

University of Montana

ScholarWorks at University of Montana

Graduate Student Theses, Dissertations, &
Professional Papers

Graduate School

1974

A sulfur isotopic and major element study of the lower Chester Vein Sunshine Mine Idaho

Richard Huntington Harris
The University of Montana

Follow this and additional works at: <https://scholarworks.umt.edu/etd>

Let us know how access to this document benefits you.

Recommended Citation

Harris, Richard Huntington, "A sulfur isotopic and major element study of the lower Chester Vein Sunshine Mine Idaho" (1974). *Graduate Student Theses, Dissertations, & Professional Papers*. 7559.
<https://scholarworks.umt.edu/etd/7559>

This Thesis is brought to you for free and open access by the Graduate School at ScholarWorks at University of Montana. It has been accepted for inclusion in Graduate Student Theses, Dissertations, & Professional Papers by an authorized administrator of ScholarWorks at University of Montana. For more information, please contact scholarworks@mso.umt.edu.

A SULFUR ISOTOPIC AND MAJOR ELEMENT STUDY OF THE
LOWER CHESTER VEIN, SUNSHINE MINE, IDAHO

By

Richard H. Harris

B.S., University of Nevada, 1972

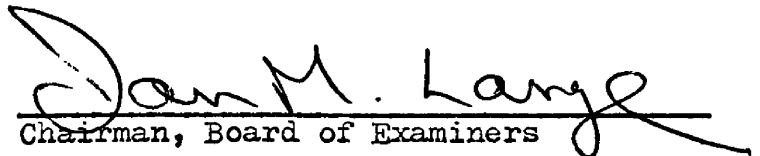
Presented in partial fulfillment of the requirements for the degree of

Master of Science

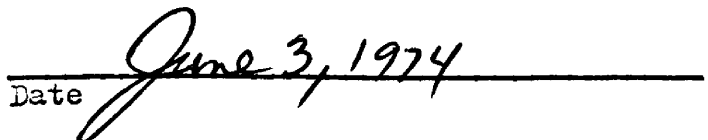
UNIVERSITY OF MONTANA

1974

Approved by:


Chairman, Board of Examiners


Dean, Graduate School


Date

UMI Number: EP38360

All rights reserved

INFORMATION TO ALL USERS

The quality of this reproduction is dependent upon the quality of the copy submitted.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if material had to be removed, a note will indicate the deletion.



UMI EP38360

Published by ProQuest LLC (2013). Copyright in the Dissertation held by the Author.

Microform Edition © ProQuest LLC.

All rights reserved. This work is protected against unauthorized copying under Title 17, United States Code



ProQuest LLC.
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106 - 1346

ACKNOWLEDGMENTS

The author is indebted to Mr. Donald Long, Chief Geologist, Sunshine Mining Co., for making this study possible, and Mr. Bill Kopp, assistant chief geologist, and Mr. Paul Hildenbrand, geologist for valuable assistance and suggestions during sampling. Many thanks are due Dr. Arnold Silverman for his interest and criticism of the thesis proposal. The author is very grateful to Dr. H. Roy Krouse and his excellent lab personnel for performing the mass spectrometry, helping with sample preparation, and making my stay at the University of Calgary Stable Isotope Laboratory an enjoyable one. In addition to reading the manuscript, Dr. Rudy Gideon gave the author a valuable awareness of the proper use and limitations of statistical methods. Dr. Jack P. Wehrenberg offered many helpful suggestions and Dr. Ian M. Lange, thesis advisor, provided valuable guidance and much needed encouragement throughout the study. Finally, a very special thanks goes to my wonderful wife, Pamela, whose help and moral support made the completion of this study possible.

TABLE OF CONTENTS

	Page
ACKNOWLEDGMENTS	ii
LIST OF TABLES	iv
LIST OF FIGURES	v
Chapter	
I. INTRODUCTION	1
II. GEOLOGY	6
Regional Geology	6
Geology of the Sunshine Mine	12
III. SAMPLE PREPARATION AND METHODS OF ANALYSIS	22
IV. ISOTOPIC AND ELEMENTAL RESULTS	26
V. DISCUSSION OF RESULTS AND SPECULATION ABOUT THE ORE-FORMING PROCESS	47
VI. SPECULATION ABOUT THE SOURCE OF THE VEIN CONSTITUENTS	58
VII. CONCLUSIONS AND RECOMMENDATIONS	62
REFERENCES	64
APPENDICES	
A. PHOTOMICROGRAPHS OF THE LOWER CHESTER VEIN ORE	70
B. SAMPLE DESCRIPTIONS AND ISOTOPE DATA	83
C. ATOMIC ABSORPTION OPERATING PARAMETERS	87

LIST OF TABLES

Table	Page
1. Sequence of Mineral Deposition in the Coeur d'Alene Mining District, Idaho	10
2. Elemental Analyses of Tetrahedrite	29
3. Comparison of Elemental Results—All Samples	35
4. Comparison of Elemental Results—Sample from the West	36
5. Comparison of Elemental Results—Sample from the East	36
6. Regressions which Yielded a Correlation Coefficient Greater than 0.10 (for elemental analyses)	38
7. Summary of Localized Elemental and Isotopic Trends for Tetrahedrite in Individual Raises	40
8. Comparison of Sulfur Isotopic Data	43
9. Linear Regression of Isotopic Data	43

LIST OF FIGURES

Figure	Page
1. Location of Coeur d'Alene Mining District	2
2. Mineral Belts	3
3. Generalized Longitudinal Section—Sunshine Mine	4
4. West Silver Belt	8
5. Generalized Section—Sunshine Mine	9
6. 3700' Level Plan	14
7. Modified Paragenetic Sequence for the Lower Chester Vein . . .	16
8A&B. Euhedral Pyrite Relationships	17
9A&B. Arsenopyrite Relationships	18
10A&B. Tetrahedrite—Chalcopyrite Relationships	19
11. Longitudinal Section—Chester Vein (Sample Locations)	23
12. 4600' Level Plan (Relationship of J and H Veins to Chester Vein)	27
13. 5000' Level Plan (Relationship of K Vein to Chester Vein) . .	28
14-18. Location of Elemental Results	30-34
19. Location of Isotopic Results	41
20. Location of Isotopic Results	42
21. Permil S ³⁴ Values for Pyrite vs. Depth	44
22. Relative Vertical Change in Cu, Fe, Zn, Ag, Cd, and δS^{34} Td 5200 - 9 Raise	45
23. Sulfur Isotopic Enrichment Factors	49
24. Eh-pH Diagram with Fe-S-O Mineral Stability Fields and δS^{34} Contours	50
25. Tetrahedrite Permil Values by Level	54

CHAPTER I

INTRODUCTION

The Sunshine Mine is located in the Coeur d'Alene mining district, Fig. 1, about two miles up the Big Creek drainage east of Kellogg, Idaho (Fig. 2). The Sunshine Mine is the leading producer of silver and metallic antimony in the United States.

The purpose of this study was to investigate the possibility and significance of zonal variations in sulfur isotope and major element compositions of important sulfide minerals in a portion of the Chester Vein. Isotopic and major element zonations if present in specific mineral species could then be used to predict position within an ore shoot or proximity to a new undiscovered ore shoot. In addition, it was hoped that data would yield some new clues about the ore forming process and source of the vein constituents.

The Chester vein was selected because of its simple geometry, structure, mineralogy, textural characteristics and ready accessibility. Also, the considerable vertical and lateral extent of the vein provided an adequate sample distribution for detection of isotopic and elemental trends.

Approximately 40 samples were collected from 30 drift, raise and stope locations between the 4200 and 5200 levels (Fig. 3). Textural and mineralogical relationships were studied in polished section. S^{34}/S^{32} ratios were determined by mass spectrometry. The elemental analyses were

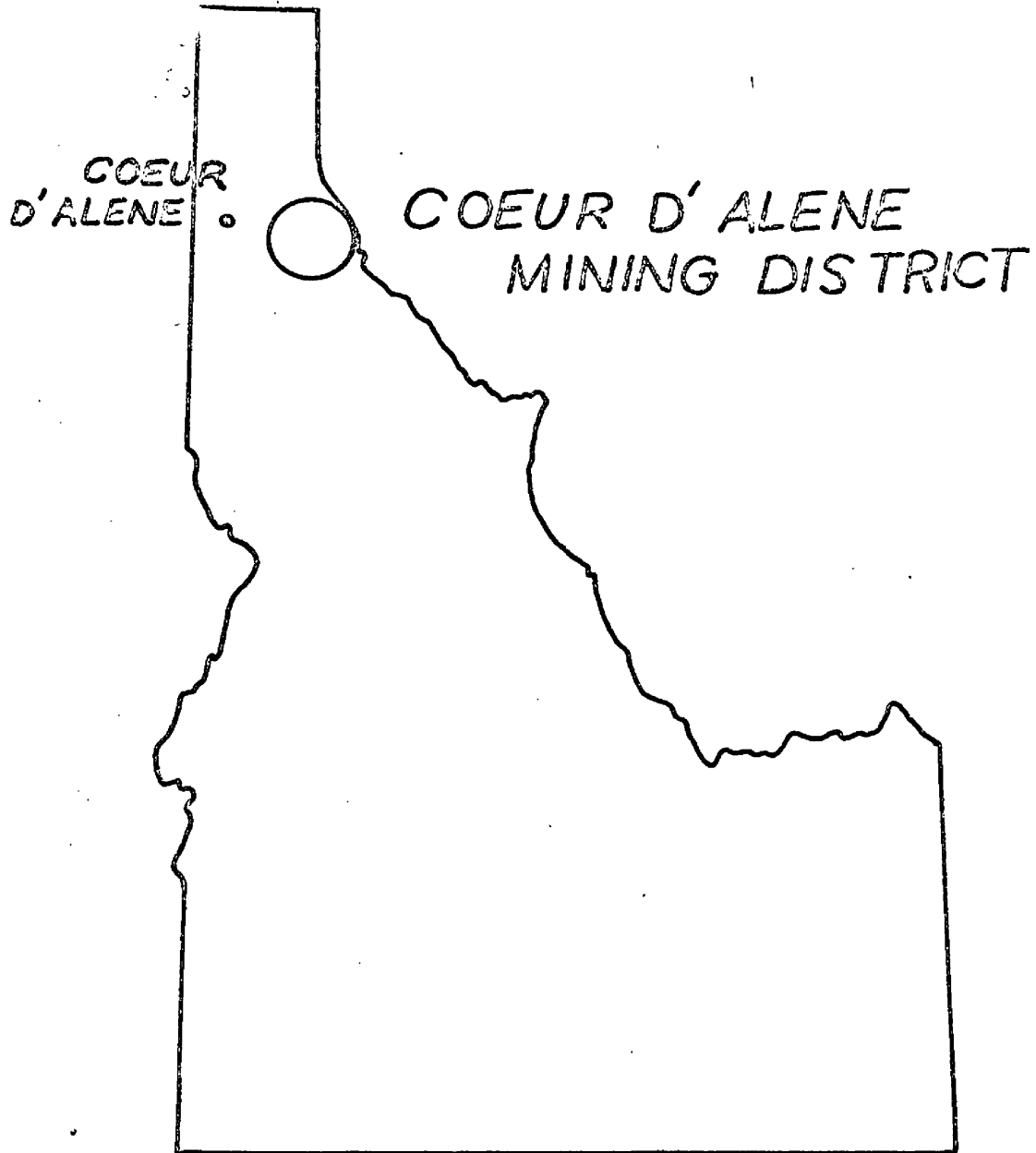


FIG. 1

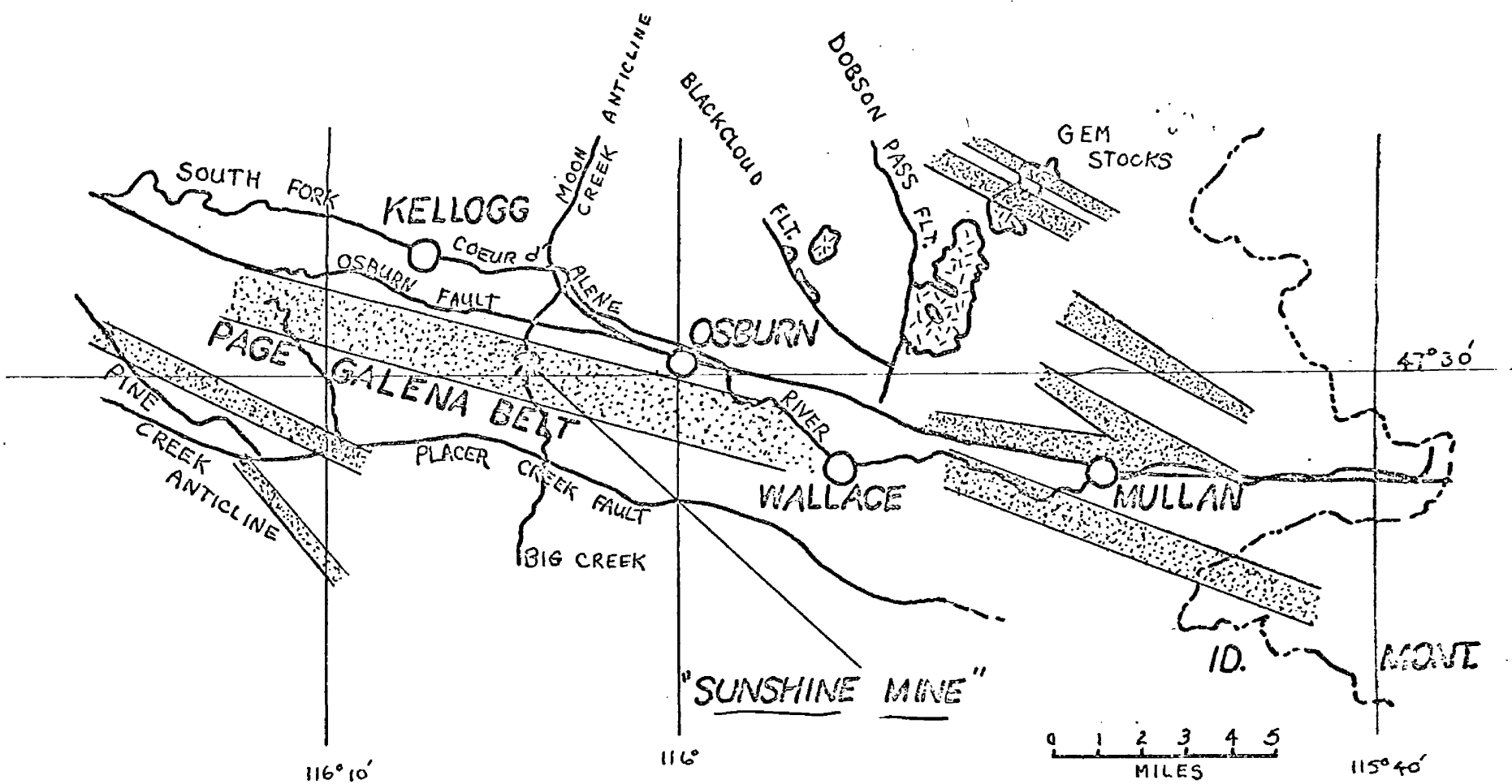


FIG. 2 MINERAL BELTS

AFTER HOBBS and FRYKLUND, 1968

GENERALIZED LONGITUDINAL SECTION - SUNSHINE MINE LOOKING EAST

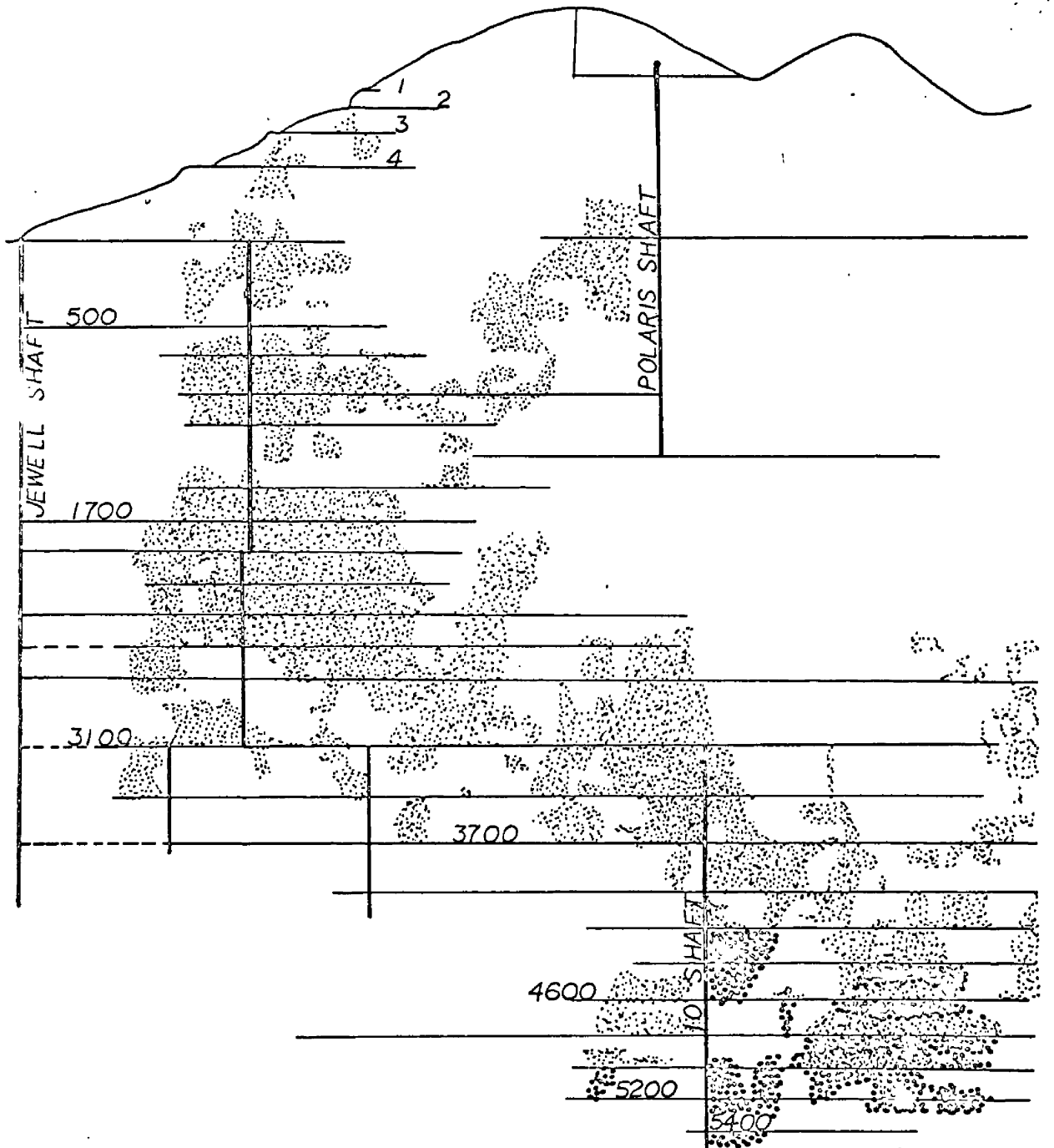


FIG. 3

0 500' 1000'

MINING COMPLETED
MINING IN PROGRESS

done with atomic absorption spectrometry. Finally, the data were examined statistically by digital computer using the Basic language.

A study of this type in the Coeur d'Alene district has not been published to date. Sorenson (1972) reported a 27 permil range in S^{32}/S^{34} ratios in sulfide samples from the Lucky Friday and other mines in the district but gave no specific details needed for proper interpretation of such results. Ault and Kulp (1960) report two δS^{34} values in galena of +3.2 and +5.4 from the 2800' and 3840' levels of the Sunshine Mine. Fryklund and Fletcher (1956) demonstrated an iron zonation in sphalerites from the Star Mine. Chan (1966), using qualitative and semi-qualitative analyses at the Galena Mine, was unable to demonstrate a systematic zonation of major elements in specific sulfide minerals. Bryan (1974) is presently conducting an elemental study of specific vein sulfides at the Lucky Friday Mine.

CHAPTER II

GEOLOGY

Regional Geology

The Coeur d'Alene mining district is located in the panhandle of northern Idaho and extends in an east-south-easterly direction for nearly 100 miles (Fig. 1). It has produced more than two billion dollars in silver, copper, lead and zinc since mining began in 1884. Detailed descriptions of the district geology can be found in Ransome and Calkins (1908), Umpleby and Jones (1923), Anderson (1940), Fryklund (1964), Hobbs and others (1965), and Hobbs and Fryklund (1968).

The district is occupied mainly by the Precambrian Belt series of fine-grained clastic sediments. These argillites, slates, and nearly pure quartzites have been slightly regionally metamorphosed. Their age has been established at 1400 m.y. (Long, Silverman, and Kulp, 1960).

The Belt series rocks have been intruded by the Cretaceous-aged Gem stocks (Fig. 2). They are predominately monzonite in composition, although the composition ranges from syenite to diorite. Tertiary diabase and lamprophyre dikes located along west-northwest trending faults commonly crosscut monzonite stocks and ore veins.

Structurally, the Coeur d'Alene district is located at the intersection of a northerly trending, broad anticlinal arch (the Trout Creek anticline), and the Lewis and Clark linement (locally called the Osburn fault) (Billingsley and Locke, 1941). The Osburn fault trends west-northwest (Fig. 2), and has approximately 16 miles of right lateral

displacement. North of the fault, the Belt sediments are moderately folded with northerly trending fold axes. South of the fault the folding is tighter and the axes trend westerly, with northern limbs commonly vertical or overturned (Fig. 4 and 5). Several periods of faulting have been superimposed on the folding. South of the Osburn fault, most major faults subparallel the Osburn fault, dip steeply to the southwest, and exhibit strike slip, normal, or reverse displacements. North of the Osburn fault, steeply dipping west-northwest and northerly trending faults predominate with reverse, normal or strike slip and reverse or normal displacements, respectively.

Fryklund (1964) outlined three periods of mineralization in the district—Late Precambrian, Late Cretaceous, and Tertiary. The sequence of mineral deposition is shown in Table 1. The Late Cretaceous or main period of mineralization has accounted for 98 percent of the production. The main period mineralization consists of tabular replacement veins along steeply dipping fault systems, which have usually experienced only small displacements. The replacement nature of the Coeur d'Alene ore deposits has been well documented by Fryklund (1964) and Chan (1966). These structurally related vein systems form a dozen subparallel mineral belts in the district which generally trend about $N65^{\circ}W$ (Fig. 2). The length of the mineral belts ranges from 1 to 14 miles, widths ranging from one-quarter to one and one-half miles.

