MINERALOGY AND CRYSTAL CHEMISTRY OF THE SULFOSALT MINERALS: BOURNONITE, SELIGMANNITE, AIKINITE, DIAPHORITE AND FREIESLEBENITE

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by

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I hereby recommend that the thesis prepared under my supervision by GERALD GENE SCHABER

entitled "Mineralogy and Crystal Chemistry of the Sulfosalt Minerals: Bournonite, Seligmannite, Aikinite, Diaphorite and Freieslebenite"

be accepted as fulfilling this part of the requirements for the degree of DOCTOR OF PHILOSOPHY

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CONTENTS

TABLES

FIGURES

PLATES

Photomicrographs

ABSTRACT

The sulfosalt minerals: bournonite $PbCuSbS_3$, seligmannite $PbCuAsS_3$, aikinite $PbCuBiS_3$, diaphorite $Pb_2Ag_3Sb_3S_8$ and freieslebenite $PbAgSbS_3$ were placed into one "group" by Dana(1892) owing to their similar cation-anion ratio of the type A_2BX_3. These minerals have long since been recognized as being of diverse structural types.

Bournonite is a common ore of lead, copper and antimony in many world-wide, hydrothermal deposits where it is associated with other sulfosalts of lead, copper, antimony and silver, as well as with most common sulfides of zinc, copper, lead and iron. Diaphorite is the second most common sulfosalt of the group while seligmannite, aikinite and freieslebenite are considered rare. All five minerals are found only in hydrothermal deposits of intermediate- to low temperatures.

Although the structures of these minerals have been studied within the past ten years, no minor element chemistry, lattice parameter variation studies or solid phase relationship investigations have been attempted. Recent high temperature phase studies in the binary systems of Pb, Sb, Ag, Bi and Cu with S have also prompted a similar look at the natural mineral groups.

This investigation is based on synthetic specimens and

many natural ores from world-wide localities and utilizes data from chemical analyses, x-ray diffraction, differential thermal analysis, single crystal studies, computer refined lattice parameters and polished section examination.

Chemical analysis of natural specimens revealed the presence of several consistent minor elements occurring in the following manner:

(1) bournonite: As(2.0-3.5 wt.%), Ag(0.10-0.46 wt.%), Bi(0.01-4.0 wt.%)

(2) seligmannite: not determined

(3) aikinite: As($\approx$1.0 wt.%), Sb($\approx$0.25 wt.%), Ag($<$0.02 wt.%)

(4) diaphorite: As(2.25-2.75 wt.%), Cu(not determined), Bi(0.08-0.14 wt.%)

(5) freieslebenite: As(2.0-3.0 wt.%), Cu(0.16-0.78 wt.%), Fe(not determined), Bi($<$0.01 wt.%)

Some limitations in minor element chemistry of bournonite are defined and related to variation of lattice parameters. The axial parameters of bournonite were found to range as follows: (a_o) 8.145Å-8.174Å, (b_o) 8.685Å-8.725Å and (c_o) 7.806Å-7.836Å.

Bismuth content of bournonite reaches a maximum at an a_o of 8.159Å and silver falls off rapidly with slight increase in weight percent arsenic. Weight percent lead and antimony were found to rise in a linear manner with

increasing a_o and b_o parameters of bournonite. A similar relationship with lead and antimony occurs with reference to the total cell volume of the bournonite lattice.

Solid solution between antimony and arsenic is not complete in the isotype structures of bournonite and seligmannite but reaches a maximum of $3\frac{1}{2}$:1 for the ratio Sb:As.

X-ray data, coupled with minor element analyses and polished section studies, indicates possible, submicroscopic, chain-like layers of exsolved, secondary sulfides or sulfosalts as inclusions in the five study minerals (especially bournonite). The situation could be analogous to the micro-perthites in the silicate system. The minor elements present are thought to be very soluble in the bournonite group minerals at high temperature, but upon cooling, they are forced out of the lattice as a secondary sulfide or sulfosalt phase.

