study of trace elements in sphalerite, galena, and chalcopyrite from the British Isles, found that indium, manganese, and tin in sphalerite, and bismuth and tin in galena, decreased away from bodies of granite in Cornwall and Devon, whereas germanium and gallium in sphalerite increased away from the granites. The distances involved in this lateral zoning are large, spanning tens of miles.

Schroll (1953) found in the Bleiberg-Kreuth district in Austria, that four distinct ages of zinc sulfide could be distinguished both by megascopic character and trace element content. Such a distinction may be analogous to the distinction in cobalt content of sphalerite at the Hanover mine, or to the other groupings found in both the Central and Bingham mining districts, although no indication of an age difference has been found in the latter cases.

Auger (1941), and later Hawley (1952), in a study of trace elements in pyrite from Canadian gold mines, found vertical zoning within veins for a number of elements. Their trends show somewhat more regularity than those of the writer, possibly because of the more deep-seated character of the deposits, and the resulting greater uniformity of temperature gradient and less erratic nature of the mineralization process.

Russell, Farquhar and Hawley (1957) demonstrate the existence of two groups of galena in the Broken Hill, Australia, district on the basis of lead isotope ratios and trace element content. One group consists of samples of galena associated with the main zinc mineralization and has lead isotope ratios indicating common lead, whereas the other group occurs as fringe deposits with anomalous lead isotope ratios as well as different trace element content.

Broderick (1929) found a zoning in arsenic content of copper ore from the Lake Superior copper deposits. The zoning was vertical within ore horizons and lateral from one ore horizon to the next.

From the above brief summary of the literature, it can be seen that the grouping and zonal relations shown by the chalcopyrite and sphalerite from the Central and Bingham mining districts are not unique. Such relations may be present in many mining districts, particularly in the larger and more complex districts.

# TRACE ELEMENTS IN PYRITE AND OTHER HYDROTHERMAL MINERALS

Table 16 lists the trace element content of pyrite samples analyzed during this study. Abbreviations and symbols have the same meaning as in tables 8 - 11. The samples from the Central mining district were chosen to represent mines and ores from all parts of the district. A great deal of variability is evident in the values. The cobalt, nickel, manganese, and tin contents are probably more meaningful than other elements because these elements are relatively concentrated in pyrite compared to other sulfides and are less likely to be present as impurities. There is a suggestion that the cobalt content of samples from Chino averages higher than in samples from the zinc mines of the district, but more work is needed to show this definitely.

The pyrite samples from Bingham were selected to test variations in trace element content of pyrite from the B limestone at the U. S. mine. It was hoped that a vertical zoning would be present. Unfortunately, the content of most trace elements is so low, and the variations across the veins are so large (see samples BIN-679a, b, and d), that the investigation was discontinued.

Table 17 shows the trace element content of various other hydrothermal minerals. The analytical methods used for the silicate and carbonate minerals were special modifications of the procedures used for spectrographic analysis of rocks at the California Institute of Technology. This method is similar in procedure and sensitivity to that used by the U. S. Geological Survey (Gordon and Murata, 1952). For the sulfide minerals, the methods were modifications of the procedures used for chalcopyrite and sphalerite.

## Table 16

## Trace Elements in Pyrite

| | Ag | As | Bi | Cd | Co | Cu(%) | Cr | In | Mn | Mo | Ni | Pb | Sb | Sn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Central mining district | | | | | | | | | | | | | | |
| CEN-325 | 1 | - | 10 | - | 150 | 1 | - | - | 15 | - | 4 | 30 | - | - |
| CEN-293 | 2 | - | - | - | 5000 | >1 | - | - | 9 | 7 | 300 | 30 | - | - |
| CEN-92 | - | - | - | - | 5 | 0.001 | - | - | - | 3 | 3 | - | - | - |
| CEN-75 | 8 | - | - | - | 800 | >1 | - | - | 150 | 5 | 100 | - | - | - |
| CEN-8 | - | - | 10 | - | 1000 | * | * | * | 1500 | - | 800 | * | - | 5 |
| CEN-2 | - | - | - | - | 2000 | * | * | * | 70 | 50 | 400 | * | - | 10 |
| CEN-7 | 1 | 150 | - | - | 8000 | * | * | * | 30 | 40 | 800 | * | - | - |
| SR-17† | - | - | - | - | 400 | * | * | - | 10 | 40 | 400 | * | - | - |
| G-18 | 40 | - | - | - | 800 | - | - | - | 100 | - | 20 | 3000 | - | - |
| CEN-10 | 10 | - | 50 | - | 200 | * | * | * | 3000 | - | 60 | * | - | 5 |
| G-4 | 3 | - | 400 | - | 900 | * | * | * | 300 | - | 500 | * | - | - |
| CEN-6 | - | - | - | - | 40 | * | * | * | 3000 | - | 200 | * | - | - |
| G-6 | - | 2000 | 1 | - | 400 | * | * | * | 60 | - | 150 | * | 200 | 5 |
| CEN-199 | 150 | - | 150 | 60 | 1000 | - | - | - | 2000 | - | 70 | 10,000 | - | - |
| CEN-225 | 100 | - | 150 | - | 700 | 0.X | 100 | - | 1000 | - | 30 | 2000 | - | - |
| CEN-209 | 10 | - | 10 | - | 50 | - | 100 | - | 3000 | 3 | 60 | 1000 | - | 20 |
| CEN-204 | 9 | - | 10 | - | 100 | - | - | - | 900 | - | 150 | 1000 | - | - |
| CEN-5 | 100 | - | 10 | - | 200 | - | - | - | 300 | - | 150 | 400 | - | - |
| CEN-237 | 4 | - | 30 | - | 400 | - | - | - | 300 | 5 | 30 | 300 | - | - |
| OS-2 | - | - | 2 | - | 100 | * | * | * | 3000 | - | 400 | * | - | 10 |
| CEN-4 | 100 | 3000 | 200 | 20 | 2000 | * | * | * | 800 | - | 500 | * | - | 20 |
| CEN-13 | 1 | - | 50 | 100 | 400 | * | * | * | >5000 | - | 150 | * | - | 8 |
| CEN-17 | 30 | 200 | 150 | - | 5000 | * | * | * | 1000 | 1500 | 10,000 | * | - | 5 |
| CEN-16 | 3 | 2000 | 300 | - | 500 | * | * | * | 3000 | - | 300 | * | 90 | - |
| CEN-12 | 10 | 200 | - | 30 | 30 | * | * | * | 200 | - | 500 | * | - | - |
| CEN-20 | - | - | - | - | 3000 | * | * | * | 150 | - | 400 | * | - | 20 |

Table 16 (Cont.)

| | Ag | As | Bi | Co | Cu | Cr | Mn | Ni | Pb | Sb | Sn |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Bingham district | | | | | | | | | | | |
| BIN-679A | 100 | 500 | 200 | - | 10 | - | 90 | 4 | >3000 | - | - |
| BIN-679B | - | 700 | - | - | 8 | - | 15 | 3 | 200 | - | - |
| BIN-679D | - | - | - | - | 6 | - | - | - | 150 | - | - |
| BIN-681 | - | - | - | - | 8 | - | 150 | - | 200 | - | - |
| BIN-682 | 30 | 3000 | - | - | >100 | - | 40 | 3 | >3000 | - | - |
| BIN-684 | 100 | 500 | - | - | 60 | - | 150 | 3 | 1500 | - | - |
| BIN-686 | 4 | 1000 | - | - | 8 | - | 30 | - | 700 | - | - |
| BIN-688 | 6 | 700 | - | - | 20 | - | 15 | 1.5 | 300 | - | - |
| BIN-690 | - | - | - | - | 3 | - | 10 | 5 | 100 | - | - |
| BIN-696 | 10 | 1500 | - | - | >100 | 90 | - | - | 150 | - | - |
| BIN-698 | 90 | 400 | 150 | - | 10 | - | - | 1 | >3000 | - | - |
| BIN-699 | - | 1000 | - | - | 10 | - | - | 2 | 400 | - | - |
| BIN-741 | - | - | - | - | 6 | - | - | 5 | - | - | - |
| BIN-744 | - | 500 | - | - | 7 | - | 200 | - | 30 | - | - |
| BIN-748 | - | 1500 | - | - | 9 | 40 | 60 | 1.5 | 60 | - | - |
| BIN-748 hp | - | 2000 | - | - | 15 | - | 50 | - | - | - | - |