Within mineral belts, ore shoots along shear systems may be from 1000 to 3000 feet wide. The dip length is usually greater than the strike length. Characteristically, ore bodies in the district are limited in

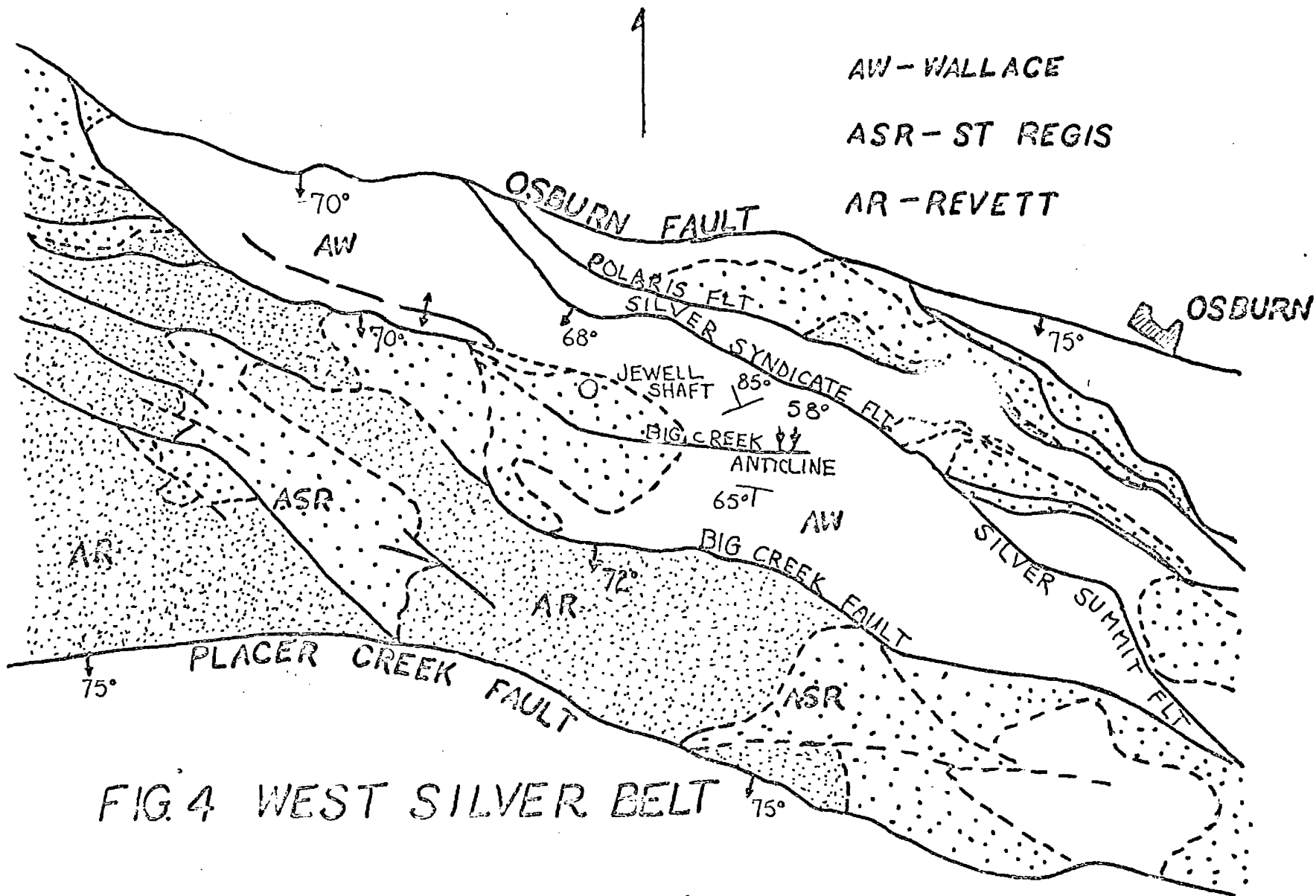
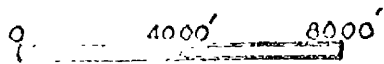
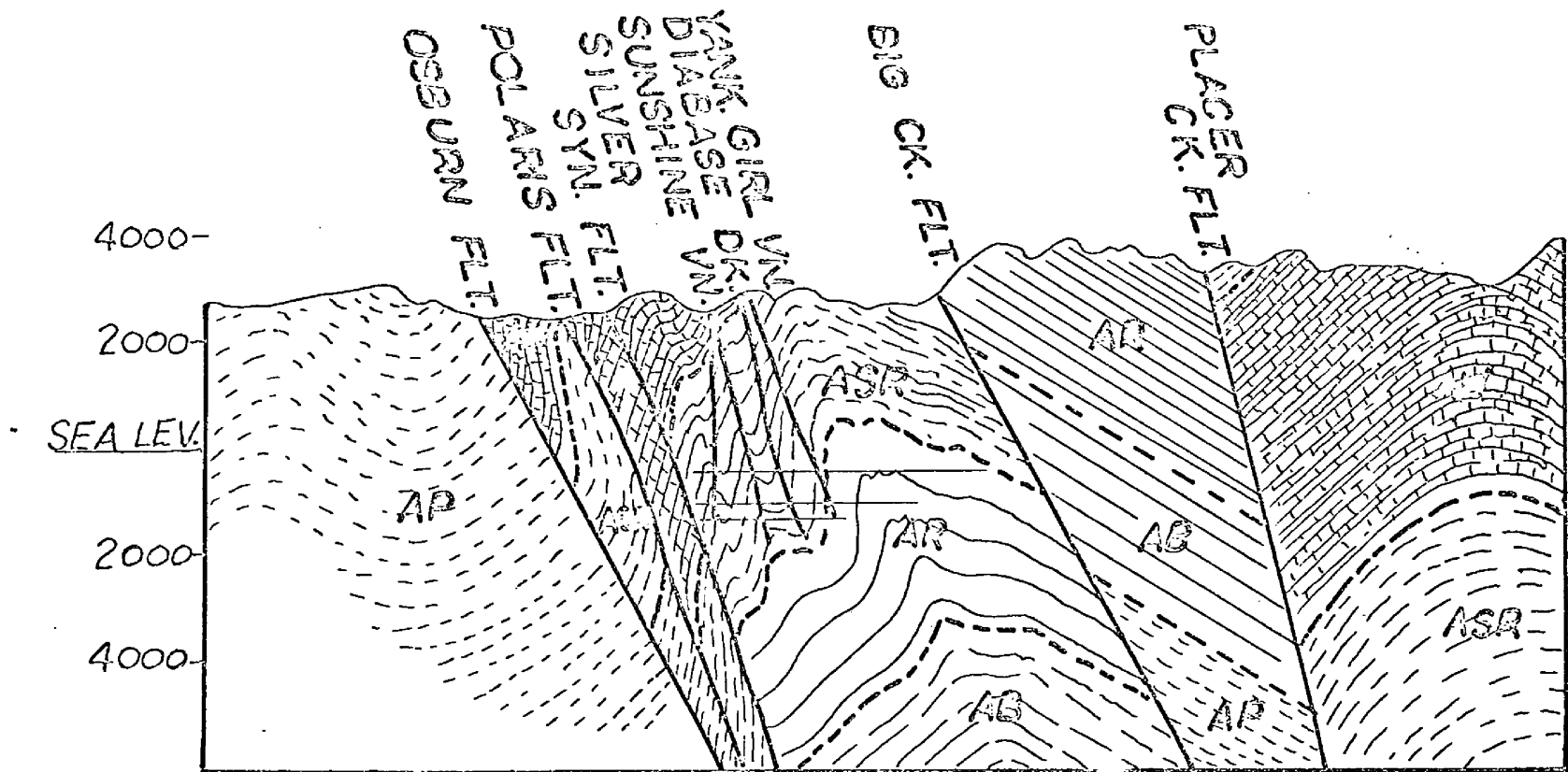


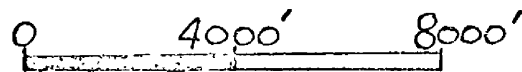
FIG. 4 WEST SILVER BELT



AFTER COLSON, 1961



GENERALIZED SECTION-SUNSHINE MINE
LOOKING EAST



- ASP-STRIPED PK.
- AW-WALLACE
- ASR-ST. REGIS
- AR-REVETT
- AB-BURKE
- AP-PRICHARD

AFTER COLSON, 1

FIG. 5

TABLE 1

SEQUENCE OF MINERAL DEPOSITION IN THE
COEUR D'ALENE MINING DISTRICT, IDAHO*

Precambrian Mineral Deposits

Disseminated arsenopyrite and pyrite
 Hydrothermal alteration (bleaching) of country rocks
 Uranium bearing veins

Late Cretaceous Mineral Deposits—Main Period of Mineralization

Country rock recrystallization (quartz)
 Silicate stages (biotite, garnet, amphiboles)
 Carbonate stage
 Barite stage
 Iron oxide stages (hematite, magnetite)
 Sulfide stages:
 Pyrite stage
 Arsenopyrite stage
 Sphalerite stage
 Tetrahedrite-chalcopyrite stage
 Galena stage
 Late sulfosalt stage

Tertiary Mineral Deposits

First period veins
 Sphalerite-galena veins
 Second period veins
 Stibnite
 Stibnite-scheelite
 Scheelite-gold
 Third period veins
 Quartz-dolomite-arsenopyrite-gold
 Other veins
 Quartz
 Calcite-pyrite

*(After Fryklund, 1964)

outcrop exposures. Hidden ore bodies with the tops of the ore shoots more than a thousand feet below the surface are common.

A variety of ore and gangue minerals occur throughout the district although only a few are abundant. The ore minerals deposited during the main period include sphalerite, galena, tetrahedrite and chalcopyrite (Table 1). The most abundant gangue minerals are siderite and quartz and locally ankerite. The main period ore and gangue minerals seem to have been deposited in separate stages of mineralization. A linear pattern of zoning is observed within individual mineral belts, beginning with chalcopyrite and tetrahedrite on the east, galena in the center, and sphalerite on the west. The major gangue minerals show no pattern of zoning. Only the early silicates and magnetite show a concentric distribution around the Gem stocks which lie north of the Osburn fault.

The age of the main period veins has been debated for some time. The most notable proponents of a Late Cretaceous age are Fryklund (1964) and Hobbs and Fryklund (1968). The Precambrian age of Long, Silverman, and Kulp (1960) is questioned on the basis of crosscutting evidence in the field. First, only one period of monzonite intrusive activity and related dike formation has been recognized. In eight mines, veins similar to main stage veins cut these dikes. Second, these veins also cut the contact metamorphic aureole and contain the same minerals, particularly the same silicate minerals, both inside and outside the aureole. Third, the veins are not located within the stocks themselves because at the time of intrusion the stocks were too plastic in character to fracture like the Belt sediments.

Zartman and Stacey (1971) favor a Precambrian age for the main period mineralization based on a single-stage lead isotope model. Cannon and others (1962) reported younger lead model ages for ore associated with the quartz monzonite North Gem stock. Ault and Kulp (1960) obtained one billion year old ages on two galena determinations from the Sunshine Mine. According to Zartman and Stacey (1971), Precambrian ages for uraninite associated with lead mineralization in the Sunshine Mine support the conclusion that the main stage veins formed synchronously with or soon after sedimentation of the Belt strata.

Intrusion of the Gem stocks may have redistributed existing vein material and possibly formed minor veins related to the stocks. Gott and Botbol (1971) recognized areas of high sulfur concentration which were coextensive with mineral belts and cut across monzonite stocks while mineral belts do not. Iron in the form of magnetite is normally common in the stocks while pyrite is common in the sulfur-rich portions of the monzonite stocks. They postulated that monzonite intruded portions of the mineral belt destroying the sulfides and using the sulfur to form pyrite. If veins which cut across monzonite dikes do not belong to the main period of mineralization (as Cannon and others, 1962, indicated), then the available data would indicate that the Gem stocks post-dated the main period of mineralization. If the lead isotope ages are accurate, the main period of mineralization is probably Precambrian in age.

Geology of the Sunshine Mine

The Sunshine Mine is located on the east end of the Page-Galena mineral belt in what is known as the "Silver Belt." The Silver Belt is

bounded on the north by the Osburn fault and on the south by the Placer Creek fault. Folded rocks of the Wallace, St. Regis, and Revett Formations outcrop in this block which has been sliced into narrow wedges by northwest trending, steeply south dipping normal and reverse faults. Within these wedges the Belt sediments are steeply folded, in some cases overturned to the north (Fig. 5, after Colson, 1961).

The Sunshine Mine is contained within the Revett and St. Regis Formations on the northern, overturned limb of the Big Creek anticline. Replacement veins occupy northwest trending faults which dip steeply (60° - 75°) to the south and generally parallel the axial plane of the Big Creek anticline (Fig. 5). Figure 6, after Colson, 1961, shows the distribution of the four main vein systems—Sunshine-Polaris, Silver Syndicate, Yankee Girl, and Chester found within the Sunshine Mine.

Ore shoots on these vein systems are characterized by massive, argentian tetrahedrite with subordinate amounts of pyrite, chalcopyrite and galena. The sulfides usually form stringers in massive siderite which in turn contains varying amounts of quartz.

Anderson (1940) described microscopic features of ore from the Sunshine Mine, presumably from the Sunshine Vein. Tibbs (1972) modified Anderson's paragenetic sequence to fit his observations of the Chester Vein. According to Tibbs (1972), pyrite and arsenopyrite were the first minerals to form and were followed by quartz which continued to form throughout subsequent mineralization. The main pulse of siderite deposition was next and it was followed by tetrahedrite and then galena. Bournonite often lies physically between galena and tetrahedrite grains and thus appears to be a reaction product between the two. Tibbs, as

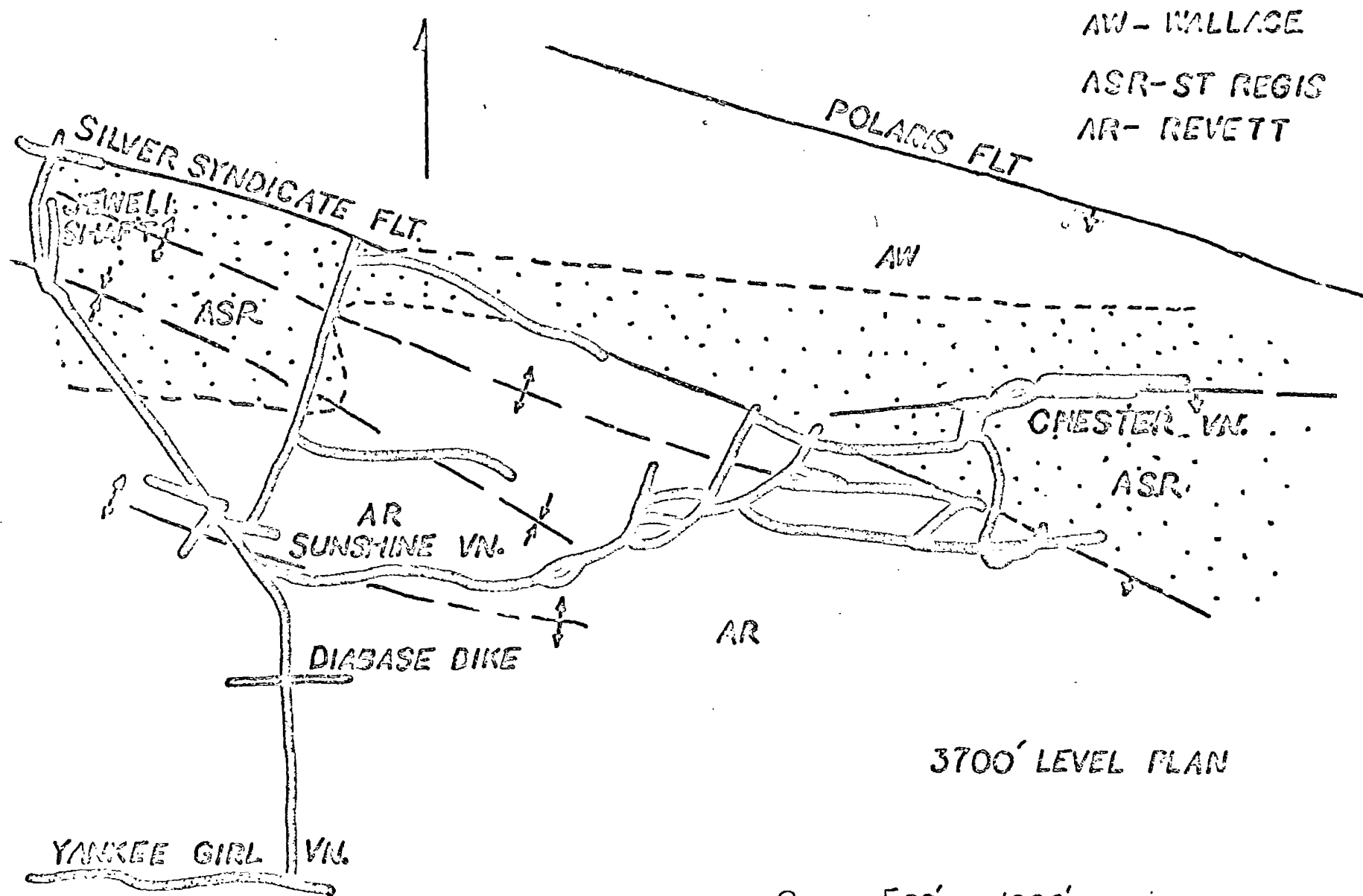


FIG. 6

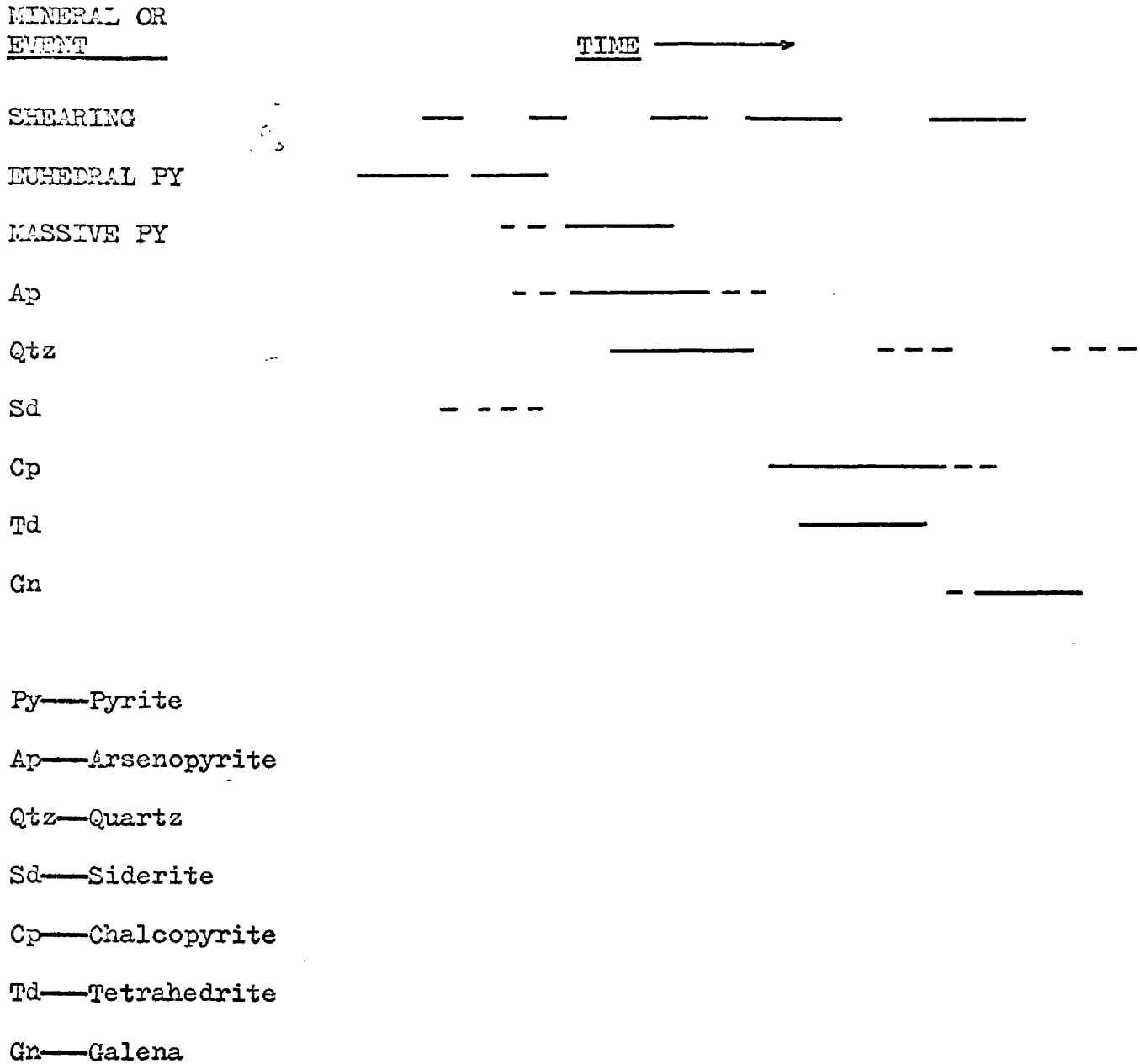
AFTER COLSON, 1961

well as this author observed boulangerite subsequent to tetrahedrite in hand specimens collected from lower levels.

An examination of 40 polished sections has led to a modification of Tibbs' paragenetic sequence (Fig. 7). Pyrite seems to have formed first as disseminated pyritehedrans in the wall rock (Fig. 8A). It was followed by shearing and introduction of minor amounts of siderite and cubic pyrite euhedra. Pyritehedrans close to these shears have been replaced by siderite and quartz (Fig. 8B). Veins of massive, allotriomorphic pyrite were observed cutting zones of disseminated pyrite euhedra. This stage of pyrite deposition may have accompanied cubic pyrite deposition but the evidence is inconclusive. Deposition of massive pyrite was accompanied by and succeeded by arsenopyrite deposition. Pyrite is commonly replaced by arsenopyrite (Fig. 9A), and the latter often forms trails of euhedra between siderite grains and cleavages (Fig. 9B) which replaces massive pyrite. Finally, evidence for tetrahedrite preceded by chalcopyrite is abundant (Fig. 10A). Chalcopyrite deposition continued during and after tetrahedrite deposition as indicated by ambiguous evidence for replacement of one by the other in the same specimen (Fig. 10B). The importance of exsolution, if present, could not be determined. Ramdohr (1969) has observed exsolved fahlore (tetrahedrite) in chalcopyrite and fine grains of chalcopyrite suggestive of exsolution in fribergite (tetrahedrite with 17 percent silver). However, exsolution is difficult to recognize in many ore minerals and can be easily confused with replacement features. No obvious exsolution patterns were observed. Photomicrographs showing other textural features and mineralogical associations are contained in Appendix A.

Figure 7

Modified Paragenetic Sequence
for the Lower Chester Vein



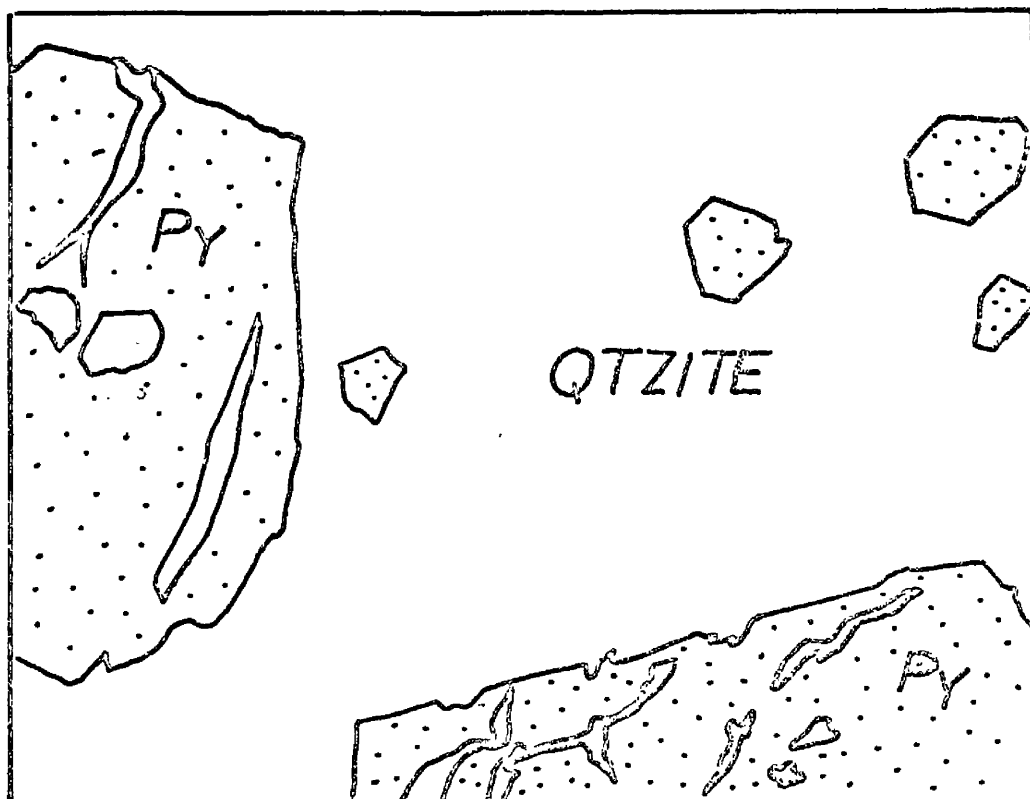


FIG. 8A

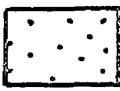
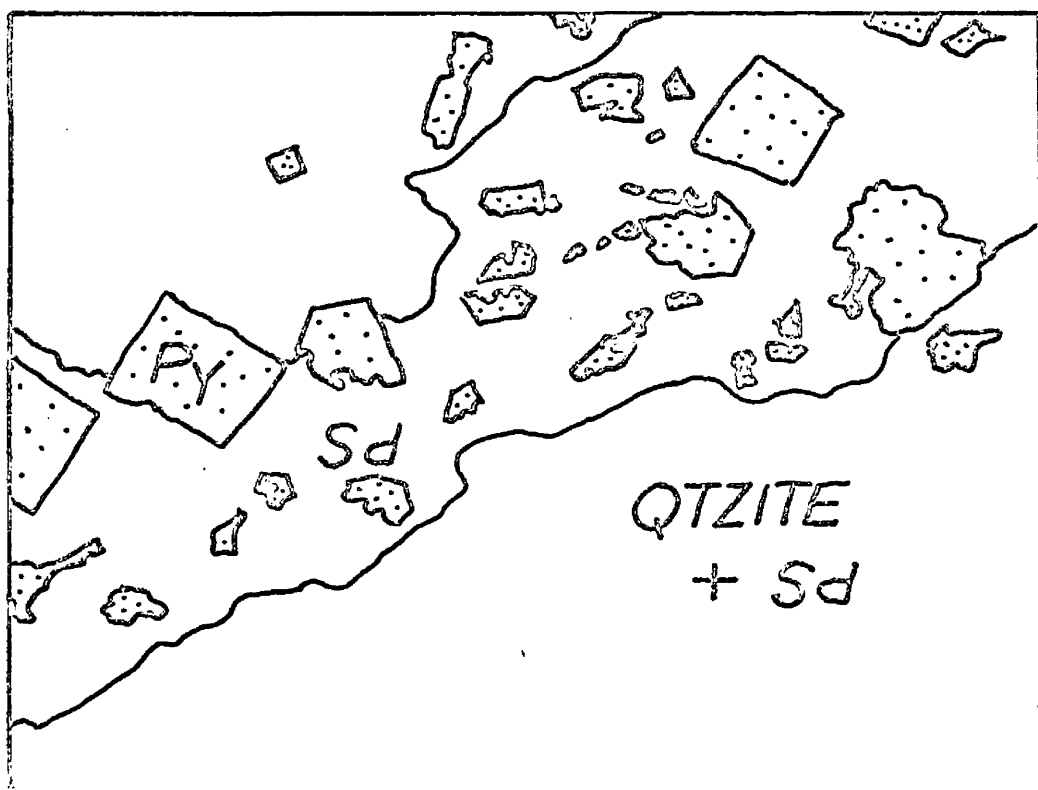