High temperature phase studies, utilizing both synthetic and natural specimens, resulted in quenching of disordered polymorphs for the minerals: aikinite, diaphorite and freieslebenite. Preliminary indexing of the previously unknown aikinite high polymorph indicates a (pseudo-tetragonal) body-centered, orthorhombic cell with $a_o \approx 6.5$Å, $b_o \approx 5.7$Å and $c_o \approx 12.2$Å. Aikinite commences disordering

at 270 degrees C and undergoes two other exothermic reactions at 465 degrees and 475 degrees C which could possibly represent additional disordering transformations of a non-quenchable nature.

Investigation of the cubic, high polymorph of diaphorite and freieslebenite(both synthetic and natural systems) generally confirmed the observations of Wernick(1960) in the pseudo-binary $AgSbS_2$-PbS.

Utilization of the four sample Nonius-Guinier powder camera resulted in the observation of many new lines in the x-ray powder patterns for the five study minerals.

INTRODUCTION

The "Bourninite Group" (Palache and others, 1944, p. 349) of the sulfosalt minerals is classified under the type formula A_2BX_3 and contains seven species:[1] bournonite $PbCuSbS_3$, seligmannite $PbCuAsS_3$, aikinite $PbCuBiS_3$, diaphorite $Pb_2Ag_3Sb_3S_8$ and freieslebenite $PbAgSbS_3$. Two minerals, klaprothite $3Cu_2S \cdot 2Sb_2S_3$ and berthonite $Pb_2Cu_7Sb_5S_{13}$ have been discredited (Nuffield, 1946, p. 374 and Thompson, 1947, p. 485, respectively) since the publication of Dana's System, vol. I. Berthonite (Buttgenbach, 1923, p. 212) has been found to be equivalent to bournonite as a result of x-ray diffraction methods but has been re-investigated by this writer. Klaprothite (Petersen, 1868-1869) has been shown to be a mixture of the minerals wittichenite $3Cu_2S \cdot Bi_2S_3$ plus emplectite $Cu_2S \cdot Bi_2S_3$.

Ultrabasite (originally $Pb_{28}Ag_{22}Sb_4Ge_3S_{53}$; Rosicky and Sterba-Bohm, 1920) has been shown to be a synonym for diaphorite as has brongniardite Ag_2PbSbS_5, (Damour, 1949, p. 227) which was previously thought to be a cubic mineral. Prior and Spencer (1900, p. 5-14) pointed out the identity of brongniardite with argyrodite - Canfieldite ($Ag_8(Ge,Sn)S_6$) and its association with diaphorite. Brongniardite was also re-investigated by this writer.

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[1] These are the best formulas from the literature and not necessarily as listed in Dana (Palache and others, 1944, p. 349).

Bournonite (Bournon, 1804) was named after Count J. L. Bournon (1751-1825), French crystallographer and mineralogist. The mineral has also been called endellionite from the locality where it was first found and wheel-ore (Radelerz, Germ.) due to its common aggregation of twinned groups. Bournonite is one of the most common sulfosalts, typically occurring in hydrothermal veins of moderate to low temperatures and is generally associated with galena, tetrahedrite, chalcopyrite, pyrite, sphalerite, siderite, barite, quartz and less frequently, bornite, zinkenite, rhodochrosite and dolomite. Since bournonite is found in many world-wide localities, the reader is referred to Dana's System of Mineralogy, vol. I and to the table of specimen localities (table #2) listed in this paper.

Seligmannite (Baumhauer, 1901, p. 110) was named after Gustav Seligmann (1849-1920), a private mineral collector of Coblenz, Germany. The mineral is the arsenic isotype of bournonite and is found associated with dolomite, tennantite, dufrenoysite, trechmannite, rathite, baumhauerite, sphalerite, pyrite and galena. Seligmannite is a rare mineral and has been reported from Binnental, Valais, Switzerland; Bingham, Utah; Butte and Emery, Montana and from Kalgoorie, Western Australia.