## Table 17

### Trace Elements in Miscellaneous Hydrothermal Minerals

### A. Assorted Hydrothermal Minerals

| Sample | Mineral | Ba | Co | Cr | Cu | Mn | Mo | Ni | Sn | Sr |
|---|---|---|---|---|---|---|---|---|---|---|
| CEN-209 | calcite | - | 3 | 40 | 20 | 4000 | - | - | 15 | 300 |
| CEN-237 | calcite | - | 3 | 10 | 7 | 8000 | - | - | 20 | 100 |
| CEN-177 | calcite | - | - | - | 4 | 4000 | - | - | - | 300 |
| CEN-404 | calcite | 70 | - | 4 | 6 | 30 | - | - | - | >2500 |
| CEN-167 | hedenbergite | 15 | 8 | - | 30 | 1.3% | - | - | 20 | 200 |
| CEN-167 | garnet | - | - | 3 | - | 6000 | - | - | - | 200 |
| CEN-167 | ilvaite | - | 9 | 6 | 200 | 1.5% | - | 3 | 40 | 200 |
| CEN-190 | epidote | - | 10 | 2000 | 50 | 4000 | 40 | - | - | 1000 |

| Sample | Mineral | Y | Zn | Zr | In | Ga | V | Ti | Sc |
|---|---|---|---|---|---|---|---|---|---|
| CEN-209 | calcite | 30 | - | ? | - | - | * | - | - |
| CEN-237 | calcite | - | - | ? | - | - | * | - | - |
| CEN-177 | calcite | 150 | - | ? | - | - | * | - | - |
| CEN-404 | calcite | 15 | - | ? | - | - | * | - | - |
| CEN-167 | hedenbergite | - | 3000 | 50 | - | - | * | - | - |
| CEN-167 | garnet | - | - | - | - | - | * | - | - |
| CEN-167 | ilvaite | 10 | 4000 | 60 | - | - | * | - | - |
| CEN-190 | epidote | - | 2000 | 200 | - | 20 | 200 | 3000 | 10 |

Looked for but not found: Au, Ag, Bi, Cd, Ge, La, Mo, Nb, Pb, W.

### B. Galenas

| | Ag | Bi | Co | In | Mo | Sn | Sb |
|---|---|---|---|---|---|---|---|
| CEN-268 | <200 | 15 | 2 | - | - | - | 400 |
| CEN-531A | 7% | >1000 | 2 | - | - | - | - |
| CEN-577 | 4000 | >200 | 2 | - | - | 10 | - |
| BIN-576 | 3000 | >200 | 2 | 20 | - | 15 | 200 |
| BIN-596 | <200 | 20 | 1 | - | - | - | 3000 |
| BIN-704 | <200 | - | 1 | - | 2 | - | 900 |
| BIN-751 | <200 | 10 | 1 | - | - | - | 800 |

Looked for but not found: Ni, Ge, Ga.

Table 17 (Cont.)

C. Miscellaneous Sulfides

| | Mineral | Ag | Bi | Cd | Co | In | Mo | Sn | Sb |
|---|---|---|---|---|---|---|---|---|---|
| BIN-542 | molybdenite | X | X0 | - | ? | - | P | - | - |
| BIN-539 | enargite | 1000 | >1000 | 100 | - | 5 | 40 | 200 | P |
| BIN-525 | bornite | 150 | >1000 | - | 2 | - | 200 | 70 | - |

| | Mineral | Ni | Pb | Re | W | Ge | Mn |
|---|---|---|---|---|---|---|---|
| BIN-542 | molybdenite | X0 | X00 | P | P | ? | - |
| BIN-539 | enargite | 70 | X00 | - | - | 30 | 800 |
| BIN-525 | bornite | 90 | X | * | * | - | - |

P = Present

The four calcites were analyzed mainly to test the hypothesis that hydrothermal calcite at Hanover contained cobalt which might otherwise have entered sphalerite. CEN-209 and 237 are hydrothermal calcites associated with low-cobalt sphalerite, CEN-177 is a partly recrystallized limestone adjacent to an ore body, and CEN-404 is a sample of Hanover limestone from several miles east of the district. The hypothesis was rejected on the basis of the analyses.

The four silicate minerals were analyzed to check on the possibility of contamination of the sphalerite samples by these minerals, and the results indicate that significant contamination is improbable.

The galenas and other sulfides were analyzed for similar reasons. Detectable amounts of silver and bismuth can clearly be added to samples by the presence of a percent or two of galena. The large range of silver and bismuth contents within both districts is also notable.

## TRACE ELEMENTS IN IGNEOUS ROCK MINERALS

It was initially planned to investigate the chalcophile trace element content of igneous rocks associated with the sulfides in hopes of finding out whether any correlation existed between the trace element content of the rocks and that of the hydrothermal minerals. A start on this program was made in the Central mining district, but much more remains to be done.

Three rocks from the district were investigated. They are the porphyritic facies of the Hanover-Fierro granodiorite (CEN-395), the equigranular facies of the same stock (CEN-389), and the Santa Rita granodiorite (CEN-145). In addition magnetite from a sample of the late quartz diorite porphyry (CEN-251) has been analyzed for zinc. For additional petrologic information on these rocks see Schmitt (1939), Kerr et al (1950), Belt (1955), and Hernon et al (1956). Trace element analyses and modes of the rocks are shown in table 18.

One of the most difficult problems in the study of the chalcophile trace element content of rocks is the significance of alteration. In this study an attempt has been made to use only the freshest possible rocks, but in a mining district fresh rocks are not easy to collect. Some alteration was observed in all the rocks. In CEN-395 and 389 the alteration was very slight, and most or all of it can be attributed to deuteric or supergene effects. In CEN-145 and 251 alteration is more obvious but still relatively slight. An attempt was made to handpick the altered-appearing grains from the mineral separates, and the analyzed material is believed to be as fresh as can be obtained. The minerals were separated by sizing, heavy liquids, and a Frantz magnetic separator, with precautions to avoid heavy metal contamination. The spectrographic analyses were done by modifications of the rock analysis method as previously discussed for the