 Py 
no.33-50
57x

FIG. 8B

 Py 
no.28-52
57x



FIG. 9A *Py*  *Td*  no1-44
228x

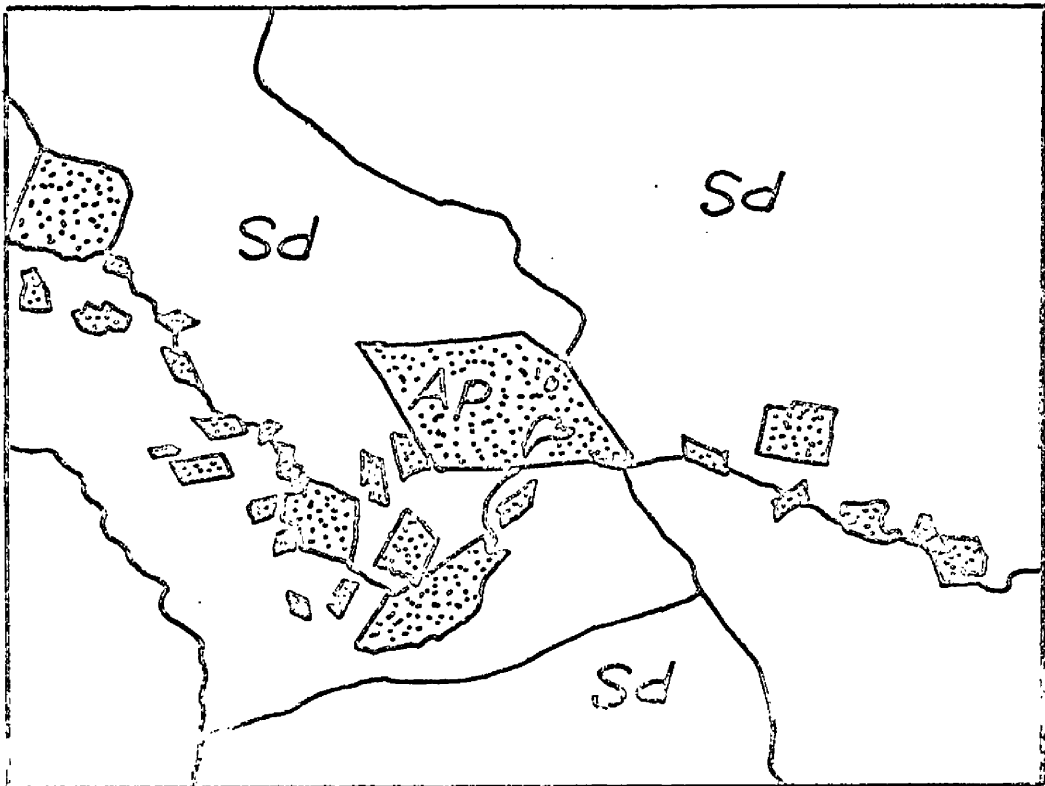



FIG. 9B *AP*  no13-50
114x

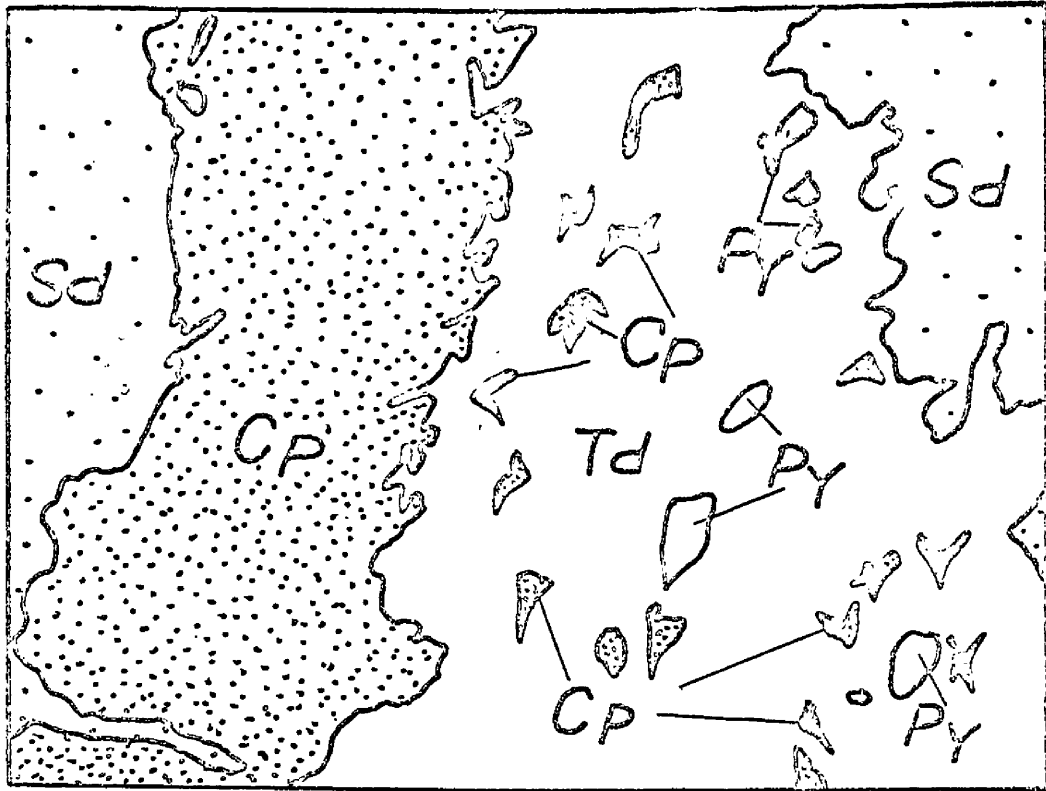


FIG. 10 A Sd  CP  43-50
57x



FIG. 10 B Sd  CP  43-50
57x

Ore shoots have been structurally and to some extent stratigraphically controlled. According to Colson (1961), ore shoots on the Silver Syndicate fault are controlled by branching of that fault. Gouge is present where branching is absent. Branching occurs along the Sunshine Vein when it passes from steeply dipping beds striking parallel to it into beds with a moderate dip and divergent strike. Splitting of the vein in this fashion decreased the ore grade. Where the Chester Vein turns north from the east end of the Silver Syndicate fault and joins with the Chester, a zone of tension fractures was formed. This area, known as the "Hook," is one of the richest portions of the vein (Fig. 6).

According to Tibbs (1972), stratigraphic control of the Sunshine Vein occurred when it bottomed out after passing from St. Regis into Revett Formation. The top of the Yankee Girl ore shoot is at the Revett-St. Regis contact. The apex of the Chester Vein is near the contact of the St. Regis and Wallace Formations on the 2300' level. This contact rakes easterly as does the contact of the ore shoot.

Bleaching of wall rocks adjacent to shear systems, both inside and outside ore zones, is common in the district. Several mines, including the Sunshine, are entirely within bleached zones. Bleached rocks are discussed in detail by Mitchum (1952) and Weiss (1964). On the basis of three pairs of chemical analyses, Weiss concluded that bleaching did not chemically change fresh wall rock, but involved alteration of hematite to goethite, degradation of green chlorite and destruction of carbonaceous material. After a detailed chemical study and statistical analyses, Tibbs (1972) found that calcium was leached in large quantities prior to the period of siderite formation which produced aureoles of

iron, manganese, magnesium and calcium near the vein. Kerr and Robinson (1953) put the time of bleaching in the Precambrian since hematite haloes about Precambrian uraninite veins in the Sunshine Mine remain unaltered.

CHAPTER III

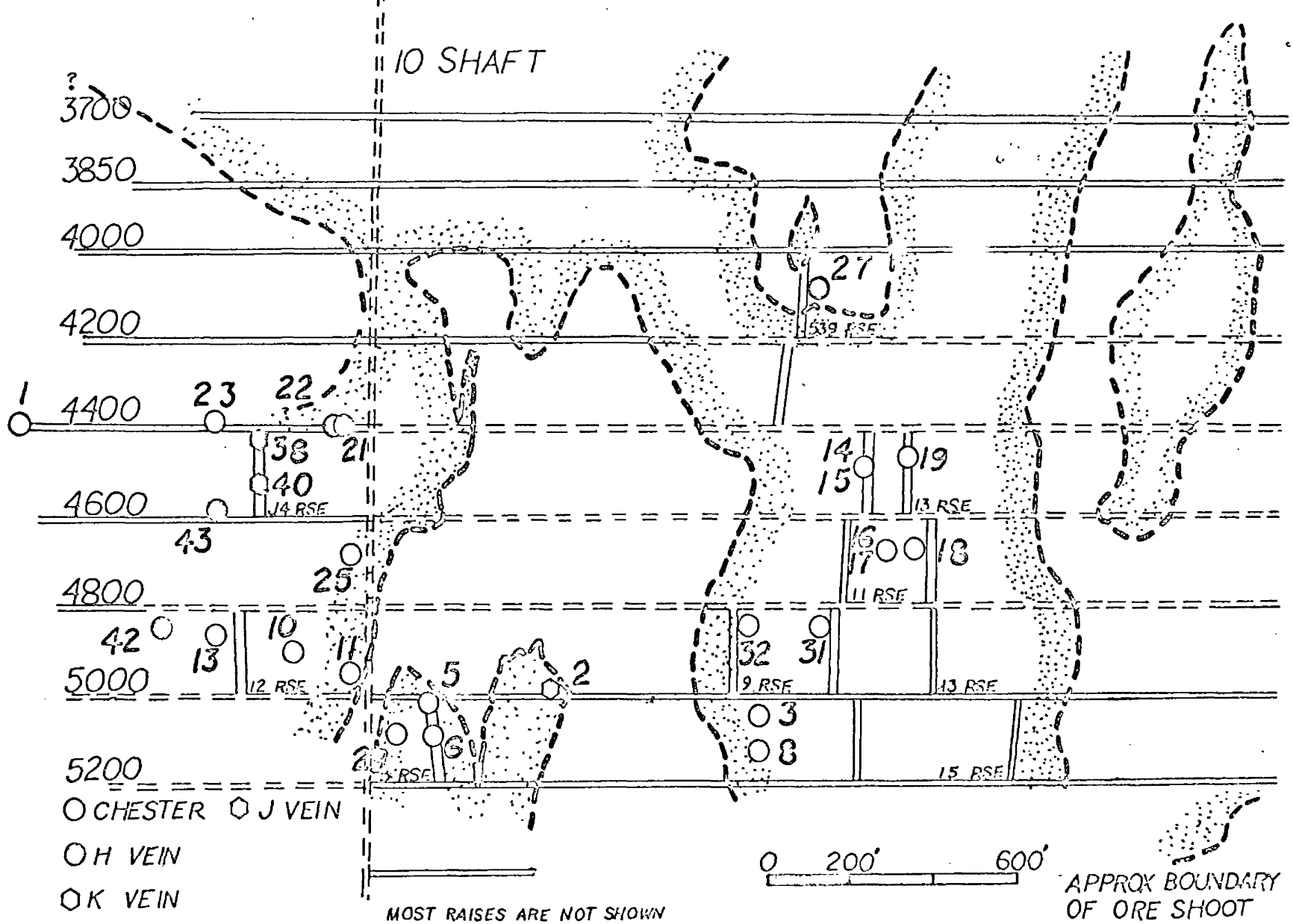
SAMPLE PREPARATION AND METHODS OF ANALYSIS

Sampling was accomplished during a four-week period in the summer of 1973. Because many parts of the mine remained closed after the fire disaster of 1972, collection sites were limited to accessible producing stopes and vein exposures. Forty-two vein samples from about 30 drift, raise and stope locations were collected between the 4200' and 5200' levels (Fig. 3) and over a lateral distance of about 2000 feet (Fig. 11). Sample descriptions and locations are given in Appendix B.

Samples were then slabbed and polished for mineralogic and textural studies. A Zeiss polarizing reflecting microscope was used for polished section examination and photomicrographs were taken with a Zeiss photomicrographic camera. Tracings were made showing important features when good contrast could not be achieved in photographs. Mineral identifications were made using optical methods and standard microchemical tests outlined in Ramdohr (1969).

After a microscopic study was completed, it was decided that reasonably pure mineral separates could be obtained from an 80-100 mesh fraction. The steps in mineral separation varied and depended on the texture encountered. Generally, samples were gently hand crushed in an iron mortar and pestal to $\frac{1}{4}$ -inch size followed by grinding in a porcelain mortar and pestal and sizing to 85-100 mesh with wood framed, silk screen sieves. Sized fractions were cleaned by rinsing in distilled water and agitating with an ultrasonic cleaner. Pyrite, quartz, siderite, and

FIG. 11 - LONGITUDINAL SECTION - CHESTER VEIN
 H, J and K VEIN SAMPLES PROJECTED ONTO PLANE OF CHESTER VEIN



tetrahedrite were separated with the Franz isodynamic separator. Residual quartz was removed with a tetrabromoethane heavy liquid treatment. Finally, purity was checked with a binocular scope and with x-ray diffraction as necessary.

Preparation of tetrahedrite and pyrite samples for mass spectrometry was done in the stable isotope lab of the University of Calgary Physics Department, under the supervision of Dr. H. R. Krouse. Preparation of SO_2 gas was done as follows: Separates were ground in an agate mortar and pestal and an amount was weighed out which would produce a required volume of SO_2 gas. This was mixed with a 1:1 mixture of $\text{CuO}+\text{Cu}_2\text{O}$ and placed in a $1\frac{1}{2}$ inch length of 10mm O.D. quartz tubing. The ends of the tube were loosely packed with quartz wool. Samples were burned in an evacuated (pressure= $10\mu\text{m}$ Hg) oven at 1050°C until all SO_2 gas had been produced. Water vapor was trapped with a 1:1 chloroform-carbon tetrachloride mixture and dry ice. CO_2 was pumped off after differential sublimation, with SO_2 trapped in frozen n-pentane. Finally, SO_2 was collected in break seal tubes after freezing with liquid nitrogen.

While pyrite samples required 30-35 minutes of combustion, tetrahedrite samples required a minimum of one hour. Tetrahedrite is often first converted to Ag_2S for combustion, in order to avoid collection of volatiles like arsenic which could foul the mass spectrometer leak system. However, since these particular tetrahedrites are known to be low in arsenic, they were burned directly.

The mass spectrometry and conversion of instrumental data to permil values was performed by Dr. H. R. Krouse and lab personnel. Sample values, in parts per thousand (per mil or 0/00), are reported relative to

the Cañon Diablo troilite standard which has an assumed S^{32}/S^{34} ratio of 22.220 (Ault and Jensen, 1962). S^{34} enrichment or depletion relative to the standard is expressed by positive or negative per mil values ($\pm S^{34}$ 0/00) respectively. Details of the calculations can be found in Ames (1962) and Lange (1968).

A Varian Techtron Model AA-6 atomic absorption spectrometer was utilized for the elemental analyses of tetrahedrite samples. The instrument is equipped with a four place digital readout system. Direct concentration readings were taken after a three-second signal integration with the instrument in concentration mode and curve correction applied. Operating parameters are listed in Appendix C.

Samples were digested using a procedure outlined by Rubeška and others (1967). Briefly .1 gm of sample was dissolved by gentle heating in a nitric-sulfuric acid mixture. Mercuric nitrate (30 mg) was added to prevent the loss of silver as the chloride. After cooling, the evaporated residue was leached with a tartaric acid solution and reheated. Tartaric acid prevented the precipitation of antimonite acid. Finally, the insoluble residue was filtered and washed with distilled water and appropriate sample dilutions were made.

The only problem encountered in the course of the analyses was the precipitation of silver or some silver compound on the nebulizer walls and the glass bead. This build-up caused a considerable memory effect from one analysis to the next. Acidifying the sample and standard solutions alleviated the problem but periodic cleaning of the nebulizer was still required.

CHAPTER IV

ISOTOPIC AND ELEMENTAL RESULTS

Elemental analyses were performed on 25 pure tetrahedrite separates (98+%). The location of analyzed samples is shown in Fig. 11. Figures 12 and 13 show the relationship of H, K, and J vein samples to the Chester Vein. The separates were analyzed for weight percent of copper, iron, zinc, silver, and cadmium. The results are listed in Table 2 and shown in Fig. 14-18. Skinner and others (1972) have experimentally determined the theoretical composition of pure tetrahedrite as $Cu_{12+x}Sb_{4+y}S_{13}$ where $0 < x < 1.92$ and $-.02 < y < .27$. Varying x and y , the minimum and maximum limits for copper content in pure tetrahedrite are 45.45% and 49.25% respectively. Iron, zinc, silver, cadmium, and other elements are known to substitute for copper in the tetrahedrite structure (Palache and others, 1944, and Radtke and others, 1969). The weight percent sum of copper, iron, silver, zinc, and cadmium should total near the lower percent limit for copper in pure tetrahedrite. Only 13 of the 25 samples analyzed exceeded this limit. The high total was 48.29%, and the low total was 42.532%. This implies the presence of some other minor component in the tetrahedral position with copper. Williston (1964) detected a mercury anomaly in surface geochemical samples over the Sunshine Mine, and Palache and others (1944) have reported up to 17% Hg in tetrahedrite from Moschellandsberg. Lead is a remote possibility but has been found in argentian tetrahedrites by Palache and others (1944) in amounts

FIG. 12

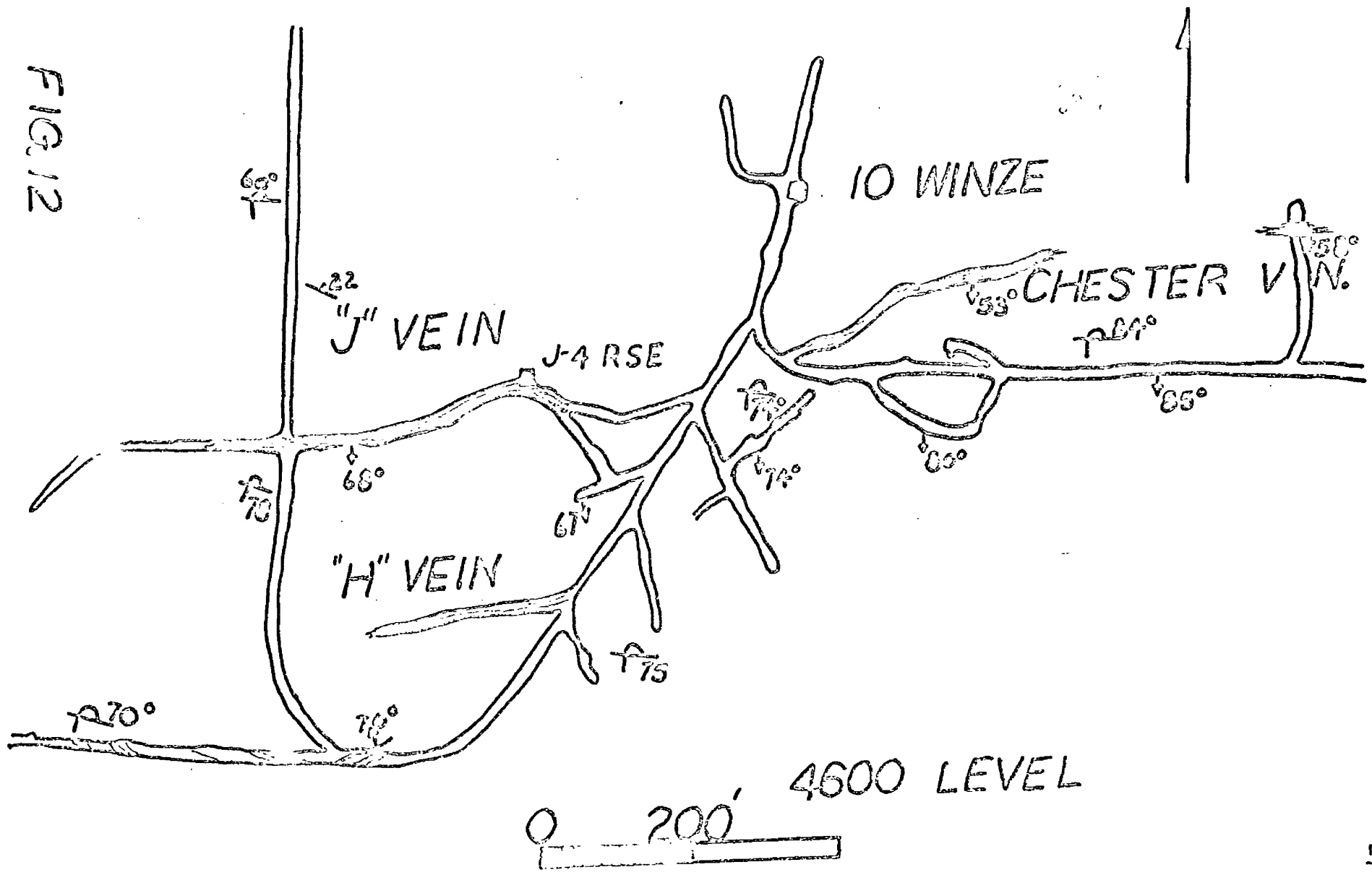


FIG. 13

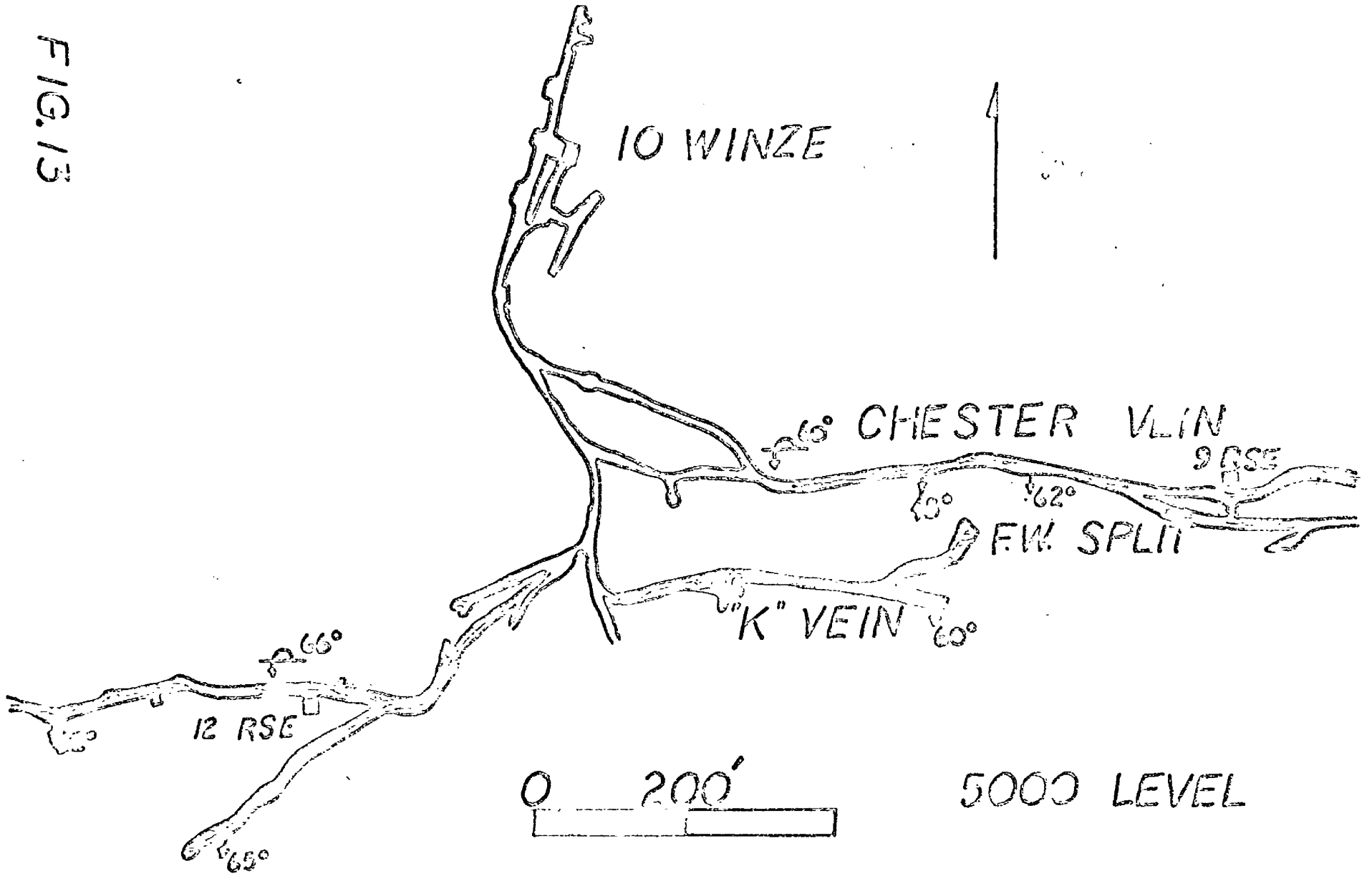


TABLE 2
ELEMENTAL ANALYSES OF TETRAHEDRITE

Sample No.	%Cu	%Fe	%Zn	%Ag	%Cd
27-42	25.97	7.17	2.42	8.45	0.12
1-44	29.36	5.43	2.28	9.32	0.07
21-44	32.72	4.57	3.40	5.29	0.16
23-44	30.16	4.41	3.41	6.63	0.16
14-46	31.46	5.79	2.73	6.52	0.09
15-46	29.95	3.84	3.25	6.99	0.13
19-46	30.33	5.92	3.04	4.23	0.13
38-46	29.41	8.11	2.10	5.85	0.05
40-46	30.98	5.89	2.48	7.75	0.09
43-46	30.94	5.97	2.19	5.49	0.12
16-48	31.69	4.81	2.67	5.18	0.16
18-48	23.21	16.00	3.08	3.29	0.14
25-48	30.91	6.49	2.51	5.55	0.11
2-50	33.63	4.15	2.69	5.61	0.09
5-50	29.63	7.42	2.13	6.86	0.11
10-50	33.19	5.47	2.35	5.32	0.16
11-50	31.49	4.79	2.35	5.34	0.11
13-50	32.16	5.14	2.23	4.70	0.18
31-50	25.73	9.91	2.25	5.76	0.07
32-50	30.76	3.73	3.18	7.12	0.13
42-50	31.15	9.25	2.30	5.42	0.16
3-52	24.81	11.35	2.85	5.63	0.11
8-52	29.20	4.86	3.40	4.95	0.12
29-52	31.02	5.49	2.00	7.58	0.06
6-52	30.97	6.53	2.09	6.84	0.11

FIG. 16 - LONGITUDINAL SECTION - CHESTER VEIN
 H, J and K VEIN SAMPLES PROJECTED ONTO PLANE OF CHESTER VEIN

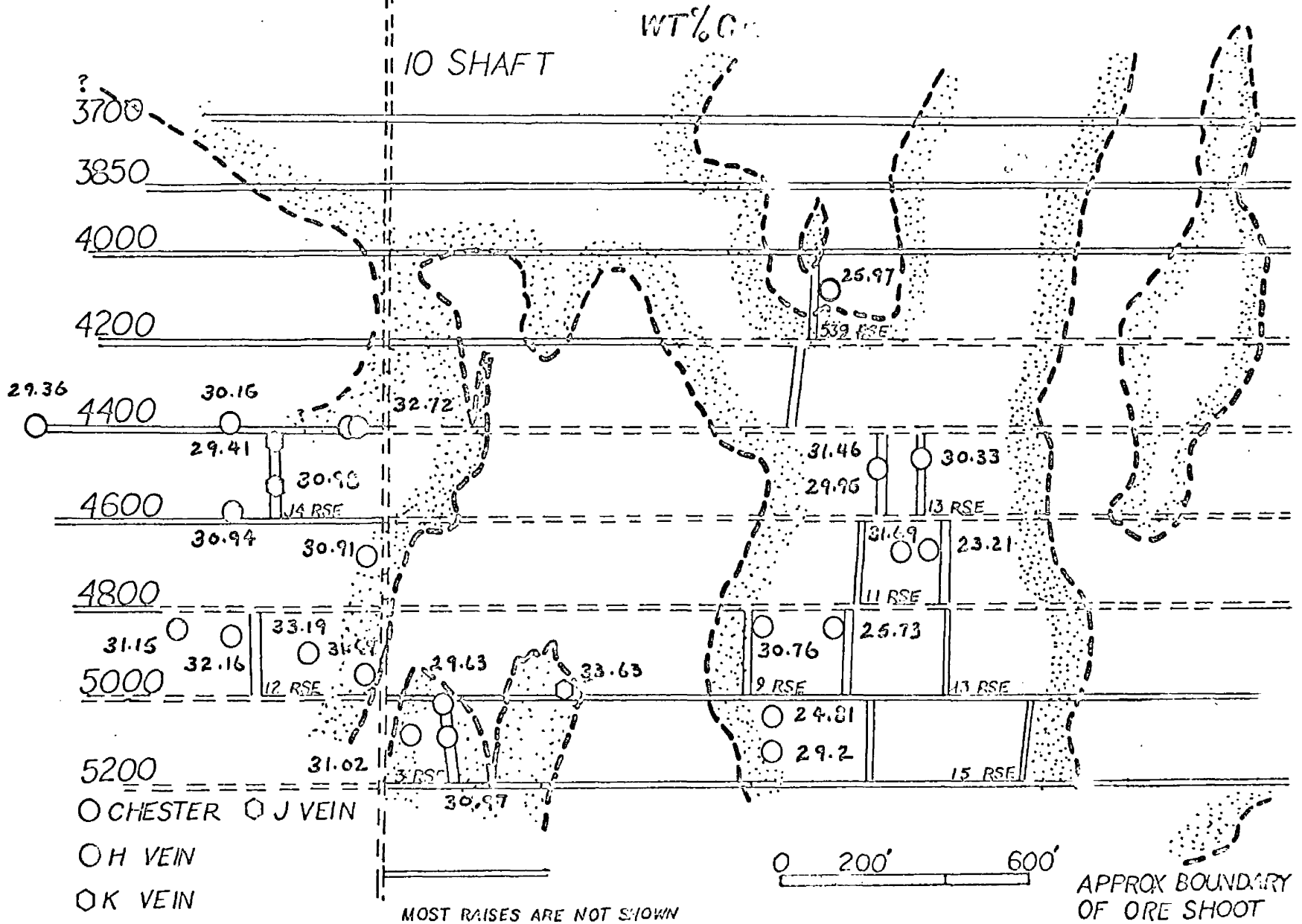


FIG. 15 - LONGITUDINAL SECTION - CHESTER VEIN

H, J and K VEIN SAMPLES PROJECTED ONTO PLANE OF CHESTER VEIN

WT% Fe

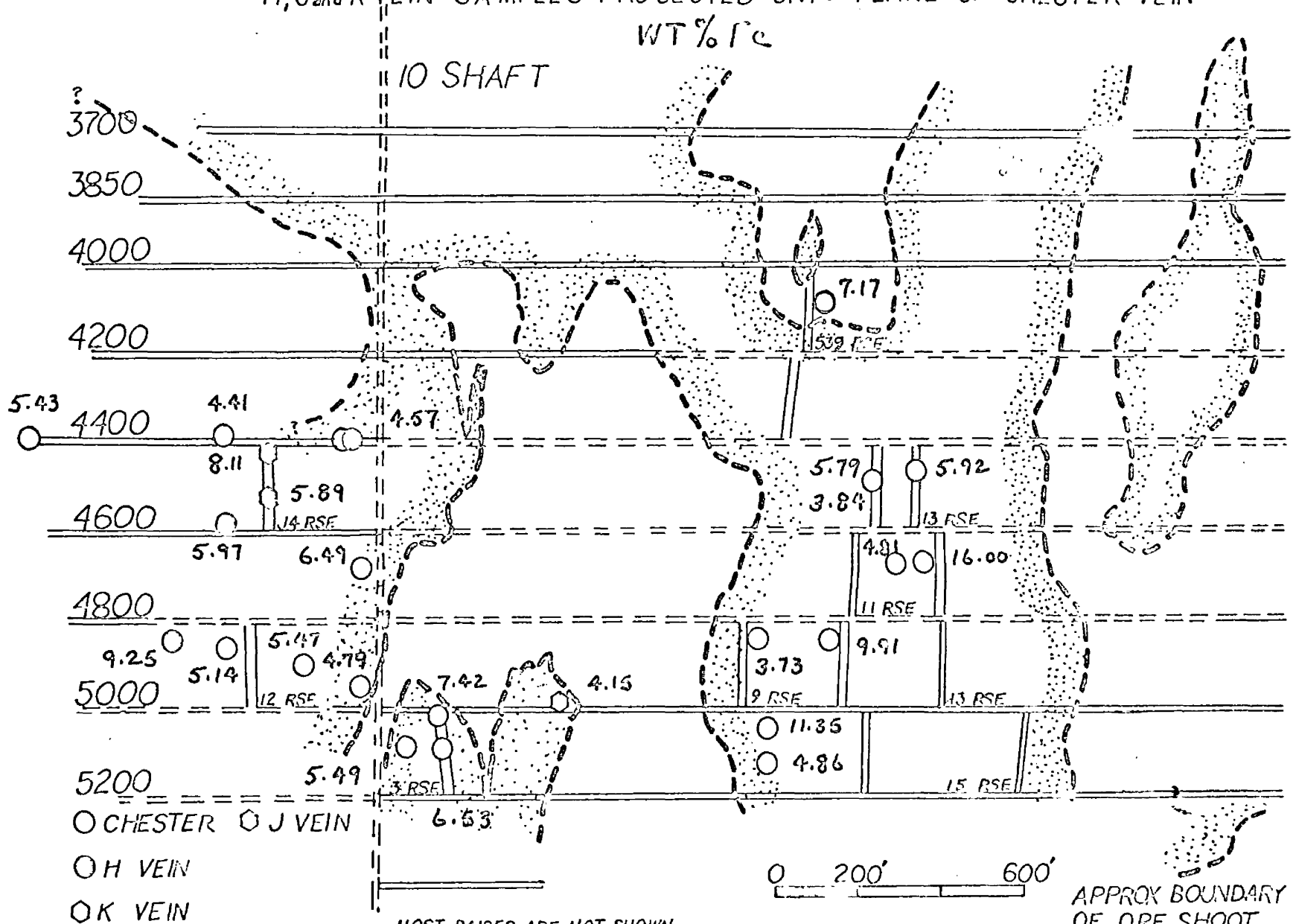


FIG. 16 - LONGITUDINAL SECTION - CHESTER VEIN

H, J and K VEIN SAMPLES PROJECTED ONTO PLANE OF CHESTER VEIN

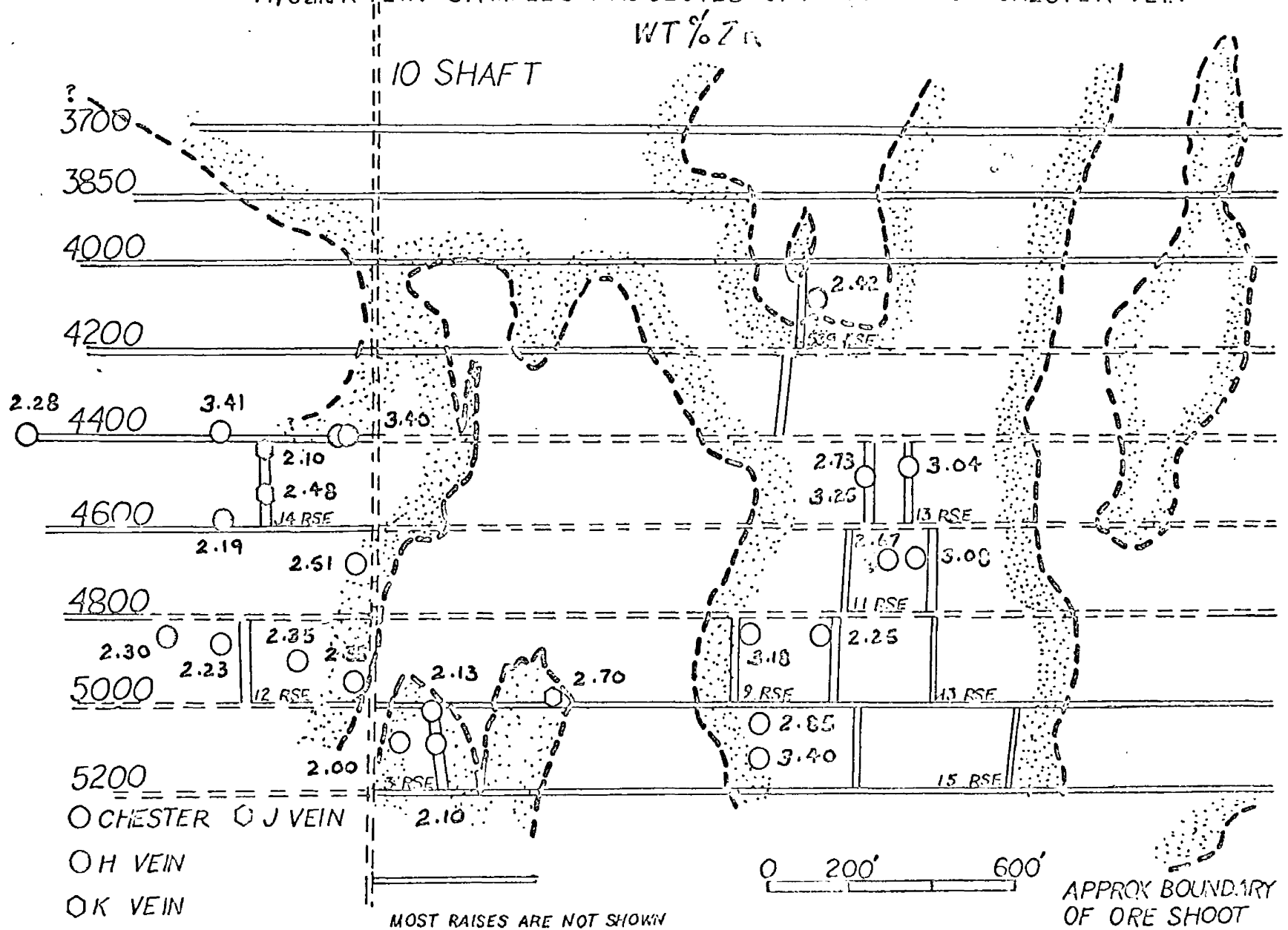
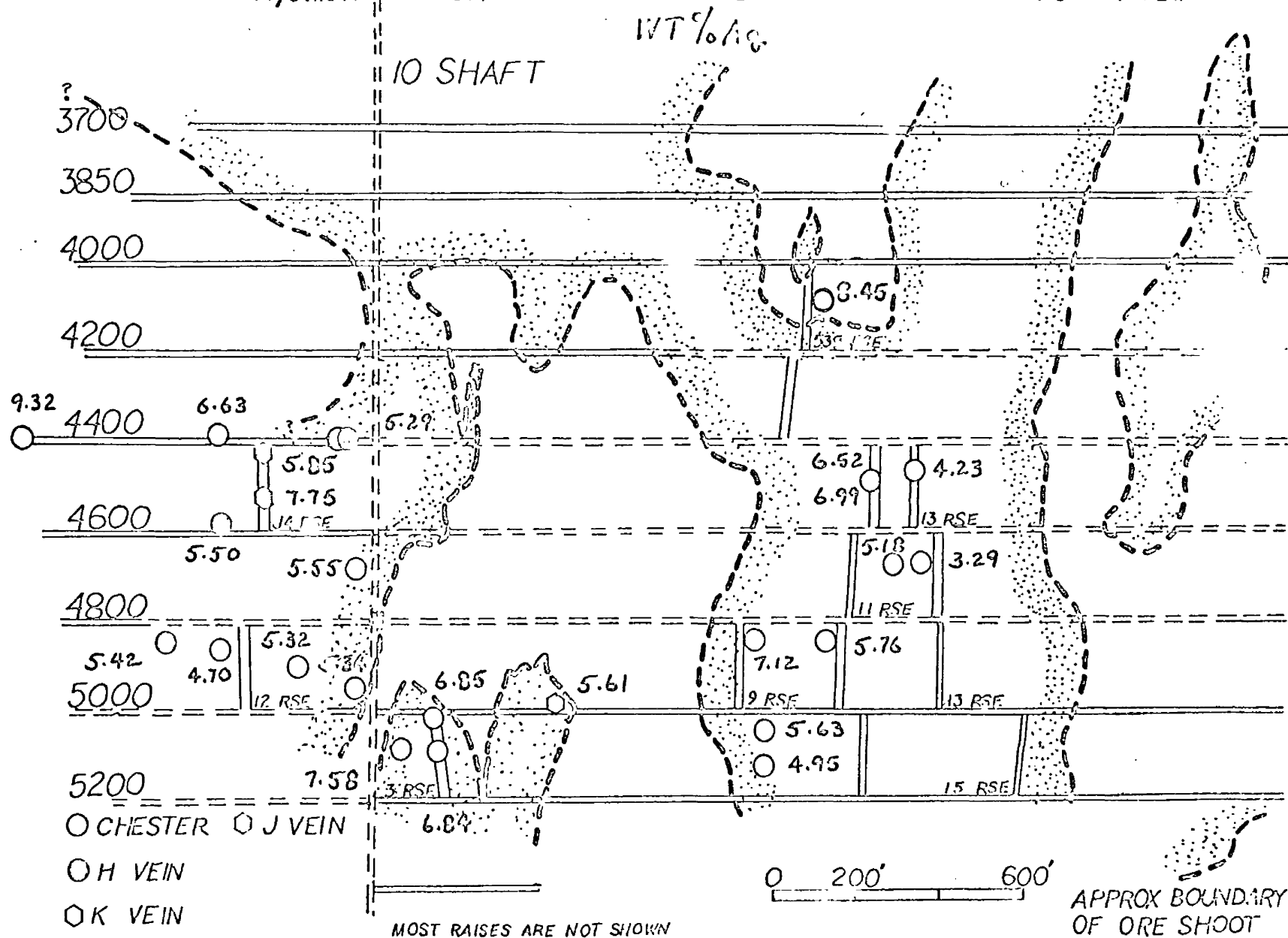


FIG.17 - LONGITUDINAL SECTION - CHESTER VEIN

H₂J and K VEIN SAMPLES PROJECTED ONTO PLANE OF CHESTER VEIN



up to 9.38%. However, unlike the Group B metals, Pb seldom enters into four-fold, or tetrahedral coordination.

Percent Cu, Fe, Zn, Ag, and Cd for all samples are compared in Table 3. Cu and Fe seem to be the most variable in abundance in all samples. Most of the variability of Cu can be explained by the variability of the elements which substitute for Cu. For example, the standard deviation for Fe, which substitutes for Cu, is of the same magnitude as that of Cu. Table 3 also compares the total Fe+Zn+Ag+Cd for all samples as a group. The sample standard deviation is very close to that of Cu.

TABLE 3
COMPARISON OF ELEMENTAL RESULTS—
All Samples (wt%)

Element	Range	Mean	Standard Deviation
Cu	23.21 - 33.63	30.03	2.569
Fe	3.73 - 16.00	6.50	2.741
Zn	2.00 - 3.40	2.62	0.461
Ag	3.29 - 9.32	6.07	1.343
Cd	0.05 - 0.18	0.12	0.034
Fe+Zn+Ag+Cd	12.25 - 22.52	15.30	2.502

The data was then divided into two other groups according to sample location—samples on the West and samples on the East (Fig. 11). Samples on the West lie principally in the "Hook" portion (Fig. 6). This group of samples is separated from the less complicated Chester Vein on the east, by approximately 1000' of barren overturned folds and sheared zones. Values for the east and west groups are compared in Tables 4 and 5.

The means and variances were compared at the 95% level of significance assuming normality, with the following results:

1. The West copper mean (31.18) is significantly higher than the East copper mean (26.43).
2. Copper is more variable on the East.

TABLE 4

COMPARISON OF ELEMENTAL RESULTS—
Sample from the West (wt%)

Element	Range	Mean	Standard Deviation
Cu	29.36 - 33.63	31.18	1.298
Fe	4.15 - 9.25	5.94	1.430
Zn	2.00 - 3.40	2.43	0.434
Ag	4.70 - 9.32	6.26	1.242
Cd	0.05 - 0.18	0.12	0.040
Fe+Zn+Ag+Cd	12.82 - 22.52	16.16	3.303

TABLE 5

COMPARISON OF ELEMENTAL RESULTS—
Sample from the East (wt%)

Element	Range	Mean	Standard Deviation
Cu	23.21 - 31.69	26.43	7.389
Fe	3.73 - 16.00	7.34	3.944
Zn	2.25 - 3.40	2.89	0.372
Ag	3.29 - 8.45	5.81	1.513
Fe+Zn+Ag+Cd	12.25 - 17.14	14.73	1.685

An attempt was made to delineate elemental trends over the entire vertical extent of sampling. Least squares linear, multiple linear and second order linear regression analyses were performed by digital computer using the Basic language. Since a method for prediction of position within an ore shoot in a vertical sense was desired, the general form of the regression equation used was $y = \beta_0 + \beta_1 X_1 + \dots + \beta_i X_i + E$ where y equals elevation in feet, β 's are regression coefficients, X 's are weight percent values for particular elements, and E is error, which is assumed to be independently normally distributed. The linear second order equation used had the form $y = \beta_0 + \beta_1 X_1 + \beta_2 X_1^2 + E$. Extremely low correlation coefficients were achieved in almost every case, signifying that the correlation between elevation and percent of one or more of the elements is poor if it exists at all in the linear or second order linear case. Those regressions which yielded a correlation coefficient, r , of 0.1 or greater are listed in Table 6. However, on a random basis, some of the correlation coefficients for the simple first order models could have been negative. Because they were all positive, the possibility of a significant multiple regression (involving more than one element) was suggested. It can be seen from Table 6 that the only regression significant at the 90% level was the multiple regression involving Cu and Zn. The second order regression for Ag has a 83% level of significance. However, the curve obtained from the regression equation did not fit the data spatially. Perhaps a more extensive sampling program would yield a useful second order model.

TABLE 6

REGRESSIONS WHICH YIELDED A CORRELATION COEFFICIENT GREATER THAN 0.10

Sample Area	No. of Samples	X's of the Regression	Correlation Coefficient	R*	Remarks
East	10	Zn	0.1066	0.57	
East	10	Ag	0.1804	0.57	
West	15	Cu	0.1221	0.45	
West	15	Zn	0.2634	0.45	
West	9	Cu	0.1141	0.61	Excluding samples not on Chester Vein
West	9	Zn	0.3509	0.61	Excluding samples not on Chester Vein
West	15	Cd, Cd ²	0.1185	0.45	
West	15	Zn, Zn ²	0.2268	0.45	
West	15	Cu, Cu ²	0.1478	0.45	
East	10	Ag, Ag ²	0.5411	0.57	
East	10	Zn, Zn ²	0.1856	0.57	
East	10	Zn, Ag	0.2374	0.57	
West	15	Cu, Zn	0.5327	0.45	
West	15	Cu, Zn, S ³⁴	0.5741	0.45	
West	9	Cu, Zn, S ³⁴	0.5939	0.57	Excluding samples not on Chester Vein

*R=Minimum correlation coefficient required for significance at the 90% level.

The lateral continuity of the sampling pattern was not sufficient for detection of statistically significant trends. This failure to identify over all vertical or lateral trends may or may not be due to frequent pinching and swelling of the vein which exists in all dimensions.

However, some consistent variations of limited vertical or lateral extent have been identified. In five adjacent raises where lateral sampling was possible, silver always increased from east to west. In three out of five examples, copper increased from east to west. Zn, Fe, and Cd were inconsistent. In seven raises sampled vertically, copper increased downward in five, Fe in four, Zn in five, and Cd in five. Ag decreased downward in five out of seven. These observations are summarized in Table 7. It must be stressed, however, that these variations are very tentative because they are sometimes smaller than the sample standard deviation of the element concerned.

The sulfur isotopic composition of 24 tetrahedrite and 13 pyrite samples was determined. The results are listed in Appendix B and located on Figures 19 and 20. Analytical precision, estimated by replicate analyses, was .4 permil or better on tetrahedrite and .2 permil or better on pyrite, except for one pyrite with a .8 permil difference in replicate analyses. Values for the three sample groupings (all samples, samples from the West, and samples from the East) are compared in Table 8.

Linear regression analyses were performed on the isotopic data in the same manner as for the elemental data (Table 9). There are essentially no linear correlation between permil δS^{34} values of tetrahedrite and elevation. However, most regressions involving pyrite were highly significant. A low correlation coefficient and low level of significance

of the eastern pyrite group was due largely to small sample size and had little influence on the correlation coefficient for all pyrites considered as one group. Figure 21, which shows a scatter diagram with the regression line drawn in for all pyrites, reveals a systematic increase in δS^{34} in pyrite with depth of nearly 0.9 permil/200 feet.

Permil S^{34} values for tetrahedrite were compared with the localized elemental trends mentioned previously (Table 7) and found to be consistent with those trends with one exception. Tetrahedrite is not consistently depleted in S^{34} from east to west as silver values increase. Figure 22 displays the trends mentioned in a vertical section of the 5200-9 raise.