## Table 18

## Trace Elements in Igneous Rock Minerals

|  | Mineral | As | Ba | Cu | Co | Ga | Cr | F% | La |
|---|---|---|---|---|---|---|---|---|---|
| CEN-395 | biotite | - | 3000 | 90 | 40 | * | 15 | 0.40 | - |
| CEN-395 | biotite | - | 2000 | 150 | 40 | * | 10 | * | - |
| CEN-145 | biotite | - | 4000 | 15 | 40 | * | 20 | 0.40 | - |
| CEN-145 | biotite | - | 4000 | 15 | 40 | * | 20 | 0.40 | - |
| CEN-395 | hornblende | - | 50 | 20 | 30 | * | 20 | 0.30 | - |
| CEN-395 | hornblende | - | 70 | 20 | 20 | * | 15 | 0.40 | - |
| CEN-389 | hornblende | - | 40 | 30 | 30 | * | 10 | 0.30 | - |
| CEN-395 | sphene | 1000 | 10 | 100 | 20 | * | 6 | * | 400 |
| CEN-395 | apatite | * | - | - | - | - | - | * | 4000 |
| CEN-145 | apatite | * | - | - | - | - | - | * | 3000 |
| CEN-389 | potash feldspar | * | 2000 | 9 | - | 8 | - | * | - |
| BIN-534 | rock | * | * | 200 | - | 10 | * | * | * |
| BIN-515 | rock | * | * | 2000 | 20 | 15 | * | * | * |
| CEN-389 | magnetite | * | * | * | * | * | * | * | * |
| CEN-251 | magnetite | * | * | * | * | * | * | * | * |
| CEN-365 | magnetite | * | * | * | * | * | * | * | * |

|  | Mineral | Nb | Mn | Mo | Ni | Pb | Sc | Sn |
|---|---|---|---|---|---|---|---|---|
| CEN-395 | biotite | - | 1500 | - | 20 | - | 10 | - |
| CEN-395 | biotite | - | 1500 | - | 30 | - | 5 | - |
| CEN-145 | biotite | - | 900 | - | 40 | - | 6 | - |
| CEN-145 | biotite | - | 900 | - | 40 | - | 6 | - |
| CEN-395 | hornblende | - | 3000 | - | 15 | - | 40 | - |
| CEN-395 | hornblende | - | 3000 | - | 10 | - | 40 | - |
| CEN-389 | hornblende | - | 3000 | - | 20 | - | 40 | - |
| CEN-395 | sphene | 500 | 700 | 10? | * | - | - | 150 |
| CEN-395 | apatite | * | 1500 | - | - | - | - | - |
| CEN-145 | apatite | * | 300 | - | - | - | - | - |
| CEN-389 | potash feldspar | * | 150 | - | - | - | - | - |
| BIN -534 | rock | * | 50 | - | 50 | - | * | - |
| BIN-515 | rock | * | 100 | - | 60 | - | * | - |
| CEN-389 | magnetite | * | * | * | * | * | * | * |
| CEN-251 | magnetite | * | * | * | * | * | * | * |
| CEN-365 | magnetite | * | * | * | * | * | * | * |

Table 18 (Cont.)

| | Mineral | Sr | Ti | V | W | Y | Zr | Zn |
|---|---|---|---|---|---|---|---|---|
| CEN-395 | biotite | 150 | 6000 | 200 | - | 15 | 300 | 200 |
| CEN-395 | biotite | 15 | 8000 | 200 | - | - | 10 | 200 |
| CEN-145 | biotite | 5 | 6000 | 200 | - | - | 15 | 150 |
| CEN-145 | biotite | 5 | 6000 | 200 | - | - | 20 | 150 |
| CEN-395 | hornblende | 100 | 2000 | 200 | - | 50 | 90 | - |
| CEN-395 | hornblende | 70 | 3000 | 150 | - | 70 | 80 | - |
| CEN-389 | hornblende | 50 | 2000 | 150 | - | 50 | 50 | - |
| CEN-395 | sphene | 40 | major | 300 | 500 | 1500 | 9000 | - |
| CEN-395 | apatite | 600 | - | - | * | 800 | - | - |
| CEN-145 | apatite | 500 | - | - | * | 700 | - | - |
| CEN-389 | potash feldspar | 800 | 150 | 30 | * | - | - | - |
| BIN-534 | rock | * | * | * | * | * | * | - |
| BIN-515 | rock | * | * | * | * | * | * | - |
| CEN-389 | magnetite | * | * | * | * | * | * | 300 |
| CEN-251 | magnetite | * | * | * | * | * | * | 900 |
| CEN-365 | magnetite | * | * | * | * | * | * | 200 |

Looked for but not found: Cd, Ag, In, Ge, Sb.

Modes of Rocks

| | CEN-395 | CEN-145 | CEN-389 |
|---|---|---|---|
| Plagioclase | 34.3 | 36.2 | 60.3 |
| Groundmass | 48.3[*] | - | - |
| Hornblende | 10.7 | 6.4 | 15.2 |
| Biotite | 2.2 | 2.4 | - |
| Quartz | 1.2 | 21.1 | 9.6 |
| Magnetite | 1.3 | 0.8 | 2.4 |
| Orthoclase | 0.6 | 30.1 | 10.9 |
| Apatite | 0.3 | 0.2 | 0.5 |
| Sphene | 0.2 | 0.2 | 0.8 |
| Miscellaneous | 0.9 | 2.6 | 0.3 |
| | 100.0 | 100.0 | 100.0 |

[*] Composed largely of quartz and orthoclase, with probably some plagioclase.

hydrothermal silicates. Analyses of two size fractions or magnetic separates were made of several of the biotites and hornblendes.

The analyses are believed to indicate the level of trace element content in the various minerals of the rocks and the partition of elements between minerals to be expected in rocks of this type. Data of this type are relatively meager in the literature up to now.

In addition, the analyses suggest some lines of investigation which seem worthy of further work. In comparing the analyses of biotite from the Hanover-Fierro and Santa Rita stocks, the only significant difference is found in the copper content of 90-150 ppm. and 15 ppm. respectively. This difference is of possible significance because of the association of a porphyry copper deposit with one stock and not with the other. The similarity in content of other trace elements in the biotites and in the apatites, as well as the similarity in chemical composition, modal composition, texture, and age relations of the rocks all suggest that the original magmas were probably closely similar in composition. If so, it is interesting to speculate that the difference in copper content is somehow related to the presence of copper mineralization in the Santa Rita stock.

The difference in zinc content of the magnetite from CEN-395 and 251 (300 and 900 ppm. respectively) is also of interest because here again a mineralization (in this case zinc) is spatially and temporally more closely related to the rock with the lower content of zinc in magnetite.

If the kinds of differences mentioned above should prove to be real, they seem to be of fundamental importance in the theory of hydrothermal ore deposits, and also of possible application as a prospecting tool. Further work of this type is strongly recommended.

# SUMMARY AND CONCLUSIONS

The purpose of this study was to determine the variability in the trace element content of sulfide minerals and to investigate the causes of any variations found. The method has been to study two mining districts, the Central mining district in New Mexico and the Bingham mining district in Utah, starting with the variations observed in single crystals and polished sections, and working up through ore bodies and mines to the district as a whole.

Investigation of variability within single crystals and single polished sections shows that the trace element content of small chalcopyrite specimens is in general uniform. In sphalerite, some elements are homogeneously distributed and others are not. In some sphalerite specimens showing significant variations of several trace elements, the variations in one element show no correlation with the variations of other elements. This lack of correlation indicates that the variations are not caused by a single factor such as temperature, as has been proposed by many previous workers. Changes in composition of the ore fluid as well as in temperature, pressure, and degree of equilibrium are all probably involved in producing the variations within single crystals and small samples.

Several studies of trace elements within single ore bodies indicate that appreciable variability occurs in both sphalerite and chalcopyrite within units of this size.

The geographic distribution of trace element values in chalcopyrite from the Central mining district indicates that chalcopyrite from certain deposits or groups of deposits contains a consistently different trace element content than other groups of deposits in the district. Five such groups have been distinguished as a result of work in the district. The deposits within several of the groups are characterized by similar geologic characters as well as geographic position, but in other groups a variety of geologic environments are represented in a single group.

Among the sphalerite samples from the Central mining district, two or possibly three groups can be distinguished on the basis of cadmium content. The groups defined by trace element content of sphalerite are consistent with those for chalcopyrite in the areas where specimens of both minerals were available.