TABLE 7

SUMMARY OF LOCALIZED ELEMENTAL AND ISOTOPIC TRENDS
FOR TETRAHEDRITE IN INDIVIDUAL RAISES

Element	East to West (5 Raises)		Up Vertically (7 Raises)	
	Element	δS^{34*}	Element	δS^{34*}
Cu	increase (3/5)	increase	decrease (5/7)	decrease
Fe	_____	_____	_____	_____
Zn	_____	_____	decrease (5/7)	decrease
Ag	increase (5/5)	increase	increase (5/7)	increase
Cd	_____	_____	decrease (5/7)	decrease

*Variations in δS^{34} in tetrahedrite are consistent with each elemental trend listed. For example, δS^{34} decreases as Cu decreases, and increases when Cu increases.

FIG. 19 - LONGITUDINAL SECTION - CHESTER VEIN

H, J and K VEIN SAMPLES PROJECTED ONTO PLANE OF CHESTER VEIN

853472

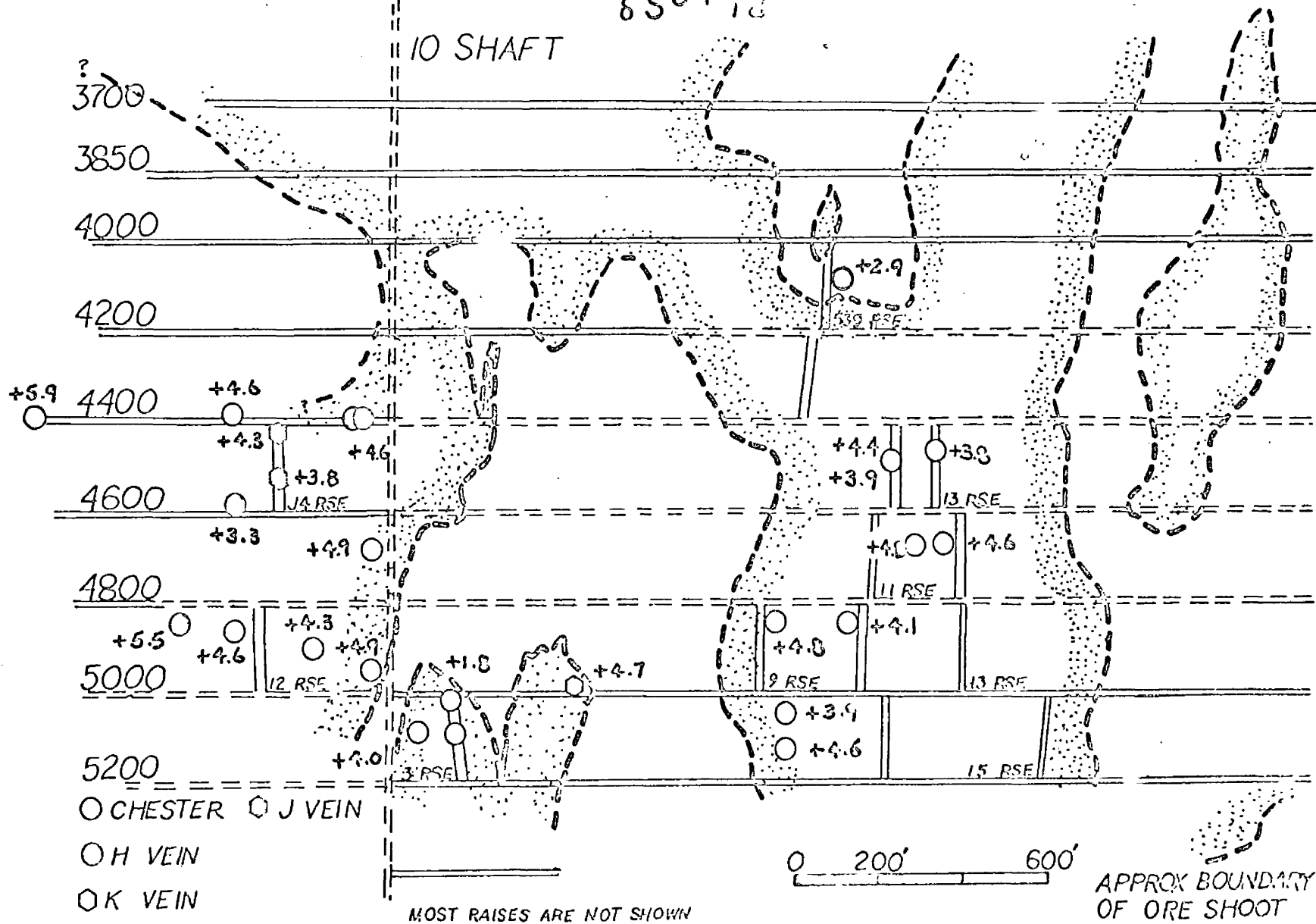


FIG.20 - LONGITUDINAL SECTION - CHESTER VEIN
 H, J and K VEIN SAMPLES PROJECTED ONTO PLANE OF CHESTER VEIN

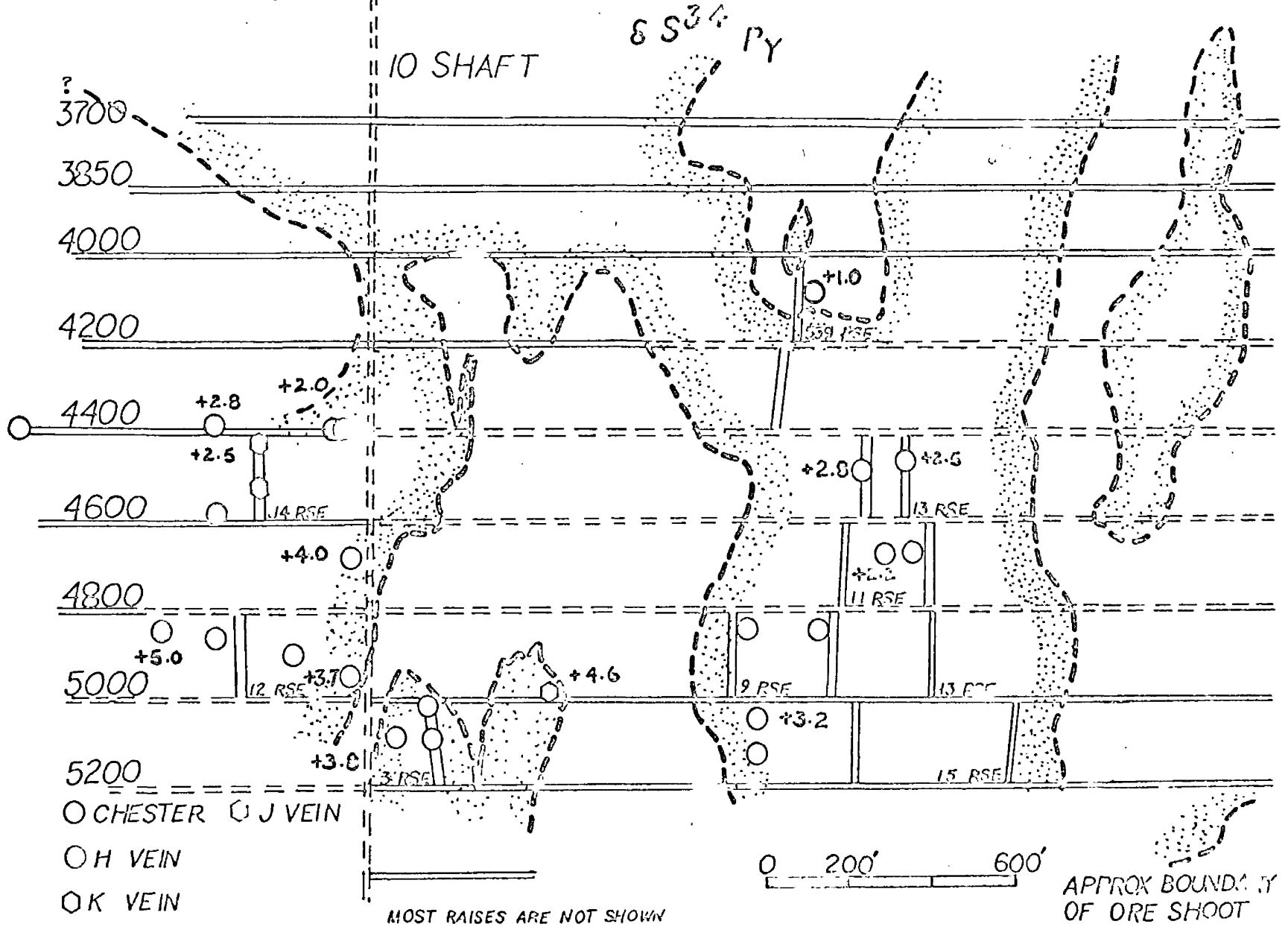


TABLE 8
COMPARISON OF SULFUR ISOTOPIC DATA

Sample Area	No. Samples	Range	Mean	Standard Deviation
<u>Tetrahedrite</u>				
All	24	+2.9 - +5.9	+4.4	0.66
West	14	+3.3 - +5.9	+4.6	0.68
East	10	+2.9 - +4.8	+4.2	0.56
<u>Pyrite</u>				
All	13	+1.0 - +5.0	+3.1	1.13
West	8	+2.0 - +5.0	+3.6	0.89
East	5	+1.0 - +3.2	+2.3	0.84

TABLE 9
LINEAR REGRESSION OF ISOTOPIC DATA

Sample Area	No. Samples	Correlation Coefficient	Level of Significance
<u>Tetrahedrite</u>			
All	24	0.06	---
West	14	0.00	---
East	10	0.39	---
<u>Pyrite</u>			
All	13	0.79	99%
West	8	0.88	98%
East	5	0.73	83%

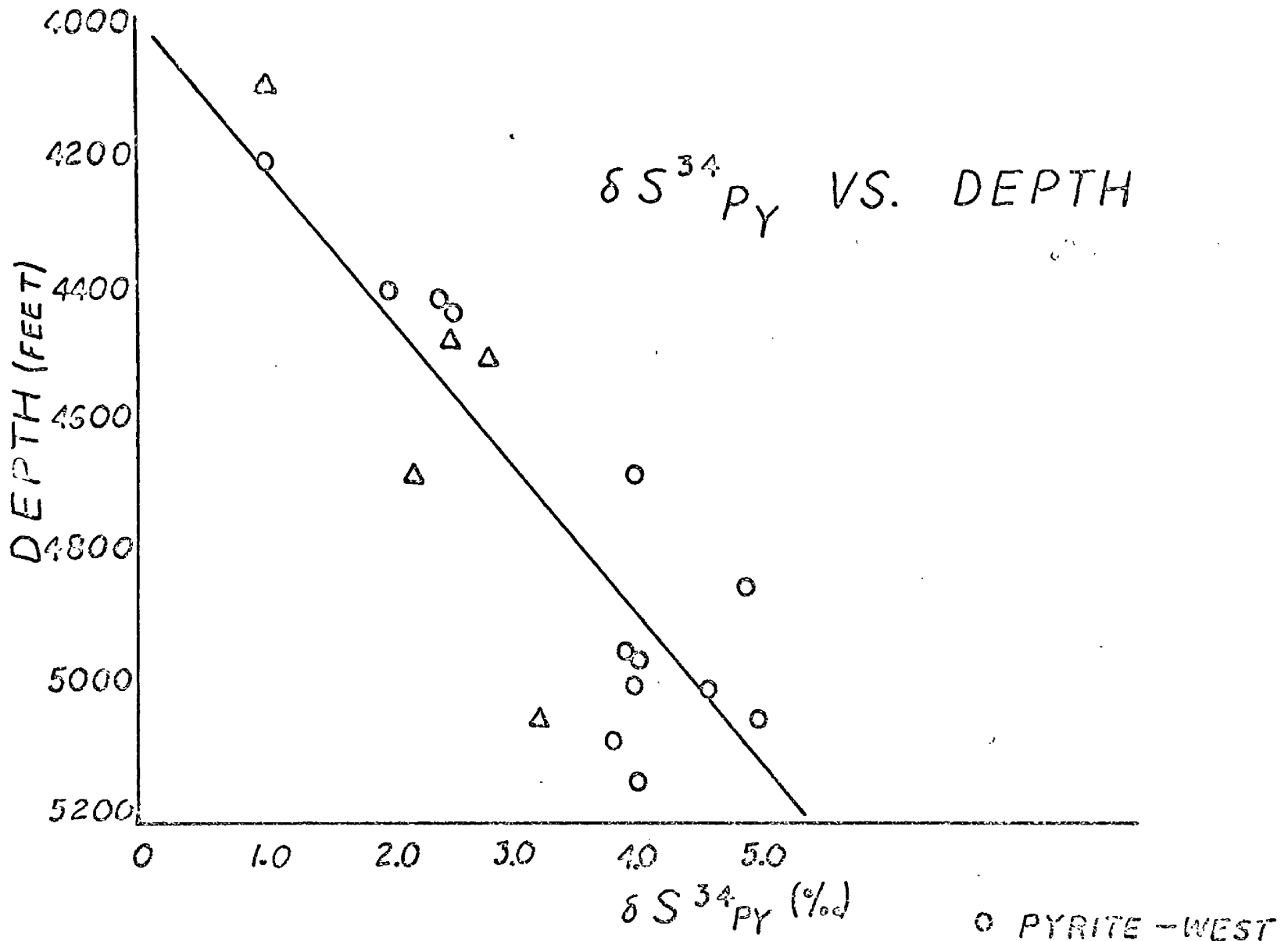
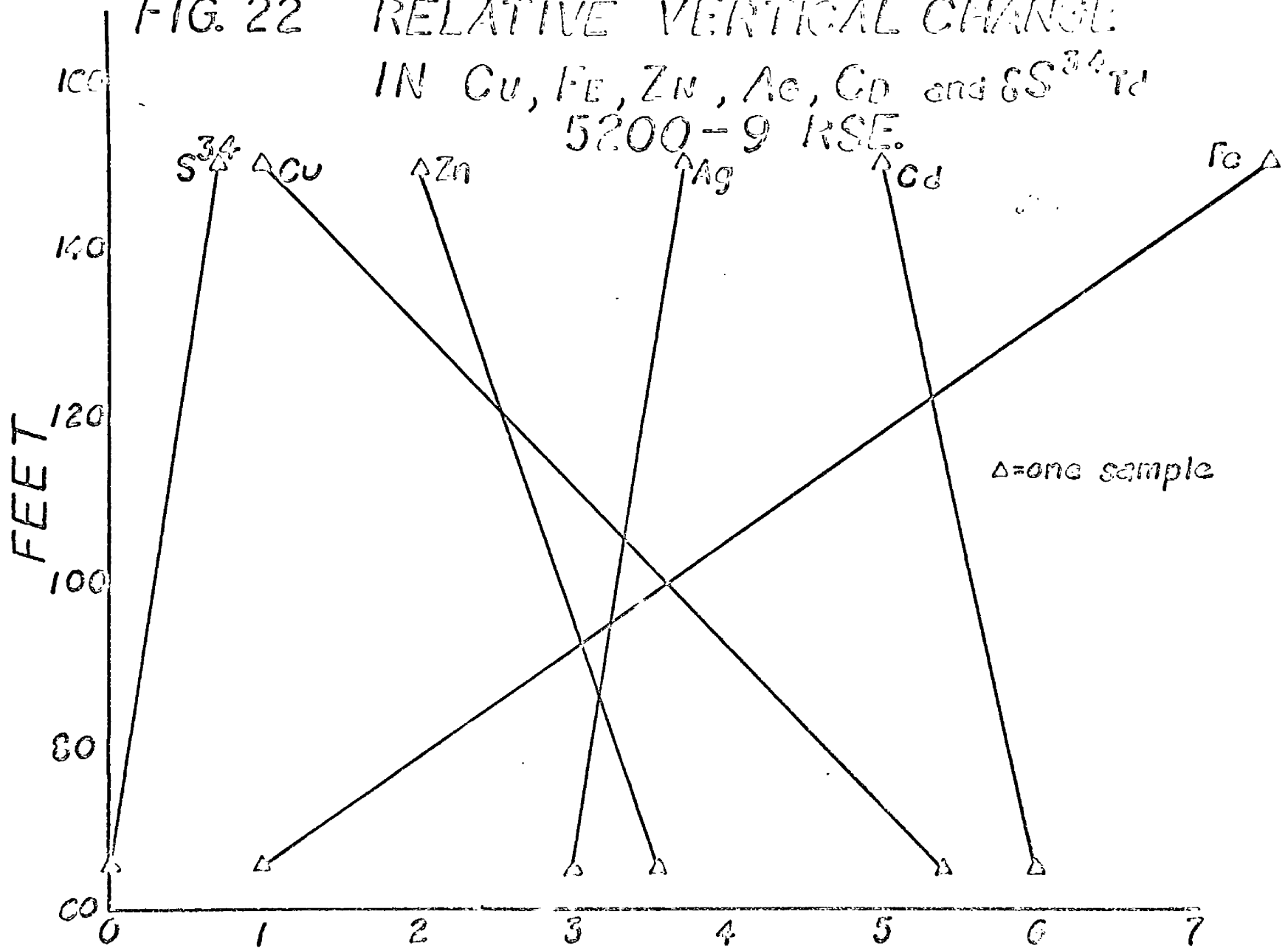


FIG. 21

FIG. 22 RELATIVE VERTICAL CHANGE
 IN CU, FE, ZN, AG, CD and S^{34} IN
 5200-9 RSE.



There was no simple relationship between one element and another in tetrahedrite. Also, attempts to correlate elemental composition with isotopic composition of tetrahedrite over a distance greater than 200' were unsuccessful. Two sources of compositional variability in tetrahedrite may be responsible for these difficulties. First, the limits on copper content in "pure" tetrahedrite vary between 44.45 and 49.25 weight percent. Second, several elements can substitute for Cu in varying proportions. Including the isotopic composition in multiple regressions involving elemental percentages versus elevation was generally unproductive. The correlation coefficient for the Cu, Zn regression mentioned earlier (Table 6) was only improved slightly with the addition of the isotopic data, while in all other similar cases the correlation coefficient was decreased. Therefore, δS^{34} tetrahedrite probably did not increase systematically with increasing depth.

Finally, an isotopic trend related to mineral paragenesis was observed. Late sulfides (tetrahedrite) were enriched in S^{34} relative to early sulfides (pyrite). Field and Moore (1971) established a primary fractionation trend with enrichment in S^{34} in the order pyrite \rightarrow sphalerite \rightarrow tetrahedrite \rightarrow galena. δS^{34} values for tetrahedrite in this study are similar to the greatest δS^{34} value for the earlier pyrite.

CHAPTER V

DISCUSSION OF RESULTS AND SPECULATION

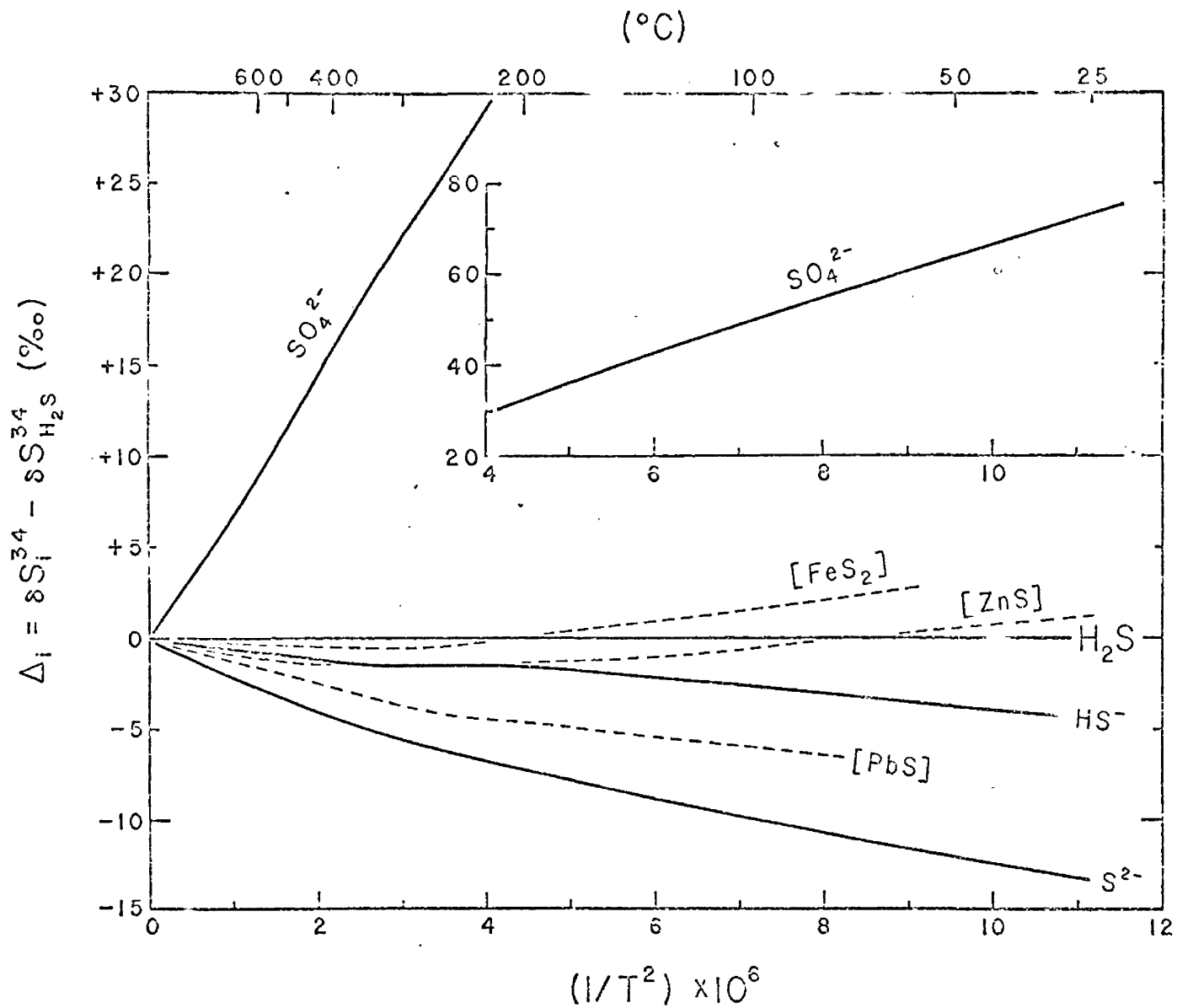
ABOUT THE ORE-FORMING PROCESS

The purpose of this study was to investigate whether systematic elemental and sulfur isotopic variations occur within the lower Chester Vein. The results of the investigation revealed a significant sulfur isotopic trend in pyrite. δS^{34} in pyrite was depleted with decreasing depth. Field and Moore (1971) observed a similar trend in the Bingham District, Utah. Tetrahedrite exhibited a weak but statistically significant elemental (Cu and Zn) trend on the west side. Consistent isotopic and elemental variations of limited spatial extent in tetrahedrite were also identified (Table 7). In addition, the paragenetically later tetrahedrite was enriched in S^{34} compared to the earlier pyrite. This isotopic trend, related to sulfide paragenesis, is opposite that observed by Field and Moore (1971), Waneless and others (1960), but similar to that found by Ames (1962).

δS^{34} values for pyrite decreased with decreasing depth at the rate of 0.9 permil/200 feet. Increasing pH with decreasing depth was probably the cause of this trend. According to Ohmoto (1972) an increase in pH could be responsible for significant depletion of S^{34} in pyrite. The pH of neutrality at 250°C (not unreasonable for a deposit of this type) for pure water in the presence of steam is 5.6 (Barnes and Ellis, 1967). This is a reasonable estimate for typically dilute ore solutions. The most probable range of pH during ore transport extends only one unit

on either side of neutrality (Barnes and Czamanske, 1967). Conditions of pH, $\log fO_2$ (f=fugacity of oxygen), and T of 5.6, -36 to -3, and 250°C respectively, would indicate H_2S as the dominant sulfur specie in solution (Ohmoto, 1972). At 250°C, H_2S is enriched in S^{34} over pyrite by only .3 permil (Fig. 23) making δS^{34} of pyrite a good estimate of the δS^{34} of total sulfur (ΣS) in solution. It seems reasonable, in light of the observed trend, that $\delta S^{34} \Sigma S$ is at least as great as the highest δS^{34} pyrite value. Using Ohmoto's (1972) data, it would be possible to deplete pyrite by about 10 permil by increasing the pH of the solution by one unit (path A-A' on Fig. 24). Therefore, only a very small change in pH is needed to produce the observed change in δS^{34} pyrite. An increase in pH fits well with the observed paragenesis. The siderite stability field can be entered from the adjacent pyrite stability field with a simple increase in pH (Carrels and Christ, 1965). It can be seen from Figure 24 that variations in δS^{34} pyrite cannot be achieved at lower fO_2 conditions within the pH range, 4.6 to 6.6.

The reservoir effect has been cited as a possible mechanism for S^{34} depletion with decreasing depth by Ryznar (1967). The progressive depletion of S^{34} in pyrite is conceivable if S^{34} is continuously removed from a finite reservoir of sulfur. The reservoir effect is thought to be untenable, geologically, because of the large amounts of sulfur supposedly available for ore deposits of this size (Both and others, 1969). However, removal of available sulfide from a finite source could lead to the precipitation of iron as siderite rather than pyrite. This is consistent with the paragenesis observed.

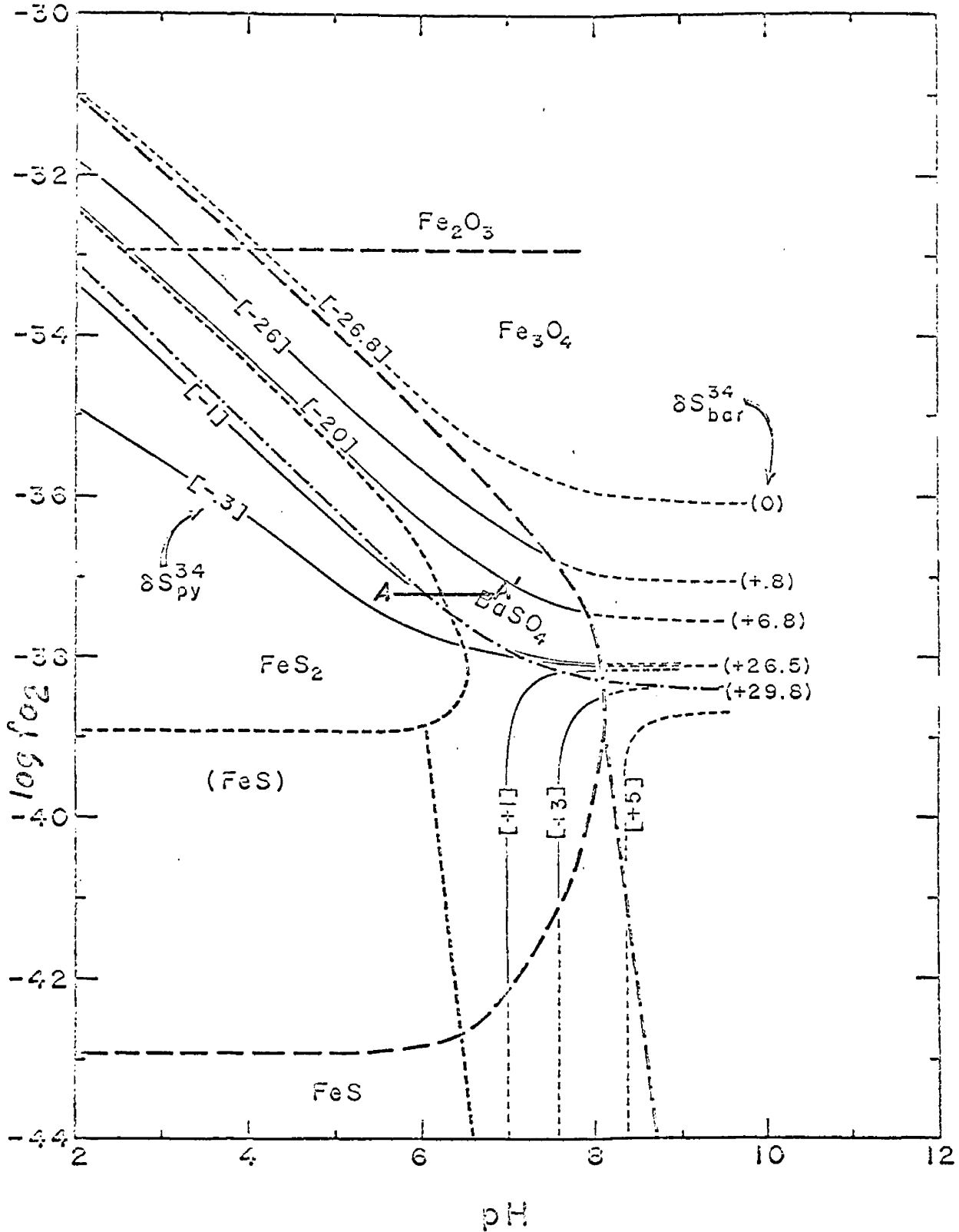


Isotopic enrichment factors for important sulfur species (based on the data by Sakai, 1968; Rye and Czamanske, 1969; Kajiura and Krouse, 1971).

FIGURE 23

after Ohmoto, 1972

FIGURE 24



Comparison of the positions of δS^{34} contours with the stability fields of Fe-S-O minerals and barite. $T = 250^\circ \text{C}$

- ~.....: δS^{34} contours. Values in [] and () are, respectively, for pyrite and barite at $\delta S^{34}_s = 0\%$.
- : Fe-S-O mineral boundaries at $\Sigma S = 0.1$ moles/kg H_2O .
- - - -: Fe-S-O mineral boundaries at $\Sigma S = 0.001$ moles/kg H_2O .
- · - · -: barite soluble/insoluble boundary at $m_{\text{Ba}^{2+}} \cdot m_{\text{S}} = 10^{-4}$.

after Ohmoto, 1972

A simple temperature decrease with decreasing depth would not have been a factor. The fractionation factor between the dominant sulfur specie in solution and the precipitating sulfide specie increases with decreasing temperature. In the case of pyrite, an enrichment in S^{34} would occur (Sakai, 1968, and Ohmoto, 1972). Also, significant cooling would probably not have occurred over a short vertical distance sampled (approximately 1000 feet) considering that the Chester Vein apexes at a present depth of about 4000 feet below the surface. Cooling, due to heat exchange with the wall rocks, is generally unimportant especially for replacement deposits in which heat of precipitation and other chemical reactions may be much more important (Toulmin and Clark, 1967). The possibility exists of increasing temperatures with decreasing depth. An increase in temperature would reduce the fractionation factor between pyrite and the dominant sulfur specie in solution (Sakai, 1968, and Ohmoto, 1972). However, the four permil change observed would not have been achieved (Fig. 24).

An increase in Eh is another possible mechanism (Ohmoto, 1972). A very small change in Eh could have produced the observed change in δS^{34} pyrite. Reaction with oxides in the wall rock would probably not have been a factor because most oxide minerals were destroyed by an earlier period of bleaching (Weiss, 1964). Mixing with meteoric or other hydrothermal solutions could also cause an increase in Eh. This would probably be accompanied by a decrease in pH, and could lead to cooling, thus producing the opposite of the observed trend (Sakai, 1968, and Ohmoto, 1972).

A positive correlation coefficient for the Cu, Zn, multiple regression indicates that, collectively, Cu and Zn in tetrahedrite on the

west show an identifiable increase in amount with increasing depth. This weak, but statistically significant, trend will be included in the following discussion of the localized variations in individual raises.

Elemental and isotopic variations of limited spatial extent force an examination of more local controls on sulfide deposition. The vein commonly pinches and swells and is rarely continuous for more than 200 feet vertically and sometimes less laterally. Fairly consistent vertical trends and very tentative lateral trends have been listed in Table 7. Only the vertical trends will be discussed.

Moving upward in specific raises, it appears that weight percent Ag in tetrahedrite increases at the expense of Cu, Zn, and Cd while S³⁴ is depleted. Fe shows no obvious, consistent variation. However, a closer look at the data suggests that Fe may have had nearly as much influence on the amount of Ag in tetrahedrite as copper did. Fe and Cu had about the same variability (Table 3). Therefore, the amount of iron available in the form of earlier siderite and/or pyrite may have been a factor. In addition, the extent of replacement of siderite and pyrite by tetrahedrite may have greatly influenced the amount of Fe included in the tetrahedrite structure. For example, consider samples 15-46 and 14-46. Both samples were collected in the same raise stope, but on different vein splits. 15-46 had abundant pyrite while 14-46 had only minor pyrite occurring with tetrahedrite. Tetrahedrite in 15-46 had 3.84 weight percent Fe, while 14-46 had 5.79 weight percent Fe. Both samples had Cu in about equal amounts but the "iron poor" 15-46 contained more silver than 14-46.

It was noted in Chapter IV that Cu was more variable on the east than on the west. In addition, a multiple regression involving Cu and Zn

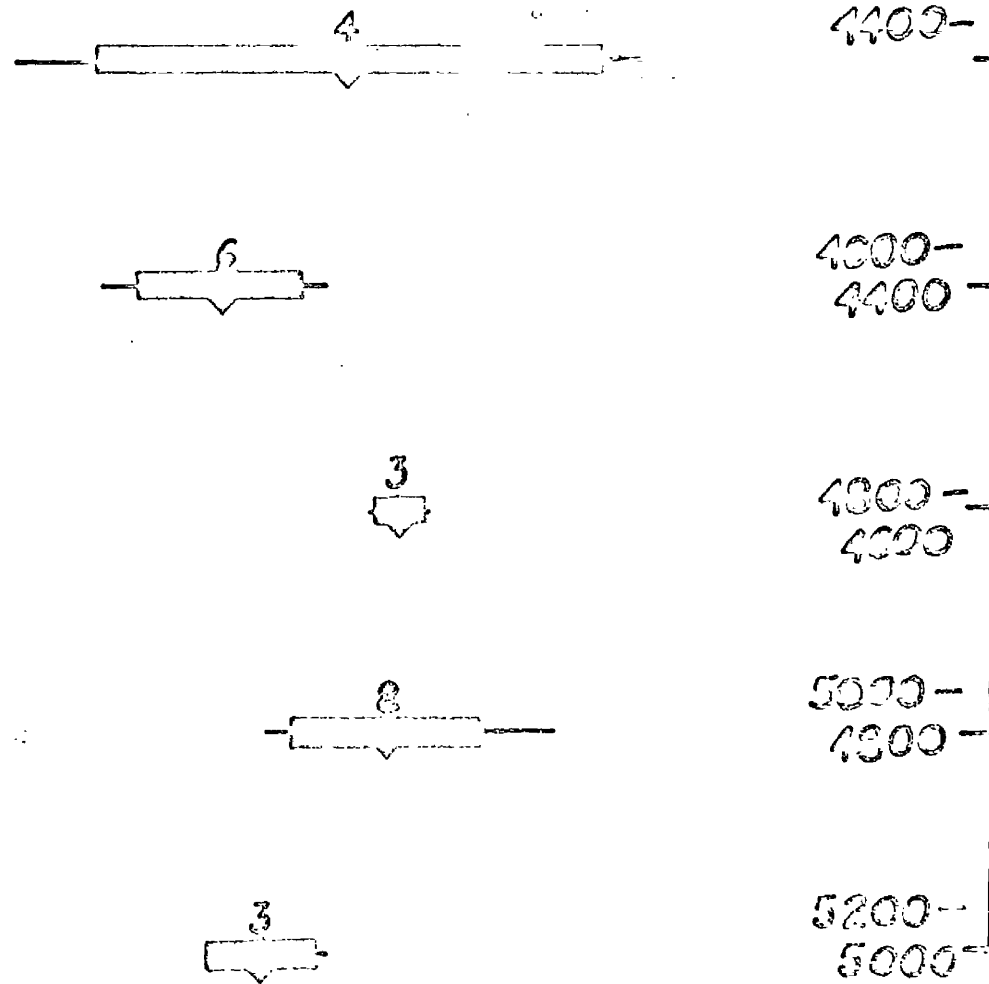
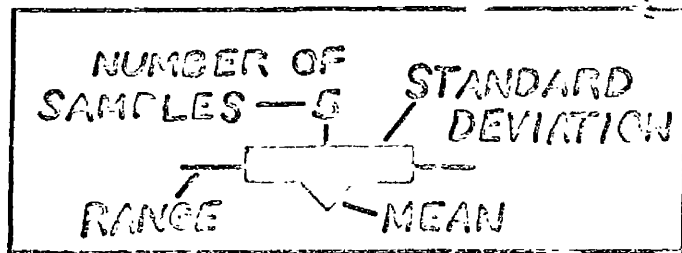
on the west yielded a correlation coefficient significant at the 90% level (Table 6); while on the east where Cu is more variable, a significant regression involving Cu was not found. Perhaps the occurrence of pyrite and/or siderite masses was more erratic on the east. Uniform replacement of variable amounts of pyrite and/or siderite by tetrahedrite could vary the amount of iron included in the tetrahedrite structure. This, in turn, could contribute to the variability of copper in tetrahedrite. This may also indicate that replacement of siderite and pyrite by tetrahedrite was not uniform and possibly that the thermochemistry of the solutions on the east was more variable than on the west. If the amount of siderite and/or pyrite available for replacement by tetrahedrite was not a factor, then solutions on the east may not have been the same as those on the west at all.

There may be two possible explanations for the observed isotopic trend with changing tetrahedrite composition. First, the isotopic variations may suggest an explanation related to the thermochemistry of the solutions. Second, it is possible that the isotopic composition is controlled by the elemental composition.

Obvious thermochemical controls on the stability of metal complexes in solution are pH, temperature, and pressure. Isotopic fractionation can be varied by changing pH and temperature, in particular (Chmoto, 1972). Significant changes in pH seem unlikely. If such changes did occur, the total change in pH over the 1000 vertical feet sampled would probably have changed the S^{34} noticeably with decreasing depth. The mean δS^{34} value of tetrahedrite was remarkably constant, vertically (Fig. 25). It is possible that the presence of earlier



FIG. 25
TETRAHEDRITE
PERMIL VALUES
BY LEVEL



formed siderite kept the solutions somewhat buffered at constant pH. However, slight changes in pH in vertical vein segments could have caused an enrichment of tetrahedrite in silver. The solubility of silver sulfide complexes decreases markedly with an increase in H_2S relative to HS^- . This can be achieved by a decrease in pH (Barnes and Czamanske, 1967). Depletion of S^{34} in tetrahedrite is not consistent with a decrease in pH. Field and Moore (1971) established a primary fractionation trend with enrichment in S^{34} in the order pyrite>sphalerite>tetrahedrite>galena. Using Ohmoto's data at $250^\circ C$ (Fig. 23), tetrahedrite would be depleted in S^{34} relative to the dominant sulfur specie in solution (H_2S or HS^-). A decrease in pH would increase the proportion of H_2S present compared to HS^- (Ohmoto, 1972). Because H_2S is enriched in S^{34} compared to HS^- (Fig. 23), the ξS^{34} of available sulfide will increase. Tetrahedrite precipitating from this sulfide solution would then become enriched in S^{34} with decreasing pH.

Cooling of the solutions can cause silver complexes to become less soluble and also cause depletion of S^{34} in tetrahedrite (Fig. 23, after Ohmoto, 1972). Very slight cooling within short vertical vein segments may have caused the small elemental and isotopic variations observed. Slight cooling may have resulted from mixing with other solutions and, according to Helgeson (1964), mixing with hydrothermal solutions of different composition can drastically alter metal complex stabilities. In addition, dilution can lead to the precipitation of portions of the dissolved sulfides (Barnes and Czamanske, 1967). Cooling over such a short vertical distance may not be a reasonable possibility, although dilution

and changing composition because of mixing with other solutions could have been responsible for the elemental variations.

Decreasing pressure can lead to sulfide deposition. According to Toulmin and Clark (1967), adiabatic expansion of ore fluids, as they rush into a fracture system through a constricted opening, has been cited as a very probable cause of sulfide deposition in many ore deposits. A certain degree of cooling also accompanies adiabatic expansion. Because the Chester Vein frequently pinches and swells, both vertically and laterally, adiabatic expansion may have been an important mechanism.

Sakai (1968) found that isotopic fractionation was proportional to the bonding strength of the mineral specie in question. For example, pyrite is enriched in S^{34} more than coexisting sphalerite because the sulfur in pyrite is more strongly bonded than in sphalerite (Bachinsky, 1969). According to Pavorennykh (1970), Cu and Zn form stronger tetrahedral bonds with sulfur than Ag does. Cu and Zn tend to stabilize SbS_3 trigonal pyramids more than Ag does. Therefore, increasing Ag and decreasing Cu and Zn in tetrahedrite might cause a corresponding depletion in S^{34} . However, this trend does not persist laterally. Therefore, the greater weight percent of Cu compared to Fe, Zn, Ag, or Cd may influence the bond strength more than Ag does.

The paragenetic trend observed, whereby pyrite is depleted in S^{34} relative to the later tetrahedrite, indicates two things. First, it confirms the textural observation that tetrahedrite did not form in equilibrium with pyrite, but formed distinctly later than pyrite. This must be the case considering the primary fractionation trend mentioned earlier (Field and Moore, 1971). Second, if this progressive enrichment

of later sulfides in S^{34} compared to earlier sulfides is suggestive of a significant change in the δS^{34} of available sulfide, it is the opposite of that observed by Field and Moore (1971) in the Bingham District, Mancless and others (1960) in the Yellowknife District, and Both and others (1969) in the Zeehan Mineral Field, but similar to the trend observed by Ames (1962) in the Tintic District. Because the sequence of mineral deposition in the Chester Vein is episodic (Fig. 7), the solutions could have undergone a change with time resulting in enrichment of available sulfide in S^{34} . There is reason to believe that this trend continued through galena deposition because two galenas had δS^{34} of +3.2 and +5.4 (Ault and Kulp, 1960). According to Field and Moore (1971) tetrahedrite is enriched in S^{34} relative to galena. These two galena analyses are similar to the δS^{34} values in tetrahedrite and, thus, may indicate continued increases in δS^{34} of available sulfide. A progressive decrease in pH would increase the proportion of H_2S in the solution and at the same time increase δS^{34} of H_2S present (Ohmoto, 1972). Sulfide precipitation from H_2S saturated solutions could release H^+ ions without increasing f_{O_2} , which would tend to produce the opposite of the observed trend. However, considering all the uncertainties in the parameters discussed, a slight increase in Eh could easily be accommodated. If an increase in Eh did occur, then the decrease in pH could be partially due to oxidation of sulfide species in solution as a result of mixing with other solutions.

CHAPTER VI

SPECULATION ABOUT THE SOURCE

OF THE VEIN CONSTITUENTS

Fryklund (1964) suggested that the so-called post-monzonitic vein constituents had a deep point source near the lower crust-mantle boundary. This point was at the intersection of a line of fractures occupied by the Gem stocks and a northwest trending shear zone now occupied by the Coeur d'Alene Mineral Belt. Hershey (1916) proposed solutions set into convective motion in highly tilted strata by monzonite intrusives. These solutions then dissolved lead-zinc mineralization in the upper Prichard Formation, depositing it in its present position. Zartman and Stacey (1971) admitted to the possibility of mobilization of low grade, stratabound lead known to exist in the upper Prichard Formation. They said, however, that large-scale movement long after initial deposition would alter the lead isotopic composition drastically from the single-stage Precambrian model they had derived. Incidentally, if this interpretation is correct, it supports a Precambrian age of vein mineralization. Krason (written communication, 1973) does not believe that the isotopic ratios of Precambrian lead would be altered in a mechanism like that proposed by Hershey (1916) regardless of the time of mobilization. Sorenson (1972) felt that sedimentary sulfides were extracted from the wall rocks by circulating hydrothermal solutions (lateral secretion). Based on the lead isotopic data, he hypothesizes that the disseminated sulfides were introduced into flat lying sediments through the ancestral

Osburn fault which tapped some deep source near the mantle. Then, in the Cretaceous, the disseminated sulfides were laterally secreted and concentrated as veins in the fractures. Barnes (1959) considered lateral secretion from the immediately enclosing wall rocks to be unworkable in most cases. He gave several examples where metal-rich shales adjacent to major ore bodies contributed only negligible amounts of metals.

Sorenson (1972) cites a wide spread in δS^{34} values of sulfides of unknown mineralogy as evidence supporting his lateral secretion theory. However, if the disseminated sulfides were dissolved and then transported in aqueous solution to the adjacent vein opening, variable fractionation should not have occurred along the vertical length of the vein. Variable δS^{34} values in vein galena at Keno Hill in the Yukon was attributed to non-uniform diffusion toward the vein, not lateral secretion. It is very likely that the wide permil spread in Sorenson's sulfur isotopic values is due to effects similar to those observed in this study with respect to pyrite. In this study, a probable increase in pH, caused a four permil variation in δS^{34} in pyrite, over a relatively short vertical distance of 1000 feet. If this is the case, the δS^{34} inferred from this study would probably apply to Sorenson's data also. This would imply that lateral secretion from the adjacent wall rocks did not occur. Instead, it may have operated at some horizon below the ore zone. The solutions probably rose into the ore zone and mineralized the fractures in hydrothermal fashion. The wide permil range probably resulted from the changing chemistry of the solutions as they migrated upward. Therefore, lateral secretion from the enclosing wall rocks is ruled out, while similar mechanisms, including convecting solutions, operating in some homogenized source

(with respect to sulfur and lead) at greater depth, remains a possibility. The nature of such a source will now be considered.

Subsidence of a thick pile of sediments could mobilize connate water, causing dissolution and mixing of disseminated sulfides. These solutions, expelled as thermal springs, could then produce strataform sulfides with a mean δS^{34} similar to the values observed in this study. Mauger (1972) found a mean δS^{34} of +4.0 with a spread of 0 to +10 permil at Ducktown, Tenn. In addition, convecting Salton Sea saline brines and pyrite (deposited from the brines) from the reservoir rocks average 1.1 permil with a narrow spread of -1.4 to +3.0 permil (White, 1968). However, the 206/204 lead isotope ratios at Ducktown (Kinkle, 1967) and many other strataform deposits (Richards, 1971) are more radiogenic than predicted on the basis of a single-stage growth curve and known age of the deposit. The Coeur d'Alene lead data rule out this type of source.

Strataform sulfides of late stage volcanic or hot spring association almost always exhibit δS^{34} with narrow spread and slightly enriched above 0 permil (Stanton, 1972). The lead isotopic ratios are very uniform and correspond to a single-stage growth curve indicating a possible deep origin of uniform U-Th-Pb ratios (Stanton, 1972). Therefore, mobilization of disseminated sulfides of volcanic association may have played a role in the formation of vein deposits in the Coeur d'Alene district.

The slight enrichment in S^{34} and the narrow range could be indicative of magmatic assimilation of a significant volume of sedimentary material. In this case the lead isotope ratios would be very uniform and could adhere to a single-stage growth curve (Stanton, 1972), as is observed in the Coeur d'Alene district.

These values also fit close to the typical "magmatic hydrothermal" category of Jensen (1967). They may not be close enough to 0 permil to indicate sulfur of upper-mantle origin (Laughlin and others, 1969; Lange and Cheney, 1971; and Rye and Sawkins, 1974), but direct introduction from some deep magmatic source is an ever-present, although mysterious, possibility.

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

Pyrite is depleted in S^{34} with decreasing depth at the rate of about 0.9 permil/200 feet. Increasing pH with decreasing depth within the Chester Vein is favored as the cause of this trend over less likely possibilities such as the reservoir effect (finite source of sulfur). The systematic variation of δS^{34} values in pyrite with depth shows potential as an indicator of position within an ore shoot, providing that pyrite and tetrahedrite have the same spatial relationship to the ore shoot.

Elemental and isotopic variations of limited spatial extent in individual raises were identified in tetrahedrite. A weak, but statistically significant, trend with respect to Cu and Zn on the west was detected. Collectively, Cu and Zn increase with increasing depth. The occurrence of earlier iron minerals (pyrite and siderite) in the vein may control the variability of iron in tetrahedrite and have some influence on the amount of silver and copper permitted to enter tetrahedrite. Elemental trends in individual raises could be explained by decreasing pH, slight cooling, dilution and mixing with other solutions, and adiabatic expansion of the solutions. The corresponding isotopic variations could be due to slight cooling (but not decreasing pH), and partly caused by changing bond strength with changing composition of tetrahedrite. A vertical zonation of Cu and Zn collectively in tetrahedrite may be

present although it is interrupted by physical irregularities of the vein and altered by the chemical variability of the ore-forming process.

Early sulfides are depleted in S^{34} compared to later sulfides. This paragenetic variation violates the primary fractionation trend involving pyrite and tetrahedrite (Field and Moore, 1971) and, therefore, confirms the textural evidence that tetrahedrite postdated the pyrite. It also indicates that the solutions probably experienced a progressive decrease in pH between pyrite and galena deposition.

It is recommended that S isotope studies of pyrite be extended to ore shoots which can be sampled in their entirety. Elemental and S isotope studies of tetrahedrite should be discontinued. The elemental and isotopic composition of tetrahedrite is probably much too dependent on the variable occurrence of pre-existing vein minerals.

Considerable work remains to be done before reasonable speculations can be made about the depositional processes involved, or the source and history of the vein constituents. Carbon, oxygen, and hydrogen isotope and fluid inclusion salinity studies could offer much information about the nature of the fluids (saline brines or magmatic fluids, for example), thermal history and pressures involved.

Selenium in sulfides has been used as an indicator of volcanic as opposed to sea water sulfur.

Finally, δS^{34} of sulfides in the Gem stocks should be determined for comparison with main stage vein sulfides and sulfides associated with the stocks.