Within the main group of sphalerites from the district, zonal changes in the average content of certain trace elements can be discerned. Cobalt and manganese decrease away from the igneous centers, whereas gallium increases. The iron content also decreases. Similar zonal changes in the Zn/Pb ratio and the silver content of ores exist. For any small area there is a relatively large spread in the content of most trace elements, and many samples are necessary to show the zoning, but lateral changes in the mean values seem undeniable.

At the Hanover mine, the association and paragenesis of sphalerite specimens of lower than average cobalt content indicate that this sphalerite was deposited late in the mineralization process. A trend toward decreasing cobalt content with time appears to have existed, but the single crystal studies make it clear that this was only a trend within which considerable fluctuations took place.

At Bingham it is possible to make a distinction between the chalcopyrite from the disseminated ore of the Utah Copper stock and the limestone replacement ores of the peripheral sediments on the basis of indium and manganese contents. Within the stock, the content of silver, bismuth, indium, and possibly nickel tends to be higher in samples containing bornite, chalcocite, or digenite. A correlation of low tin content with replacement chalcopyrite (in contrast to vein chalcopyrite) also appears to exist.

In the sphalerite samples from Bingham, two groups of samples are indicated on the basis of differences in the gallium and iron contents and the relationships between these two elements and tin. Within any one structural unit all the sphalerite generally belongs to either one group or the other, although both groups are found relatively close together.

The tin and iron contents of sphalerite from the B limestone in the United States mine show a poorly developed vertical zoning. The tin content increases and the iron content decreases upward in the structure. A vertical zoning can also be found in the data for tin content of all the sphalerites from the U. S. mine, but in this case the presence of samples from both of the groups makes the interpretation uncertain.

A lateral zoning in the gallium content of the samples from the U. S. mine is also apparent, but here again the presence of both the groups confuses interpretation.

Consideration of the mode of occurrence of trace elements in sulfides is believed to be important in understanding the causes of trace element variations. Several kinds of substitution in the crystal lattice are possible. In addition, trace elements may occur in flaws in the crystal, as adsorbed constituents, and as trace minerals. The properties of defect structures, already known in the case of pyrrhotite and chalcopyrite, are suggested as a possible explanation for trace element occurrences which were previously explained by coupled substitution, such as gallium (coupled with arsenic) in sphalerite.

In discussing the causes of trace element variations in hydrothermal minerals, it is believed that many previous writers have overlooked the fact that ore deposition takes place in an open system, possibly under non-equilibrium conditions, and that changes in the composition of the ore fluid probably take place with time. Theoretical and experimental considerations indicate that changes in temperature, composition of the ore fluid, and degree of chemical equilibrium are possible causes for appreciable variation in the trace element content of hydrothermal minerals. Pressure is probably a relatively unimportant factor. Variations in the trace element content of the hydrothermal fluid may be the result of processes occurring at the source of the fluid, during movement of the fluid from the source to the site of deposition, and at the site of deposition.

On the basis of the above considerations, several hypotheses are set up to explain the grouping found in the samples of sphalerite and chalcopyrite from both districts. It is concluded from consideration of geologic factors that differences in the composition of the ore fluid that deposited the minerals, probably originating at or near the source of the ore fluid, are responsible for the differences between groups. It is believed that a knowledge of the existence of groupings within a mine or district may assist in working out the geology and history of the deposit. The concept of groupings is also of potential significance in the exploitation of metals present in small amounts in a deposit.

The cause of the lateral zoning found in the two districts is less certain. Either a temperature gradient or concurrent changes in fluid composition and site of most intense mineralization seem plausible explanations of the available facts. For the vertical zoning in the B limestone, a temperature gradient seems the best explanation, but other explanations are possible. Zoning of trace element content is of possible application in discovering the centers or sources of mineralization in a district or mine.

A number of assumptions are shown to be involved in the use of Kullerud's (1953) phase diagram of the FeS-ZnS system for determining the temperature of deposition of sphalerite. Among the assumptions discussed are the correctness of the phase diagram, the pressure correction, equilibrium with pyrite rather than pyrrhotite, complications introduced by chalcopyrite, and deposition out of chemical equilibrium. Because of the possibility that one or several of the assumptions are not valid, the writer recommends that the temperatures derived from the iron content of sphalerite be regarded as minimum temperatures, that is, deposition took place at <u>or above</u> the temperature indicated by the iron content applied to the FeS-ZnS phase diagram. This conclusion is possible because failure of almost any of the assumptions results in sphalerite of lower iron content than given by the phase diagram, and thus results in a sphalerite giving a lower apparent temperature than the true deposition temperature. Several specimens or groups of specimens analyzed in the present study show that some of the above assumptions are not met in certain natural cases, and that the minimum temperature concept can still give useful information. Using this hypothesis, temperatures at the Cleveland mine in the Pinos Altos district are believed to have reached at least 600°C, at Hanover at least 550-600°C, at the Groundhog mine at least 350°C, and at Bingham at least 550°C. At the Cleveland mine and at Hanover these temperatures are consistent with temperatures derived from most other lines of evidence.

In order to find the number of samples needed to adequately determine the average trace element content of sulfides in a district, standard deviations of the analyses for a number of elements and districts have been calculated, using data from Burnham (1955), Fryklund and Fletcher (1956), and this study. The number of samples necessary is found from this data using an assumption of lognormal distribution. For most elements, four or more samples from a district are recommended, but fewer samples may be adequate for some purposes. The specimens should be selected in such a way as to be a valid sample of the district, and the possibility of grouping and zoning should be kept in mind in setting up the sampling procedure.

While the work of Burnham (1955) does not in general meet these recommendations, the agreement of Burnham's trends with other geologic features in Arizona and the similar findings of a European study are believed to indicate the correctness of the concept he proposed, namely, regional beltlike variations in the trace element content of sulfides. The causes of the regional variations are not as certain.

The phenomena of grouping and zoning as found in this study have also been found in a number of other trace element studies, and are probably relatively common within many mining districts, especially the larger and more complex ones. Details of the patterns differ from district to district however.

A few analyses of minerals from igneous rocks in the Central mining district suggest some interesting hypotheses concerning the content of chalcophile metals in igneous rocks associated with ore deposits, and indicate that information of significance might be gained from more intensive investigation of this subject.

# REFERENCES

Ahrens, L. H., 1954a, The lognormal distribution of the elements: Geoch. et Cosmoch. Acta, v. 5, p. 49-73; v. 6, p. 121-131.

Ahrens, L. H., 1954b, Quantitative spectrochemical analysis of silicates, a scheme of quantitative D.C. arc analysis of the silicate minerals, rocks, soils, and meteorites: London, Pergamon Press

Ahrens, L. H., and Liebenberg, W. R., 1950, Tin and indium in micas: Am. Min. v. 35, p. 571-578.

Allen, E. T., Crenshaw, J. L., and Johnson, J., 1912, The mineral sulfides of iron: Am. Jour. Sci., v. 33, p. 169-236.

Allen, V. T., and Fahey, J. J., 1953, Rhodonite, johannsenite, and ferroan johannsenite at Vanadium, New Mexico: Am. Min., v. 38, p. 883-890.

Allen, V. T., and Fahey, J. J., 1957, Some pyroxenes associated with pyrometasomatic zinc deposits in Mexico and New Mexico: Bull. Geol. Soc. Am., v. 68, p. 881-895.

Auger, P. E., 1941, Zoning and district variations of the minor elements in pyrite of Canadian gold deposits: Econ. Geol., v. 36, p. 401-423.

Barton, P. B. Jr., and Kullerud, G., 1957, Preliminary report on the system FeS-ZnS-S and implications regarding the use of the sphalerite geothermometer (abstract); Bull.Geol. Soc. Am., v. 68, p. 1699.

Belt, C. B., 1955, A petrographic and alteration study of the Hanover-Fierro intrusive, New Mexico: Columbia University master's essay.

Boutwell, J. M., Keith, A., and Emmons, S. F., 1905, Economic geology of the Bingham mining district, Utah, with a section on areal geology and an introduction on general geology: U. S. Geological Survey Professional Paper 38, 413 p.

Brewer, F. M., Cox, J. D., and Morris, D. F. C., 1955, The occurrence of germanium in blende: Geoch. et Cosmoch. Acta, v. 8, p. 131-136.

Broderick, T. M., 1929, Zoning in Michigan copper deposits and its significance: Econ. Geol., v. 24, p. 149-162, 311-324.

Buerger, M. J., 1934, The pyrite-marcasite relation: Am. Min., v. 19, p. 37-61.

Buerger, N. W., 1934, The unmixing of chalcopyrite from sphalerite: Am. Min., v. 19, p. 525-530.

Burnham, C. W., 1955, Metallogenic provinces of southwestern United States and northern Mexico: Ph.D. Thesis, California Institute of Technology, 180 p.

Butler, B. S., and Loughlin, G. F., 1920, The ore deposits of Utah: U. S. Geological Survey Professional Paper 111, 672 p.

Chayes, F., 1954, The lognormal distribution of the elements; discussion: Geoch. et Cosmoch. Acta, v. 6, p. 119-120.

Cochran, W. G., 1947, Some consequences when the assumptions for the analysis of variance are not satisfied: Biometrics, v. 3, p. 22.

Couilliette, J. H., 1943, Spectrographic determination of Ni and Cr in stainless steel: Ind. and Eng. Chem. Anal. Ed. v. 15, p. 732-734.

Devore, G. W., 1955, Crystal growth and the distribution of elements: Jour. Geol., v. 63, p. 471-494; The role of adsorption in the fractionation and distribution of elements: Jour. Geol., v. 63, p. 159-190.

Dieke, G. H., and Crosswhite, H. M., 1943, The use of iron lines as intensity standards: Jour. Opt. Soc. Am., v. 33, p. 425-434.

Dixon, W. J., and Massey, F. J., 1951, Introduction to statistical analysis: New York, McGraw Hill, 370 p.

Duriez, L. H., and Neumann, J. V., 1948, Geology and mining practice at the Bayard, New Mexico, property: Mining and Met., v. 29, p. 559-561.

Edwards, A. B., 1947, The textures of the ore minerals: Aust. Inst. Min. and Met., Melbourne, 185 p.

Edwards, A. B., 1955, Cadmium in the Broken Hill lode: Proc. Aust. Inst. Min. and Met., no. 176, p. 71-96.

Edwards, A. B., 1956, Manganese and iron in Broken Hill sphalerite: Proc. Aust. Inst. Min. and Met., no. 180, p. 97-117.

El Shazly, E.M., Webb, J. S., and Williams, D., 1957, Trace elements in sphalerite, galena, and associated minerals from the British Isles: Bull. Inst. of Min. and Met., v. 66, p. 241-271.

Eugster, H. P., 1955, The cesium-potassium equilibrium in the system sanidine-water: Carnegie Inst. of Washington Yearbook, no. 54, p. 112-113.

Fleischer, M., 1955, Minor elements in some sulfide minerals: Econ. Geol. Fiftieth Ann. vol., p. 970-1024.

Frondel, C., Newhouse, W. H., and Jarrell, R. F., 1942, Spatial distribution of minor elements in single crystals: Am. Min., v. 27, p. 726-745.

Fryklund, V. C., and Fletcher, J. D., 1956, Geochemistry of sphalerite from the Star mine, Coeur d'Alene district, Idaho: Econ. Geol., v. 51, p. 223-247.

Gilluly, J., 1932, Geology and ore deposits of the Stockton and Fairfield quadrangles, Utah: U. S. Geol. Survey Professional Paper 173, 191 p.

Golsdchmidt, V. M., 1954, Geochemistry: Oxford, Clarendon Press, 730 p.

Gordon, M., and Murata, K. J., 1952, Minor elements in Arkansas bauxite: Econ.Geol. v. 47, p. 169-179.

Gordon, L., and Rowley, K., 1957, Coprecipitation of radium with $BaSO_4$: Anal. Chem., v. 29, p. 34-37.

Haberlandt, H., 1952, Die Systematischen Grundlagen und die Fortschritte in der Erforshung der Spurenelemente als Geochemische Leitelemente in Mineralien und Erzen: Fortschritte der Mineralogie, v. 31, p. 76-89.

Hawley, J. E., 1952, Spectrographic studies of pyrite in some eastern Canadian gold mines: Econ. Geol., v. 47, p. 260-304.

Hernon, R. M., Jones, W. R., and Moore, S. L., 1953, Some geological features of the Santa Rita quadrangle, New Mexico: New Mexico Geol. Soc. Guidebook, Fourth Field Conference, p. 117-130.

Hernon, R. M., et al, 1956, Geologic map of the Santa Rita quadrangle, U. S. Geol. Survey, open file map.

Hunt, J. P., 1957, Rock alteration, mica, and clay minerals in certain areas in the United States and Lark Mines, Bingham, Utah: Ph.D. thesis, University of California (Berkeley).

Hunt, R. N., 1924, The ores in the limestones at Bingham, Utah: Trans. A. I. M. E., v. 70, p. 856-883.

Hunt, R. N., 1933, The Bingham mining district: 16th International Geological Congress Guidebook, Excursion C-1, The Salt Lake region, p. 45-56.

Hunt, R. N., and Peacock, H. G., 1948, Lead and lead-zinc ores of the Bingham District, Utah: in Symposiom on the geology, paragenesis, and reserves of the ores of lead and zinc, 18th Int. Geol. Cong., London, p. 92-96.

Kendall, M. G., 1955, Rank correlation methods, 2nd ed: New York, Hafner Pub. Co., 196 p.

Kerr, P. F., Kulp, J. L., Patterson, C. M., and Wright, R. J., 1950, Hydrothermal alteration at Santa Rita, New Mexico: Bull. Geol. Soc. Am., v. 61, p. 275-347.

Kniffen, L. M., 1930, Mining and engineering methods and costs of the Hanover-Bessemer Iron and Copper Company, Fierro, New Mexico: U. S. Bureau of Mines Inf. Circ. 6361, 20 p.

Kroger, F. A., 1940, Solid solutions in the ternary system ZnS-CdS-MnS: Zeits. Krist., v. 102, p. 132-135.

Kruskal, W. A., and Wallis, W. H., 1952, The use of ranks in one criterion variance analysis: Jour. Am. Statistical Assoc., v. 47, p. 583-621.

Kullerud, G., The FeS-ZnS system, a geological thermometer: Norsk. Geologisk. Tidskrift, v. 32, p. 61-147.

Lasky, S. G., 1936, Geology and ore deposits of the Bayard area, Central mining district, New Mexico: U. S. Geol. Survey Bull. 870, 144 p.

Lasky, S. G., 1942, Ground Hog mine, Central district, New Mexico: in Ore deposits as related to structural features, W. H. Newhouse, ed., Princeton Univ. Press, p.244.

Lasky, S. G., and Hoagland, A. D., 1948, Central mining district, New Mexico: in Symposium on the geology, paragenesis, and reserves of the ores of lead and zinc, 18th Int. Geol. Cong., London, p. 86-97.

Leroy, P. E., 1954, Correlation of copper mineralization with hydrothermal alteration in the Santa Rita porphyry copper deposit, New Mexico: Bull. Geol. Soc. Am., v. 65, p.739-768.

Lindgren, W., 1933, Mineral Deposits: New York, McGraw Hill, 1049 p.