REFERENCES

REFERENCES

- Ames, R. L., 1962, Sulfur isotopic study of the Tintic Mining Districts, Utah: Unpublished Ph.D. dissertation, Yale University.
- Anderson, R. J., 1940, Microscopic features of ore from Sunshine Mine, Idaho: *Econ. Geol.*, v. 35, pp. 659-667.
- Angino, E. E. and Billings, G. K., 1972, Atomic Absorption Spectrometry in Geology, Amsterdam: Elsevier,
- Ault, W. U. and Jensen, M. L., 1962, Summary of sulfur isotopic standards: in *Biogeochemistry of Sulfur Isotopes*, ed. M. L. Jensen: Proc. N.S.F. Symposium, Yale University, pp. 16-29.
- _____ and Kulp, J. L., 1960, Sulfur isotopes and ore deposits: *Econ. Geol.*, v. 55, pp. 73-100.
- Bachinsky, D. J., 1969, Bond strength and sulfur isotopic fractionation in coexisting sulfides: *Econ. Geol.*, v. 64, pp. 56-65.
- Barnes, H. L., 1959, The effect of metamorphism on metal distribution near base metal deposits: *Econ. Geol.*, v. 54, pp. 919-943.
- _____ and Czamanske, G. K., 1967, Solubilities and Transport of Ore Minerals: *Geochemistry of Hydrothermal Ore Deposits*, ed. H. L. Barnes, New York: Holt, Rinehart, and Winston, pp. 334-381.
- _____ and Ellis, A. J., 1967, Appendix 2—Ionization in Aqueous Solutions: *Geochemistry of Hydrothermal Ore Deposits*, ed. H. L. Barnes, New York: Holt, Rinehart, and Winston, pp. 636-649.
- Belcher, R., Dagnall, R. M., and West, T. S., 1964, An examination of the A.A. of silver: *Talanta*, v. 11, pp. 1257-1263.
- Billingsley, P. R. and Locke, Augustus, 1939, Structure of ore deposits in the continental framework: *A.I.M.E. Trans.*, v. 144, pp. 9-64.
- Both, R. A., Rafter, T. A., Solomon, M., and Jensen, M. L., 1969, S isotopes and zoning of the Zeehan Mineral Field, Tas.: *Econ. Geol.*, v. 64, pp. 618-628.
- Boyle, R. W., Waneless, R. K., and Stevens, R. D., 1970, Sulfur isotope of Pb-Zn-Ag-Cd deposits of the Keno Hill-Galena Hill area, Yukon, Canada: *Econ. Geol.*, v. 65, pp. 1-10.

- Bryan, T. S., 1974, Mineralogical and chemical zoning in the Lucky Friday Mine, Mullen, Idaho: Unpublished Master's thesis, University of Montana.
- Cannon, R. S., Pierce, A. P., Antweiler, J. C., and Buck, K. L., 1962, Lead isotope studies in the Northern Rockies, U.S.A.: in Petrological Studies—a volume in honor of A. F. Buddington: New York, Geol. Soc. America, pp. 115-131.
- Chan, S. S. M., 1966, Mineralogical and geochemical studies of the vein material from the Galena Mine, Idaho:
- Colson, 1961, Geology of the Sunshine Mine: in Guidebook to the Geology of the Coeur d'Alene Mining District, Idaho: Bureau of Mines and Geology Bull. 16, pp. 30-34.
- Crosby, G. M., 1969, A preliminary examination of trace mercury in rocks, Coeur d'Alene District, Idaho: Quart. Col. School of Mines, v. 64, pp. 169-194.
- Field, C. W., and Moore, W. J., 1971, Sulfur isotope study of the "B" Limestone and Galena Fissure ore deposits of the U. S. Mine, Bingham Mining District, Utah: Econ. Geol., v. 66, pp. 48-62.
- Fryklund, V. C. and Fletcher, T. D., 1956, Geochemistry of sphalerites from the Star Mine, Coeur d'Alene District, Idaho: Econ. Geol., v. 51, pp. 223-247.
- _____, 1964, Ore deposits of the Coeur d'Alene District, Idaho: U.S. Geol. Surv. Prof. Paper 445, pp. 103
- Garvels, R. M. and Christ, C. L., 1965, Solution, Minerals, and Equilibria, New York: Harper and Row, 437 pp.
- Goldschmidt, V. M., 1954, Geochemistry, Oxford: Clarendon Press, 725 pp.
- Gott, G. B. and Botbol, J. M., 1971, Zoning of some ore associated metals in the Coeur d'Alene District, Idaho: (abs.) Econ. Geol., v. 66, p. 1266.
- Helgeson, H. C., 1964, Complexing and Hydrothermal Ore Deposition, New York: Pergamon Press, 123 pp.
- Hershey, O. H., 1916, Origin and distribution of the ore in the Coeur d'Alenes: published by the author, 32 pp.
- Hobbs, S. W., Griggs, A. B., Wallace, R. E., and Campbell, A. B., 1965, Geology of the Coeur d'Alene District, Shoshone County, Idaho: U.S.G.S. Prof. Paper 478, 139 pp.

- Hobbs, S. W., and Fryklund, V. C., 1968, The Coeur d'Alene District, Idaho: in *Gratton and Sales volume, Ore Deposits of the U.S. 1933/1967*, v.2, ed. John D. Ridge: New York, A.I.M.E.
- Jensen, M. L., 1967, Sulfur Isotopes and Mineral Genesis: Geochemistry of Hydrothermal Ore Deposits, ed. H. L. Barnes, New York: Holt, Rinehart, and Winston, pp. 143-165.
- Kerr, P. F. and Robinson, R. F., 1953, Uranium mineralization in the Sunshine Mine, Idaho: *A.I.M.E. Trans.*, v. 196, pp. 495-511.
- Kinkel, A. R., 1967, The Ore Knob copper deposit, North Carolina and other massive sulfide deposits of the Appalachians: *U.S. Geol. Surv. Prof. Paper* 588.
- Krason, J., 1973, Written communication.
- Lange, I. M., 1968, Sulfur isotope geology of Butte, Montana: Unpublished Ph.D. dissertation, University of Washington.
- Lange, I. M. and Cheney, E. S., 1971, Sulfur isotopic reconnaissance of Butte, Montana: *Econ. Geol.*, v. 66, pp. 63-74.
- Laughlin, A. W., Rehrig, W. A., and Mauger, R. L., 1969, K-Ar chronology, S, Sr isotope ratios at the Questa Mine, New Mexico: *Econ. Geol.*, v. 64, pp. 903-909.
- Long, A., Silverman, A. J., and Kulp, J. L., 1960, Isotopic composition of lead and Precambrian mineralization of the Coeur d'Alene District, Idaho: *Econ. Geol.*, v. 55, pp. 645-658.
- Malik, H. J. and Mullen, K., 1973, *A First Course in Probability and Statistics*, Massachusetts: Addison-Wesley Publishing Co., 355 pp.
- Mauger, R. L., 1972, A sulfur isotope study of the Ducktown, Tennessee District, U.S.A.: *Econ. Geol.*, v. 67, pp. 497-510.
- Mitchum, T. W., 1952, Indicator minerals, Coeur d'Alene Silver Belt: *Econ. Geol.*, v. 47, pp. 414-450.
- Ohmoto, H., 1972, Systematics of sulfur and carbon isotopes in hydrothermal ore deposits: *Econ. Geol.*, v. 67, pp. 551-578.
- Palache, C., Berman, H., and Frondel, C., 1944, Elements, sulphides, sulfosalts, oxides, v. 1 of *The system of mineralogy of James Dwight Dana and Edward Salisbury Dana (7th ed.)*, New York: John Wiley and Sons, Inc., 834 pp.
- Povarennykh, A. S., 1971, Crystallochemistry of complex sulfides of arsenic, antimony and bismuth: in *Joint Symposium*, v. , IMS-IGOD, Special Issue No. 2, *Geochemistry and Crystallography of Sulfide Minerals in Hydrothermal Deposits*.

- Radtke, A. S., Taylor, C. M., and Morris, H. T., 1969, Micromineralogy of galena ores, Burgin Mine, East Tintic District, Utah: U.S. Geol. Surv. Prof. Paper 614 A, 17 pp.
- Ramdohr, P., 1969, The Ore Minerals and Their Intergrowths (3rd ed.), Oxford: Pergamon Press, 1171 pp.
- Ramirez, Munoz, 1968, Atomic Absorption Spectroscopy, New York: Elsevier, 457 pp.
- Ransome, F. L. and Calkins, F. C., 1908, The geology and ore deposits of the Coeur d'Alene District, Idaho: U.S. Geol. Surv. Prof. Paper 62, 203 pp.
- Richards, J. R., 1971, Major lead ore bodies—mantle origin?: Econ. Geol., v. 66, pp. 425-434.
- Rubeška, I., Sulcek, Z., and Moldon, B., 1967, The determination of silver in sulfide minerals by atomic absorption spectrophotometry: Anal. Chem. Acta., v. 37, pp. 27-32.
- Rye, R. O. and Sawkins, F. J., 1974, Fluid inclusions and stable isotope studies on the Casapalca Ag-Pb-Zn-Cu deposit, Central Andes, Peru: Econ. Geol., v. 69, pp. 181-205.
- Ryznar, G., Campbell, F. A., and Krouse, H. R., 1967, Sulfur isotopes and the origin of the Quemont ore body: Econ. Geol., v. 62, pp. 664-678.
- Sakai, H., 1968, Isotopic properties of sulfur compounds in hydrothermal processes: Geochem. Journal, v. 2, pp. 29-49.
- Skinner, B. J., Luce, F. D., and Malzovicky, E., 1972, Studies of the sulfosalts of CuIII phases and phase relations in the system Cu-Sb-S: Econ. Geol., v. 67, pp. 924-938.
- Sorenson, A. H., 1972, Age and Mode of Origin of the Coeur d'Alene Ore Deposits, Idaho, New York: Carlton Press, Inc.
- Stanton, R. L., 1972, Ore Petrology, New York: McGraw-Hill Book Co., 699 pp.
- Steiner, A. and Rafter, T. A., 1966, S isotopes in py, pyrr, alunite, and arhydrite from steam wells, in the Taupo Volcanic Zone, New Zealand: Econ. Geol., v. 61, pp. 1115-1129.
- Tibbs, N., 1972, Wall rock geochemistry of the Chester Vein, Sunshine Mine, Idaho: Unpublished Ph.D. dissertation, University of Missouri, Rolla.

- Toulmin, P. and Clark, S. P., 1967, Thermal aspects of ore formation: Geochemistry of Hydrothermal Ore Deposits, ed. H. L. Barnes, New York: Holt, Rinehart, and Winston, Inc., pp. 437-464.
- Umpleby, J. B. and Jones, E. L., 1923, Geology and ore deposits of Shoshone Co., Idaho: U.S. Geol. Surv. Bull. 732, 156 pp.
- Waneless, R. K., Boyle, R. W., Lowdon, J. A., 1960, Sulfur isotope investigation of the Au-ztz deposits of the Yellowknife District: Econ. Geol., y. 55, pp. 1591-1621.
- Weiss, P. L., 1964, Bleaching: in Ore Deposits of the Coeur d'Alene District, Idaho: U.S. Geol. Surv. Prof. Paper 445, pp.
- White, D. E., 1968, Environments of generation of some base metal ore deposits: Econ. Geol., v. 63, pp. 301-335.
- Williston, S. H., 1964, The mercury halo method of exploration: Eng. Mining Jour., v. 1965, no. 5, pp. 98-101.
- Zartmen, R. E. and Stacey, J. S., 1971, Lead isotopes and mineralization ages in belt supergroup rocks, Northwestern Montana and Northern Idaho: Econ. Geol., v. 66, pp. 849-860.

APPENDIX A

PHOTOMICROGRAPHS OF THE LOWER CHESTER VEIN ORE

PHOTOMICROGRAPHS OF LOWER CHESTER VEIN ORE

Symbols Used—

Qtz—quartz

Py—pyrite

Qtzite—quartzite

Td—tetrahedrite

Sd—siderite

Cp—chalcopyrite

Ap—arsenopyrite

Gn—galena

Fig. A-1. Chan (1966) noticed that Td was often associated with earlier Ap in the Silver Vein at the Galena Mine. This tracing of a photomicrograph shows Td growth beginning at a cluster of earlier Ap in Sd. (no. 10-50, 57x)

Fig. A-2. This tracing of a photomicrograph shows a composite of Sd-Td-Cp partially replaced by Gn. Ap appears to have spanned a period of Sd deposition. Some Ap grains are corroded while others have euhedral shapes. (no. 38-46, 57x)

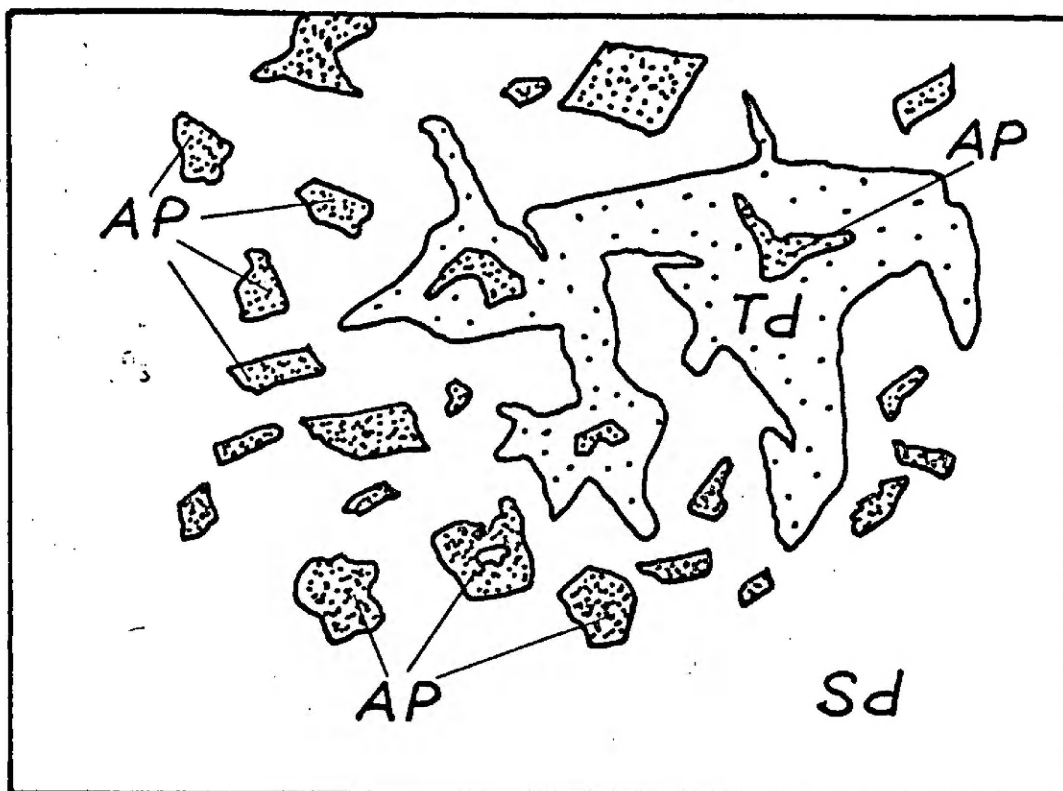
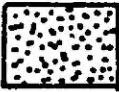
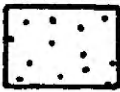


FIG. A-1 Ap  Td  10-50
114x

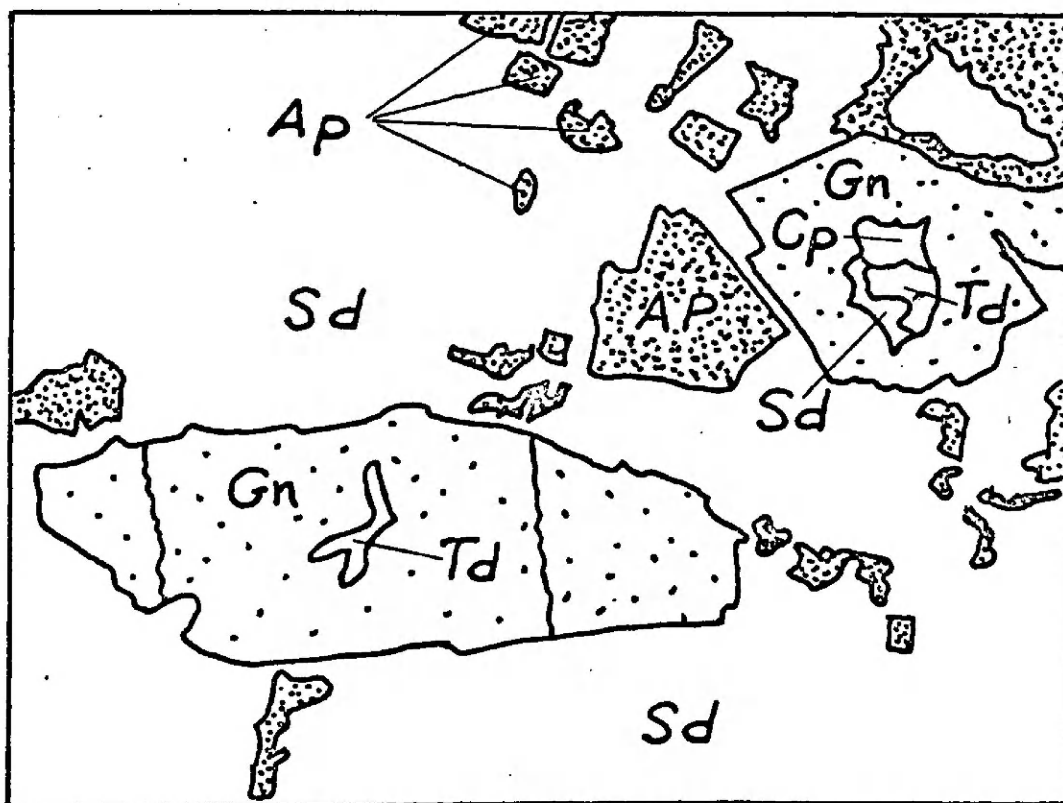


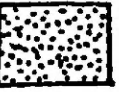
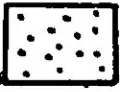
FIG. A-2 Ap  Gn  3846
57x

Plate 3 - Intensely sheared Sd has
been partially replaced by Td.
The bar scale represents 0.2 mm
(no. 31-50, 57x)

Plate 4 - Td has infiltrated brecciated
Sd with minor replacement.
The bar scale represents 0.2 mm.
(no. 16-48, 57x)

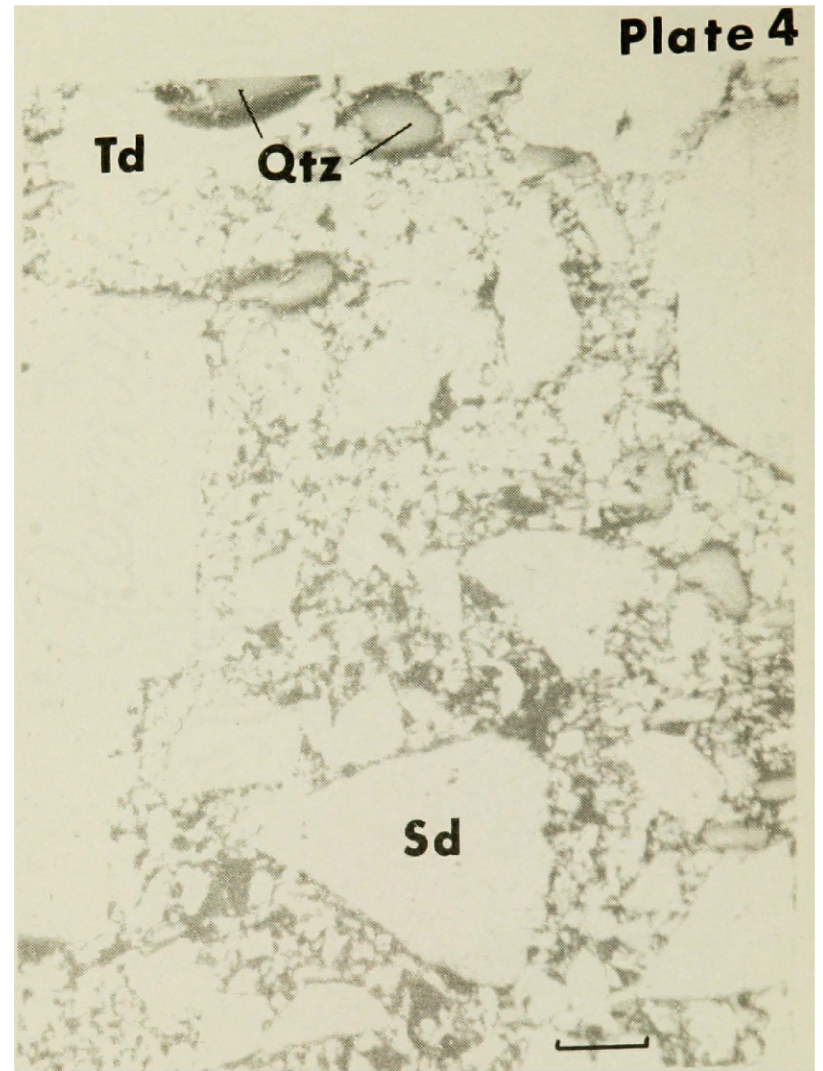
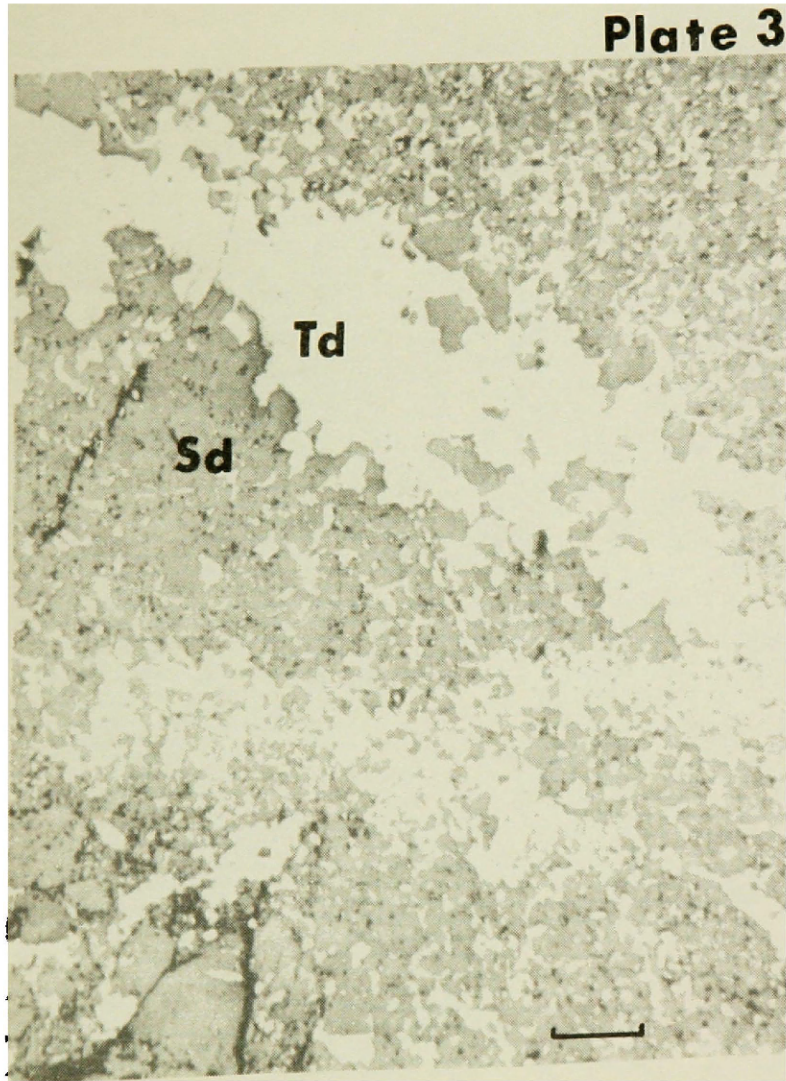


Plate 5 - Replacement of Sd by Td has begun along a fracture perpendicular to Sd twin lamellae.
The bar scale represents 0.2mm.
(no.31-50, 57x, x nic.)