Lindgren Volume Committee, 1933, Ore deposits of the Western States: A.I.M.E., New York, 797 p.

Miller, R. L., and Goldberg, E. D., 1955, The normal distribution in geochemistry: Geoch. et Cosmoch. Acta, v. 8, p. 53-62.

Mortimore, D. M., and Romans, P. A., 1952, X-ray spectroscopy as a control method in the production of hafnium and zirconium: Jour. Opt. Soc. Am., v. 42, p. 673-677.

Mullen, D. H., and Storms, W. R., 1948, Copper Flats zinc deposit, Central mining district, Grant County, New Mexico: U. S. Bureau of Mines Report of Investigation, 4228, 8 p.

Myers, A. T., 1951, Improved cutting tool for spectrographic electrodes: Anal. Chem., v. 23, p. 209-210.

Noble, J. A., 1950, Ore mineralization in the Homestake gold mine, Lead, South Dakota: Bull. Geol. Soc. Am., v. 61, p. 221-252.

Ordonez, G., Baltosser, W. W., and Martin, K., 1955, Geologic structures surrounding the Santa Rita intrusive, New Mexico: Econ.Geol., v. 50, p. 9-21.

Paige, S., 1916, Description of the Silver City quadrangle: U. S. Geol. Survey, Geol. Atlas, folio 199, 19 p.

Peacock, H., 1948, An outline of the geology of the Bingham district; Mining & Met., v. 29, p. 533-534.

Russell, R. D., Farquhar, R. M., and Hawley, J. E., 1957, Isotopic analyses of leads from Broken Hill, Australia: Trans. Am. Geoph. Union, v. 38, p. 557-565.

Sales, R. H., and Meyer, C., 1948, Wallrock alteration at Butte, Montana: Trans. A.I.M.E., v. 178,p. 9-35.

Salutsky, M. L., Stites, J. C., and Martin, A. W., 1953, Fractionation of barium-radium mixtures as chromates: Anal. Chem., v. 25, p. 1677-1681.

Schaller, W. T., 1938, Johannsenite, a new manganese pyroxene: Am. Min., v. 23, p. 575-582.

Schmitt, H., 1935a, Structural association of certain metalliferous deposits in southwestern United States and northern Mexico: Trans. A.I.M.E., v. 115, p. 36-58.

Schmitt, H., 1935b, The Central mining district, New Mexico: Trans. A.I.M.E., v. 115, p. 187-208.

Schmitt, H., 1939, The Pewabic mine: Bull. Geol. Soc. Am., v. 50, p. 777-818.

Schmitt, H., 1942, Certain ore deposits in the southwest; Central mining district, New Mexico: in Ore deposits as related to structural features, W. H. Newhouse, ed., Princeton Univ. Press, p. 73-79.

Schroll, E., 1955, Uber das Vorkommen einiger Spurenmetalle in Blei-Zink-Erzen der ostalpiner Metall provinz: Tschermaks Mineralog. Petrog. Mitt., v. 5, p. 183-208.

Schroll, E., 1953, Uber Minerale und Spurenelemente, Vererzung, und Entstehung der Blei-Zink Lagerstatte Bleiberg-Kreuth, Karnten, Osterreich: Osterreich. mineralog. Ges. Mitt., Sonderheft no. 2, p. 1-60.

Schwartz, G. M., 1923, Chalmersite at Fierro, New Mexico: Econ Geol., v . 18, p. 270-277.

Shaw, D. M., 1952, The geochemistry of indium: Geoch. et Cosmoch. Acta, v. 2, p. 185-206.

Shaw, D. M., and Bankier, J. D., 1954, Statistical methods applied to geochemistry: Geoch. et Cosmoch. Acta, v. 5, p. 111-123.

Soule, J. H., 1947, Peerless lead-zinc mine, Grant County, New Mexico: U. S. Bur. of Mines, Report of Investigation 4044, 8 p.

Soule, J. H., 1948, West Pinos Altos lead-zinc deposit, Grant County, New Mexico: U. S. Bur. of Mines, Report of Investigation 4237, 8 p.

Spencer, A. C., and Paige, S., 1935, Geology of the Santa Rita mining area, New Mexico: U. S. Geol. Survey Bull. 859, 78p.

Storms, W. R., and Faust, J. W., 1949, Mining methods and costs at the Kearney zinc-lead mine, Central mining district, Grant County, New Mexico, U. S. Bur. of Mines, Inf. Circ. 7507, 11 p.

Stringham, B., 1953, Granitization and hydrothermal alteration at Bingham, Utah: Bull. Geol. Soc. Am., v. 64, p. 945-992.

Warren, H. V., 1935, Distribution of silver in base metal ores: Trans. A.I.M.E., v. 115, p. 81-88.

## Sample locations and mineralogy

In the following table are listed the location and mineralogy of samples from the Central mining district, New Mexico. The coordinates used are mine coordinates except in the case of the Cleveland mine.

Under Mineralogy the minerals identified in the hand specimen and polished section are listed (in the form of numbers appearing in the table below) in terms of relative abundance in the hand specimen. The most abundant mineral is listed first. Minerals present in amounts less than 5% are enclosed in parentheses.

### Key to mineral numbers

1. pyrite
2. sphalerite
3. chalcopyrite
4. galena
5. magnetite
6. garnet
7. hedenbergite
8. carbonate minerals
9. marcasite
10. pyrrhotite
11. hematite
12. quartz
13. clay
14. epidote
15. chlorite
16. bornite
17, covellite, chalcocite
18. rhodonite
19. amphibole
20. cosalite(?)
21. barite
22. tetrahedrite
23. opal
24. ilvaite
25. clay
26. forsterite
27. molybdenite
28. serpentine

## Sample locations and mineralogy

### Central mining district

| Sample | Mine and location in mine. | Mineralogy |
|---|---|---|
| CEN-2 | Chino, 2300S, 2700E 2650 level. | |
| -3 | Super Cobre mine, dump. | |
| -4 | Oswaldo #1 mine, dump. | |
| -5 | Hanover mine, dump | |
| -6 | Groundhog mine, dump. | |
| -7 | Chino mine, 1250S, 300E. | |
| 8 | Chino mine 22 H. 1262, 343'. | |
| -10 | Groundhog mine, dump of Star shaft. | |
| -12 | Slate Hill mine, dump. | |
| -13 | Oswaldo #2 mine, dump. | |
| -16 | Jim Fair mine, dump. | |
| -17 | Union Hill mine, dump. | |
| -20 | Copper Flats mine shaft #2, dump. | |
| 30 | Chino mine 580S, 1240E. | granodiorite, 3, 12. |
| 31 | Chino mine 580S, 1240E. | " 3, 12, 1, (5, 11) |
| 32 | Chino mine, 580S, 1240E | 3, 12, (1, 5, 11.) |
| 42 | Chino mine, 540S, 900E | granodiorite, 3, 1, 11, 12, 25. |
| 45 | Chino mine, 330S, 730E | " 3, 1, 12, (5, 9, 11). |
| 58 | Cleveland mine, 275N, 300E. | 12, 2, 1, (3, 8, 10). |
| 60 | Cleveland mine, 275N 460E. | 1, 2, 12, 10, 3, (8, 9, 20). |
| 61 | Cleveland mine, 200N, 110E. | 2, 1, 10, 12, (3, 8, 9). |
| 62 | Atlas #2 mine. | 12, 1, 2, 8 (3, 4, 10). |
| 63 | Atlas #2 mine. | 1, 2, 12, (3, 4, 9). |
| 64 | Houston-Thomas mine. | 2, (1, 12, 3, 4). |
| 65 | Chino mine 22H. 1263, 683'. 400S 1700W | 25, 14, 19, 1, 3, (5, 12) |
| 67 | Chino mine, 22 H. 1263 75' | 14, 25, (1, 3, 12, 17, 5). |
| 71 | Chino mine 22. 12[illegible] 555' | 12, 25, 1, 3 (5, 10). |
| 72 | Chino mine 22 H. [illegible]63 [illegible]2 | |

| Sample No. | Mine and location in mine. | Mineralogy. |
|---|---|---|
| CEN-15 | Chino mine, DDH. 1263 417'. | 12, 3, [illegible], 5, 14, (11). |
| 12 | Chino mine, 1400S, 240E. | 1. |
| 145 | " " , [illegible] N. [illegible] Pit. | Fresh granodiorite porphyry. |
| 147 | Pewabic mine, 4100N, 1615E, 160-104 | 2, 3, 7, 10, [illegible]. |
| 150 | " " 4725N, 1450E, 60-13 stope | 2, (6, 8, 1, 3, 4, 11). |
| 151 | " " 4750N, 1800E, 34 stope. | 2, 6, 12, (3, 5, 10, 11). |
| 152 | " " " " " | 2, [illegible], 1, 5, 7, 6, 11, 8, 12). |
| 153 | " " 3725N, 1675E, 300-7 stope. | 2, hornfels, (3, 5). |
| 158 | " " 300-33 stope. | [illegible] (12, 3). |
| 160 | Grant County mine. | 2, hornfels, (3, 4, 11, 12). |
| 162 | " " " . | 2, 7, (6, 1, 3, 4, 5, 8, 9, 10, 11, 12) |
| 167 | Hanover mine, 6940N, 4240E. | |
| 168 | Hanover mine, 7130N 4240E. | 2, 24, (3, 1). |
| 172 | " " 7180N 4260E | |
| 174 | " " 7320N, 4300E. | 2, 8, 12, (6, 7, 1, 5, 4). |
| 177 | " " 7880N, 3700E. | |
| 178 | " " 7700N, 3720E | 2, 7, 12, 8, (1, 4, 3, 11). |
| 180 | " " 5980N, 4500E. | 2, 6, (1, 3, 8). |
| 183 | " " 6090N, 4490E. | 2, 6, 7, (1, 11). |
| 185 | " " 6200N, 4560E. | 3, 1, 4, 2, (5, 6, 11). |
| 186 | " " 5750N, 4610E. | 2, 8, 4, (1, 12, 3, 11). |
| 188 | " " 5740N, 4700E. | 2, 8, 12, 1, (3, 4). |
| 189 | " " 5500N, 4760E. | 2, 14, (1, 3, 11). |
| 190 | " " 5580N, 4760E. | |
| 193 | " " 5320N, 4860E. | 2, 6, 5, (3, 4, 11, 1, 10). |
| 194 | " " 5190N, 4920E. | 2, 6, 7, (8, 1, 3, 11, 12). |
| 195 | " " 5220N, 4980E. | 2, 6, 7, (1, [illegible] |
| 196 | " " 4040N, 4980E. | [illegible] 3, 11, 8, 12). |

| Sample No. | Mine and location in mine. | Mineralogy |
|---|---|---|
| CEN-197 | Hanover mine, 4450N, 5090E. | 2, 6, (3, 8). |
| 198 | " " 4620N, 5880E. | 2, 1, 6, 7, 12, (5, 3, 11, 8, 20). |
| 199 | " " 4450N, 6430E. | 7, 2, (8, 12, 4, 3, 1). |
| 203 | " " 4150N, 6920E. | 2, 7, 8, 11, 6, (1, 3, 2). |
| 204 | " " 4040N, 7300E. | 1, 2, 12, 7, 4, 6, (3, 8, 15). |
| 207 | " " 3980N, 7370E. | 2, 7, (1, 6). |
| 208 | " " 4060N, 7770E. | 2, 1, 7, 3, 4, 8, 2. |
| 209 | " " 4120N, 8200E. | 8, 12, (3, 4). |
| 211 | " " 4670N, 8580E. | 2, 6, (1, 3, 4). |
| 212 | " " 4140N, 8460E. | 7, 2, 24, 1, (6). |
| 213 | " " 4740N, 8460E. | 7, 2, 6, (1, 3, 5, 11, 8, 12). |
| 213A | " " 4320N, 8430E. | 2, 8, 7 (1, 3, 4, 12, 25). |
| 214 | " " 4600N, 8670E | 2. |
| 21[illegible] | " " 3910N, 8030E. | 2, 8, 10, 4 (1, 11, 3). |
| 218 | " " 3850N, 7650E. | 2, 8, 12, 3, (2, 1). |
| 219 | " 3670N, 6240E. | 2, 6, (1, 3, 4, 10, 12). |
| 220 | " " 3680N, 6300E. | 2, 7, (3, 4, 12). |
| 221 | " " 3960N, 6460E. | 6, 2, 26, 2, (1, 3, 8, 4. |
| 222 | " " 3920N 6390E. | 1, 2, 12, (3, 4, 26). |
| 225 | " " 3570N, 4500E. | 2, 6, 7, 1, (3, 4, 11). |
| 227 | " " 4080N, 4820E. | 2, 1, 8, (3, 4, 12). |
| 229 | " " 4010N, 5060E. | 2, 6, 7, 3, (1, 8, 12). |
| 230 | " " 3800N, 5100E. | 2, 6, 7, 1, (1, 3). |
| 233 | " " 7210N, 3790E. | 2, 7, 3, 4. |
| 236 | Kearney mine 150N, 250E, 109 stope. | 2, 24, (6, 1, 3, 4, 5, 12). |
| 237 | " " 220N, 400E. | 6, 1, 2, 11, 12, (8, 3, 4. |
| 238 | " " 350N, 1400E. | 2, 6, (1, 3, 10, 8, 12). |
| 239 | " " 475N, 1800E 500 level. | 2, 6, (8, 11). |

| Sample No. | Mine and location in mine. | Mineralogy |
|---|---|---|
| CEN-240 | Kearney mine, 350N, 2050E, 500 level. | 2, 7, 6, (1, 3, 4, 12). |
| 241 | " " 475N, 1075E, 500 level. | 2, 7, 1, 8, 9, 25, (12, 3, 4). |
| 243 | Pearson mine, dump | 5, 6 12, 3, 1, 8. |
| 251 | Small quarry west of Central-Bayard highway near Central. Late quartz diorite porphyry. | |
| 253 | Groundhog mine, 1850 level. | 2, 7, 8 3 4, (1, 12). |
| 256 | " " " " | 2, 3, 4, (1, 8, 7). |
| 257 | " " " " | 2, 12, 5, (13, 8, 4, 11, 16). |
| 261A | " " " " | 3, 1, 2 (4, 12). |
| 262A | " " " " | 2, 12, 4 3, 1, (11). |
| 263A | " " " " | 12, 2, 3, 1, 4, 25, (8). |
| 264 | " " " " | 2, 4, 1, (3). |
| 265 | " " 1830 level. | 2, 1, 4, 8, (3). |
| 266 | " " 1800 level. | 2, 4, (8, 1, 3). |
| 267 | " " 1800 level | 2, 1, 7, (3, 4). |
| 268 | " " 1860 sublevel. | 1, 2, 3, 4, 7, (8). |
| 269 | " " 1860 sublevel. | 2, 7, 3, 4, (1, 8). |
| 271 | " " 1815 level. | 2, 3, (1, 4, 11). |
| 274 | " " 1980 level. | 2, 1, (13, 3, 4, 5). |
| 275 | " " 1980 level. | 2, 3, 4 (3, 1, 8). |
| 281 | Dump along road near W edge of SE ¼ of SW ¼ of Sect 6, T 17S, R 13W, Pinos Altos district. | |
| 285 | Cleveland mine, 200N, 125E. | 2, 12, 1, 3, (8, 6). |
| 286 | " " 180N, 160E. | 2, 1, 12, 3. |
| 287 | " " 350N 200E. | 2, 1, 12, 3, 8, (10). |
| 289A | " " 260N, 350E. | 2, 12, 3, 1, (9, 10, 25). |
| 290 | " " 220N 330E. | 12, 4, 8, 2, 1, (5). |
| 313 | Chino mine, 2920S, 170E | |
| 320 | Cleveland mine 340N, 110E. | 2, 3, 12 (1, 10, 8). |
| 321 | " " 850N 425E. | 2, 12, 5, 8, (1, 4, 20, 3). |