Plate 6 - Td growth has begun at the junction of several Sd grains and then infiltrated Sd grain boundaries.
The bar scale represents 0.1 mm.
(no. 5-50, 114x)

Plate 5

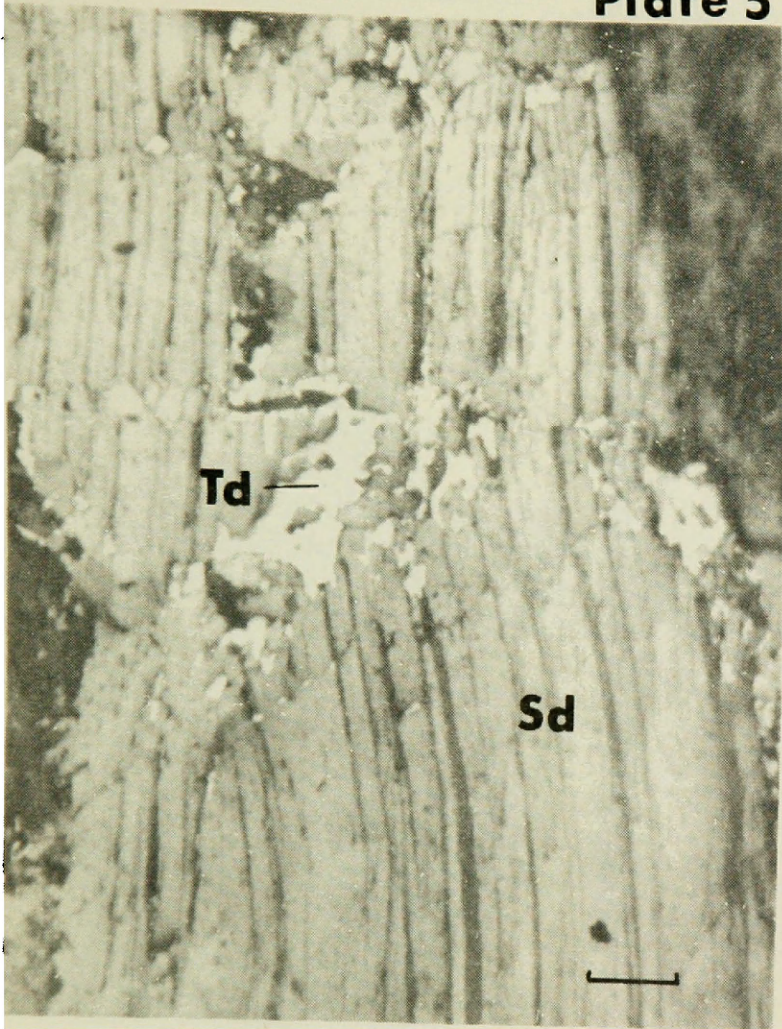


Plate 6

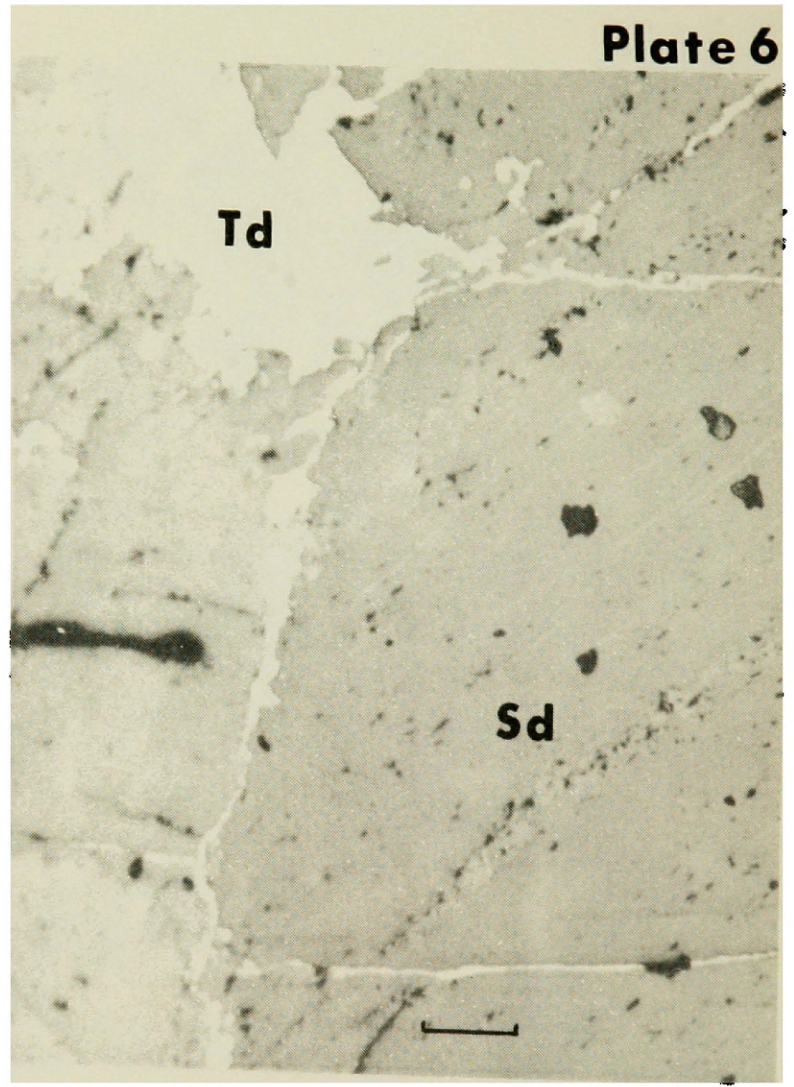


Plate 7 - This photomicrograph shows what appears to be open space filling of a Qtz lined vug in Sd by Td. The bar scale represents 0.2 mm. (no.23-44, 57x)

Plate 8 - Td is shown replacing Sd and Qtz along a sheared Qtz veinlet in Sd. The bar scale represents 0.1 mm. (no. 11-50, 114x)

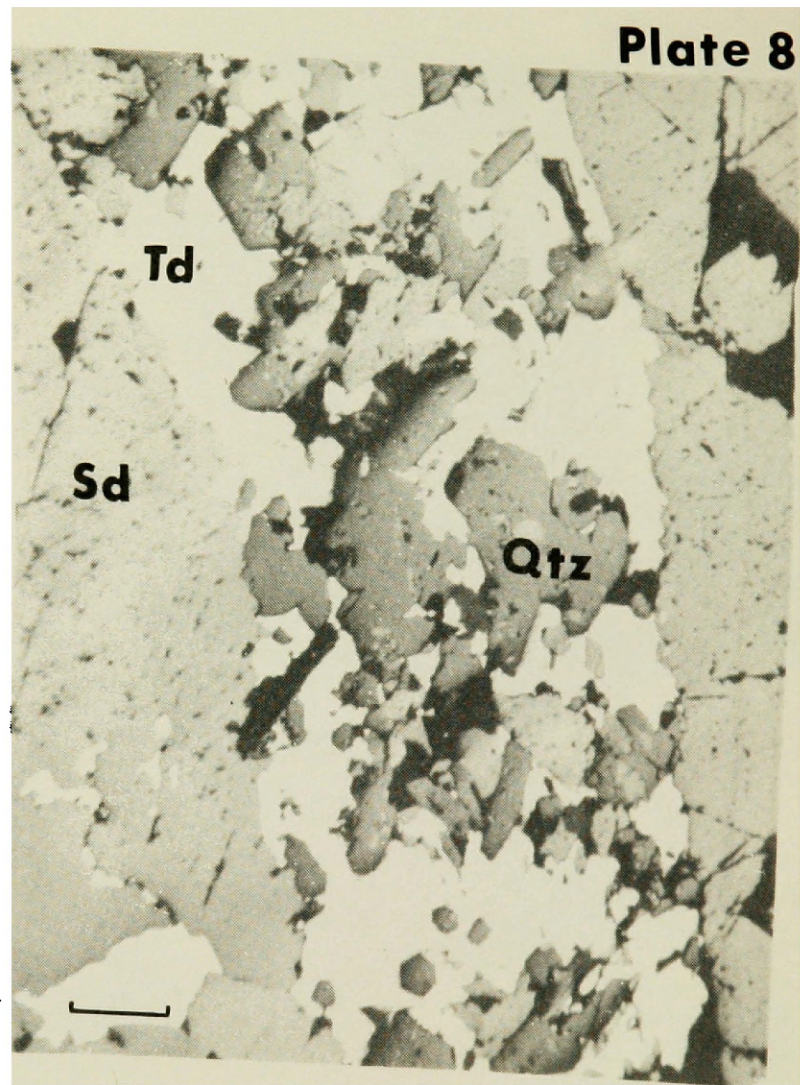
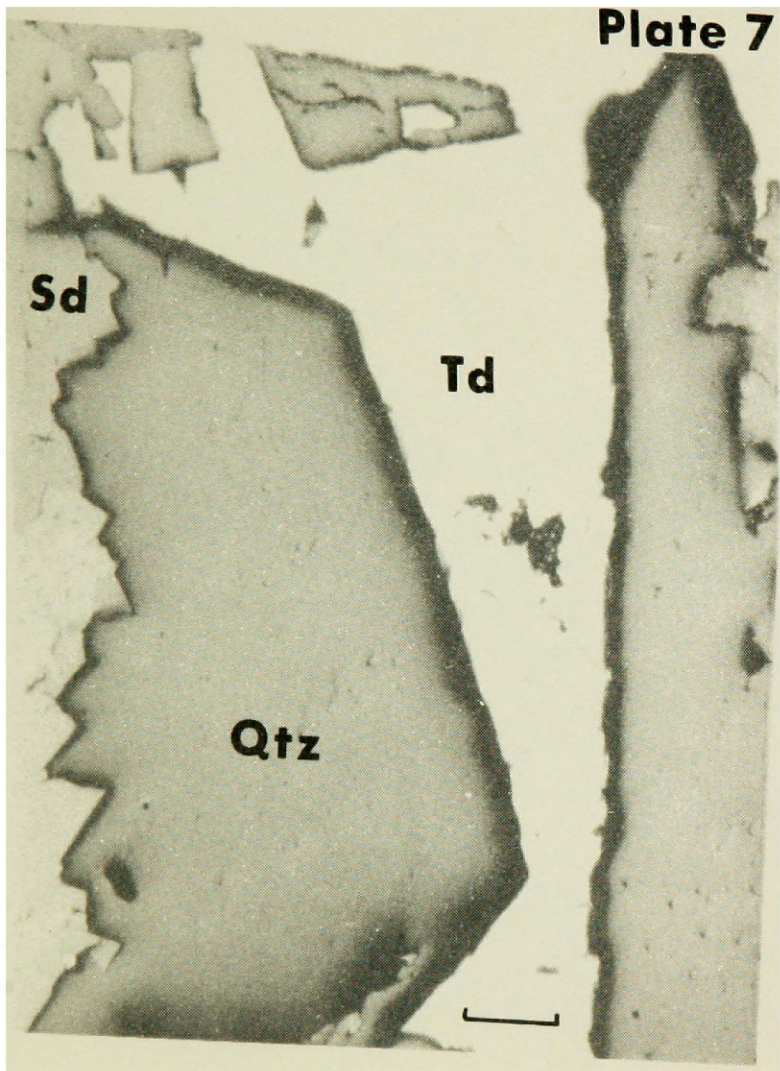


Plate 9 - This photomicrograph shows advanced replacement of Py by Td forming a network texture of Td in gangue which is typical of Chester Vein ore.
The bar scale represents 0.2 mm.
(no. 39-46, 57x)

Plate 10 - the paragenetic sequence, Py-Qtz-(Sd)-Td is illustrated in this Photomicrograph.
The bar scale represents 0.2 mm)
(no. 27-42, 57x)

Plate 9



Plate 10

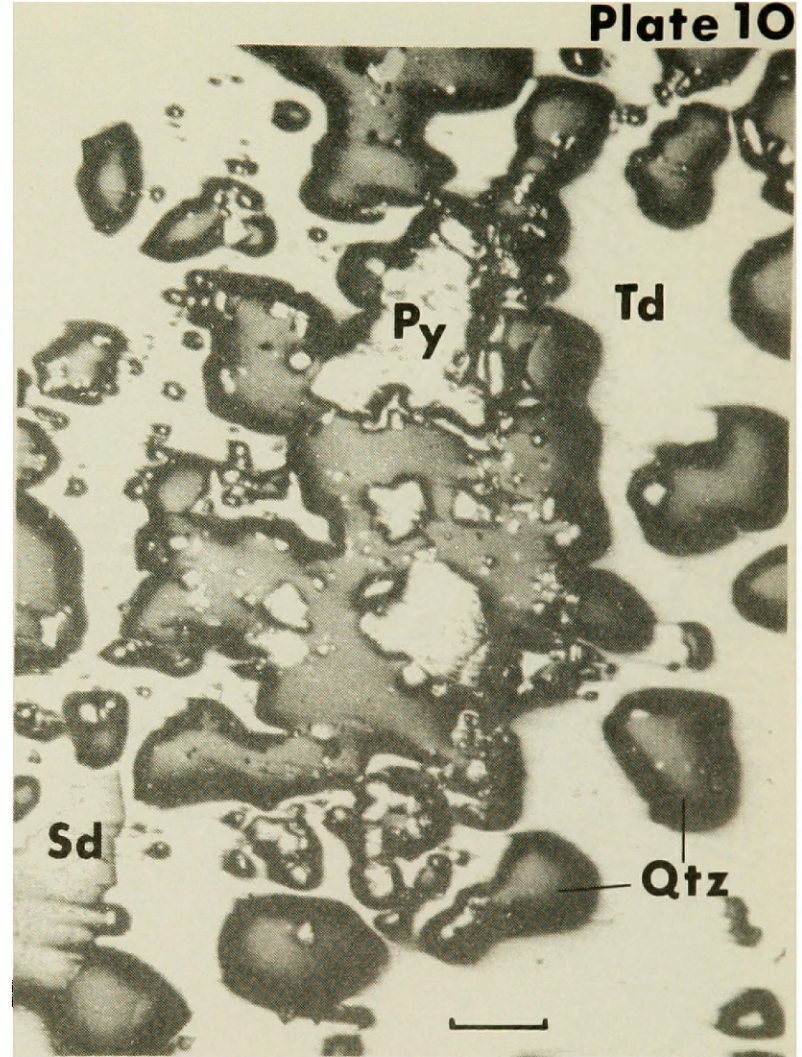


Plate 11 - Pyritehedrans in Qtzite have been corroded due to sideritization of the wall rock.
The bar scale represents 0.2 mm.
(no. 28-52, 57x)

Plate 12 - Td has been partially replaced by Gn revealing polygonal grain boundaries in "massive" Td.
The bar scale represents 0.2 mm.
(no. 16-48, 57x)

Td - Gn grain boundaries have been accented.

Plate 11

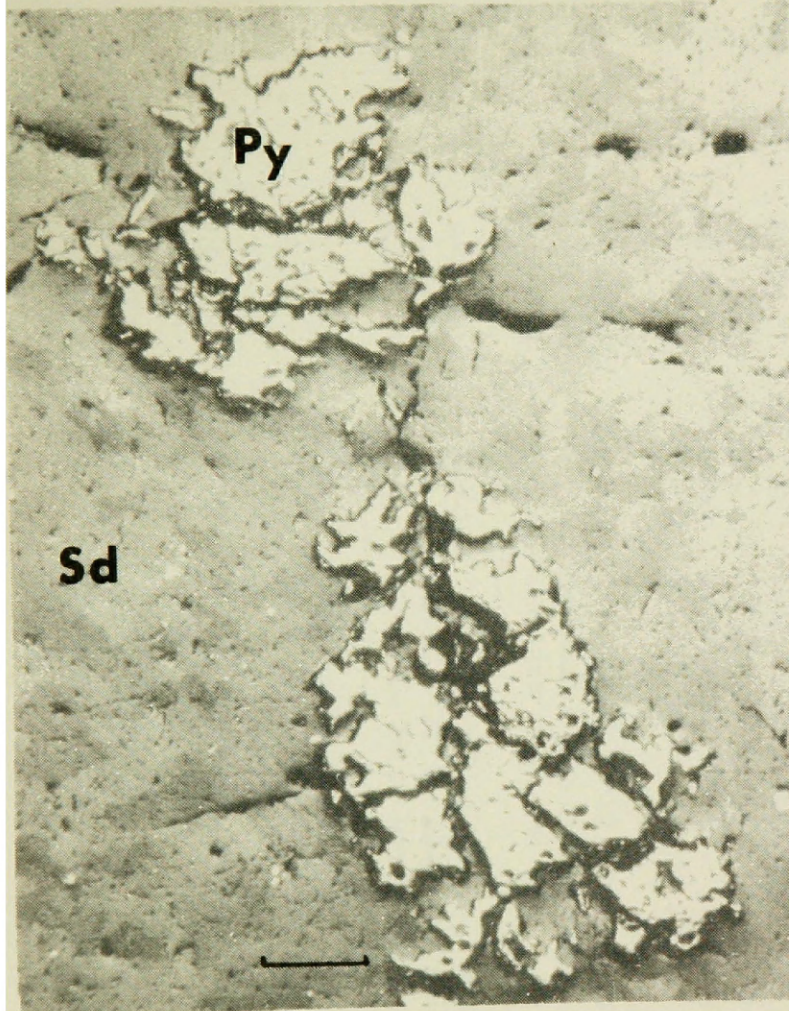
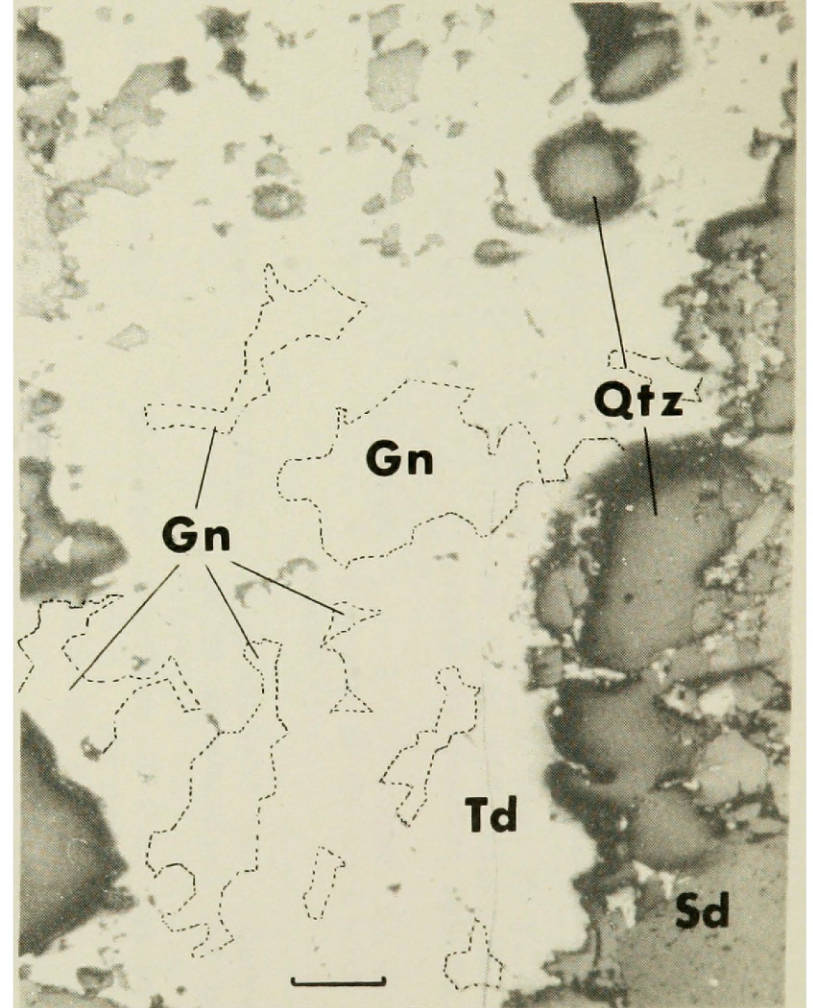


Plate 12



13

APPENDIX B

SAMPLE DESCRIPTIONS AND ISOTOPE DATA

SAMPLE DESCRIPTIONS AND ISOTOPE DATA

SAMPLE NO.	MINERAL	S^{34}	VEIN	REMARKS
27-42	Td	+2.9	Chester	110 up 539 rse, 25 E. sulfides next to FW of FLT. Minor Td replacing abundant massive Py, Sd
	Py	+1.0		
1-44	Td	+5.9, +5.9	Chester	2 W. drift stope, 65 W. sta. 14. 6 veins of Td in 2 wide massive Sd. Minor Py
21-44	Td	+4.6	H Vein	8 up 4400-10 rse. Narrow veinlets of Td in abundant Qtz gangue
22-44	Py	+2.0	Chester	Junction of 2 S. lat with J vein drift. Narrow veinlets of Td, minor Sd, Py
23-44	Td	+4.6, +4.9	No-name	75 W. of 4400 J-6 rse. Very narrow Td veinlet in equal amounts of Qtz, Sd, minor Py
	Py	+2.4, +3.2		
14-46	Td	+4.4	Chester	120 up 4600-11 rse. 11 E. FW vein split 2 wide Td vein in 5 wide Sd vein. Abundant Py
	Py	+2.8		
15-46	Td	+3.9	Chester	Same Loc. 14-46, 11 E. HW Sheared Td, Sd with minor Py
19-46	Td	+3.8, +3.7	Chester	145 up 4600-13 rse. 6 vein Td with abundant Py, minor Cp. Sheared massive Qtz and Sd
	Py	+2.5, +2.6		
38-46	Td	+4.3	J Vein	180 up 4600-J4 rse. Very narrow vein. Td veinlets 1 to 6, equal amounts Sd. Minor Qtz, Cp, Py, Gn
	Py	+2.5		
19-46			J Vein	150 up 4600-J4 rse. Narrow vein, fine intergrowth Td, Cp, Py, Sd
40-46	Td	+3.8	J Vein	80 up 4600-J4 rse. 6 veinlet Td after Sd, Py
43-46	Td	+3.3	H Vein	57 W. 4600-H6 rse. 17 up H6 pillar stope. Sd vein 5 wide, 8 to 1 wide Td, Cp veinlets

SAMPLE NO.	MINERAL	S ³⁴	VEIN	REMARKS
16-48	Td	+4.8	Chester	140 up 4800-13 rse. 6 to 1 wide veinlets Td in massive Sd, with minor Gn Brecciated
17-48	Py	+2.2, +2.2	Chester	Same Loc. as 16-48 but separated by vein pinch Td, minor Cp after massive Py
18-48	Td	+4.6	Chester	145 up 4800-11 rse. 100 E. Entire vein 10 wide, 6 Td veinlets with minor Gn, Py, Qtz
25-48	Td	+4.9	Chester	125 up 4800-4 rse. Narrow veinlets of Td with minor Py, Cp in Massive Sd
	Py	+4.0		
2-50	Td	+4.7	K Vein	40 in on K5 branch before FW split. Narrow veinlets of Td after Cp with minor Py, Gn in massive Sd
	Py	+4.6		
5-50	Td		Chester	Top of 5200-3 rse. Td after minor Cp. Vein 1 wide bounded on FW and HW sides by sheared Sd
10-50	Td	+4.3	Chester	100 up 5000-10 rse. Very narrow veinlets of Td in equal amounts Sd, Qtz
11-50	Td	+4.9	Chester	45 up 5000-4 rse. 20 W. FW. Very narrow veinlets Td with minor Cp in sheared Sd with minor Qtz
12-50	Py	+3.7, +3.9	Chester	Same Loc. 11-50, HW. Euhedral Py in Sd and Qtzite
13-50	Td	+4.6	Chester	140 up 5000-12 rse. 40 W. Narrow veinlets Td with minor Cp, Ap, Gn in massive Sd, minor Qtz
31-50	Td	+4.1	Chester	160 up 5000-11 rse. HW. 8 to 1 zone of narrow Td veinlets in massive Sd vein 4 wide with minor Qtz, Py
32-50	Td	+4.8	Chester	150 up 5000-9 rse. 30 E. HW. Vein complex 14 wide. Td veinlets 1 to 1 wide in massive Sd

<u>SAMPLE NO.</u>	<u>MINERAL</u>	<u>S³⁴</u>	<u>VEIN</u>	<u>REMARKS</u>
33-50 34-50			Chester	45 up 5000-4 rse. 30 W. Euhedral Py in HW portion of Sd, Qtzite
42-50	Td Py	+5.5 +5.0, +4.9	H Vein	150 up 5000 H8 rse. Td with minor Cp in minor Sd, Qtz
3-52	Td Py	+3.9 +3.2	Chester	150 up 5200-9 rse. Narrow veinlets of Td after Py in minor Sd, Qtz
8-52	Td	+4.6, +4.2	Chester	65 up 5200-9 rse. Very narrow veinlets of Td in minor Sd, Qtz
28-52			Chester	100 up 5200-3 rse. 90 W. HW Euhedral, disseminated Py in Qtzite
29-52	Td Py	+4.0 +3.8	Chester	Same Loc 28-52. Td vein zone 8 to 1 wide with minor Cp replacing 3 wide Sd vein with minor Qtz
6-52			Chester	100 up 5200-3 rse. FW. Narrow Td veinlets in Sd with minor Qtz

APPENDIX C

ATOMIC ABSORPTION OPERATING PARAMETERS

ATOMIC ABSORPTION OPERATING PARAMETERS

Element	Wavelength (nm)	Slit Width (nm)	Lamp Current (ma)	Burner Height	Fuel Pressure	Support Pressure
Cu	327.4	0.5	3	7.0	1.5	5.5
Fe	248.3	0.5	5	7.5	2.5	5.5
Zn	213.9	0.5	5	6.5	1.6	5.5
Ag	338.3	0.2	3	7.5	1.6	5.5
Cd	228.8	0.5	3	7.0	1.6	5.5