| Sample No | Mine and location in mine. | Mineralogy. |
|---|---|---|
| CEN-325 | Chino mine | |
| 334 | Tiptop shaft, dump, Pinos Altos district. | 2, 12, 3, 4, (8). |
| 337 | Aztec shaft, " " " " | 8, 3, 12, 2, (1, 4). |
| 338 | " " " " " " | 3, 4, 8, 12, 1, 2 |
| 341 | Shingle Canyon mine, dump. | 2, 4, shale, (1, 3). |
| 343 | Small pit north of Hanover Mtn. | 3, (11, 12). |
| 348 | Hobo mine, dump. | |
| 349 | Pit, southwest side Hanover Mtn, north of Fierro | 5, 6, 3, (1, 10, 12). |
| 354 | Super Cobre mine, dump. | 3, diorite, 8, (12). |
| 355 | Copper Flats mine, shaft #4, dump. | hornfels, 2, 6, 5, (12, 3, 11). |
| 355A | " " " " " " | 2, 5, 1, 3, 8, (11). |
| 356 | " " " " #2 " | 2, 5, (11, 1). |
| 358A | Continental mine, dump. | 2, 6, 8, 3, 1, (4, 11). |
| 358B | " " " | 6, 2, 12, 3, (11). |
| 359 | Republic iron mine, dump | 5, 2, 1, (8, 6). |
| 360 | Hearst mine, Pinos Altos district. | 1, 3, 12, (4). |
| 361 | Manhattan mine, Pinos Altos district. | 12, 2, 1, (3, 4). |
| 363 | " " " " " . | 2, 12, 21. |
| 368 | Snowflake Iron mine, dump | 5, 3, 8, 12, (2, 4). |
| 369 | " " " " | 5, 3, 1. |
| 371 | Ivanhoe mine, dump. | |
| 374A | Slate Hill mine, dump. | 8, 2, 4, 1, (3, 12). |
| 376 | Bullfrog mine, dump. | 1, 2, 12, 25 (3, 4). |
| 377 | Princess mine, dump. | 2, 6, (9, 1, 4 (3, 5, 10, 11). |
| 378 | Peerless mine, dump. | 2, 3, 4, 15. |
| 389 | Equigranular facies, Hanover-Fierro granodiorite 1500' N45W from Pewabic shaft. | |
| 390 | Oswaldo #2 Mine, dump. | 5, 1, 3, 12, (4, 6, 9, 11). |
| 395 | Porphyritic facies, Hanover-Fierro granodiorite, 400' S 70°E of NW cor. Sect 15, T17S, R12W in RR. cut. | |

| Sample No | Mine and location in mine. | Mineralogy. |
|---|---|---|
| CEN-404 | Hanover limestone, road cut on highway 180 near west edge of section 19, T17S, R11W. | 8. |
| 503 | Prospect pit [illegible] of Snowflake Iron mine. | 1, 3, 12, (2, 4, 11, 27). |
| 506 | Republic Iron mine, central area of pit. | 5, 28, (3, 1, 11). |
| 507 | " " " " " " ". | 5, 2, 12. |
| 513 | Bullfrog mine, ore bin. | 2, 12, 25, 1, (3, 4, 16). |
| 514 | Snowflake tunnel, about 300' from entrance. | 1, 3, 12, 5, (8, 9). |
| 516 | Oswaldo #2 mine, DDH. 0-2-170, 70' 2515N, 350W. | 5, 14, 1, 3. |
| 518 | " " " " 0-2-163, 25' 3180N, 1040W. | 1, 8, 2, (3, 6, 11). |
| 518A | " " " " 0-2-163, 49', 3180N, 1020W. | 2, 3, 6, 8, (12, 1, 4, 11). |
| 519 | " " " " 0-2-162, 38' 2650N, 300W. | 1, 2, 6, 7, (3). |
| 520 | " " " ", 0-2-144, 1', 2380N, 100W. | 2, 6, 12, 3, 1, 7, (24, 9, 4, 5, 9, 11). |
| 521 | " " " ", 0-2-143, 40' 2380N, 125W. | 6, 2, 12, 3, 4, [illegible] |
| 522 | " " " " 0-2-123, 91', 2580N, 0E. | 2, 7, (1, 3). |
| 528 | " " " " 1125A, 360', 2600N, 408E. | [illegible] |
| 530 | Hanover mine, 3790N, 7800E | 2, 12, (1, 3, 4, 11, 5, 8). |
| 531 | " " " " | See text. |
| 531A | " " " " | 2, 4, 12, 8, (1, 3, 11). |
| 533 | " " DDH-225, 61' | 7, 2, (1, 6, 3, 8, 11). |
| 534 | " " " 63' | |
| 535 | " " " 64' | |
| 536 | " " " 66' | 7, 2, 3, (1, 4, 11, 16, 17). |
| 537 | " " " 68' | 7, 2, 3, (1, 11, 16, 17). |
| 538 | " " " 72' | 2, 7, (3, 1, 7). |
| 538A | " " " 82' | 3, 6, 2, (1, 11, 12, 16, 17). |
| 539 | " " DDH-7, 16' | |
| 541 | " " 7150N, 3750E. | 2, (7, 1, 4, 8, 12). |
| 542 | " " " " | 2, 7, (8, 12). |
| 543 | " " " " | 2, 7, (1, 3, 4, 5, 11). |

| Sample No | Mine and location in mine. | Mineralogy. |
|---|---|---|
| CEN-544 | Hanover mine, 7150N, 3950E. | 2, 7, 24, (3, 4, 5). |
| 545 | " " " " | 2, (1, 3, 4). |
| 546 | " ", float. | 7, 2, (1, 3, 8, 12). |
| 547 | Small pit about 1500' S of Slate Hill mine, just north of main road. | 2, 12, (1, 3, 4). |
| 551 | Continental mine, ore pile | 5, 3, 6, 8, 1, (2). |
| 552 | " " " " | 3, 5, (6, 12, 1, 2, 11). |
| 553 | " " " " | 3, 6, 5, 8, (1, 2, 11, 12). |
| 554 | " " " " | 5, 3, (6, 2, 8, 1, 12). |
| 570 | Oswaldo #1 mine, DDH 0-404, 125', 3860N, 3440W. | 6, 3, (1, 2, 11). |
| 576 | Chino mine, 2000S, 500E. | granodiorite, 3, 12. |
| 577 | Kearney mine, 600 level. | 3, 2, 6, 1, (5, 9, 11). |
| 578 | " " 500 " , 89 stope. | 3, 2, 6, (1, 4, 8, 10, 11, 12) |
| 579 | Chino mine South wall South pit | qtz. monz. [illegible] |
| 580 | " " 800S, 1500E. | hornfels, (1, 3). |
|  |  |  |
|  |  |  |
|  |  |  |
|  |  |  |
|  |  |  |
|  |  |  |
|  |  |  |
|  |  |  |
|  |  |  |
|  |  |  |
|  |  |  |
|  |  |  |
|  |  |  |
|  |  |  |