Aikinite (= patrinite) (Nadelerz, 1804, p. 726) is the bismuth-bearing mineral of the group and was named after Dr. Arthur Aikin (1773-1854), a founder and secretary of the Geological Society of London. The mineral occurs with native gold, galena, tetrahedrite, covellite, malachite, cryscolla, pyrite and quartz. Aikinite is also rare and is reported from Beresovok, Ekaterinburg, Urals; France, Germany, Tasmania, Ontario, Arizona and Utah.

Diaphorite (Zepharovich, 1871, p. 130) received its name from the Greek word, διάφορά, meaning "difference", because of its being distinct from freieslebenite, a supposed dimorphous form. Diaphorite is found associated with sphalerite, galena, miargyrite, pyrargyrite, pyrite, tetrahedrite, siderite, quartz and dolomite. The reader is again referred to Dana's System and table #2 of this paper for specimen localities.

Freieslebenite, (DeLisle, 1773) named after Johann Karl Freiesleben (1774-1846), mining commissioner of Saxony, has been found to be very similar in both physical and chemical properties to diaphorite. It is found associated with argentite, galena, sphalerite, ruby silver and quartz. The mineral is considered rare and has been reported from

Hiendelencina, Spain; Guerrero, Mexico; Gunnison Co., Colorado; Saxony, Germany; Pribram, Bohemia; Kapnik and Felsobanya, Roumania.[2]

This paper presents results of a study of chemical composition, high temperature, phase-field relationships, structural variations and polished section, data of a large number of specimens from world-wide localities (table #2). The group was selected for high temperature studies since the structure of the included five minerals had been recently investigated by Hellner (1956, 1957, 1958), Leineweber (1956) and Wickman (1953). Thus, any high polymorph, phase fields of a quenchable nature could be better related to structural translations and cation disordering from the known structure of the low temperature, ordered phases. Three high phases were synthesized and quenched to room conditions during the course of the present study. These were indexed and given a preliminary study.

X-ray diffractometer, Nonius-Guinier powder camera, Buerger Precession camera and digital computer techniques were utilized to refine and interpret axes parameters and to index both low and high temperature mineral phases.

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[2]Reference should be made at this time to table #1 which summarizes the nomenclature for the Bournonite Group as used in the above section.

TABLE # 1

SUMMARY OF NOMENCLATURE FOR
BOURNONITE GROUP SULFOSALTS

MINERAL	BEST FORMULA	FIRST DESCRIBED	STRUCTURAL INVESTIGATIONS	SYNONYMS
Bournonite	$PbCuSbS_3$	from Endellion; Bournon (1804) Hatchett (1804)	Oftedal (1932) Hellner and Leineweber (1956)	berthonite? endellionite wheel-ore
Seligmannite	$PbCuAsS_3$	from the Binnental; Baumhauer (1901)	Frondel (1941) Hellner and Leineweber (1956)	- - - - -
Aikinite	$PbCuBiS_3$	Nadelerz (1804)	Peacock (1942) Wickman (1953)	patrinite
Diaphorite	$Pb_2Ag_3Sb_3S_8$	Zepharovich (1871)	Winchell (in Palache) (1938) Hellner (1958)	polybasite brongniardite
Freieslebenite	$PbAgSbS_3$	de Lisle (1773)	Winchell (in Palache) (1938) Hellner (1957)	- - - - -

TABLE #1 CONT.

DISCREDITED MINERALS
OF BOURNONITE GROUP

MINERAL	GIVEN FORMULA	FIRST DESCRIBED	DISCREDITED	SYNONYMS
Berthonite	$Pb_2Cu_7Sb_5S_{13}$	Buttgenbach (1923)	Thompson(1947)	bournonite?
Klaprothite	$Cu_6Bi_4S_9$	Petersen(1868-1869)	Nuffield(1946)	equivalent to wittichenite ($3Cu_2S \cdot Bi_2S_3$) plus emplectite ($Cu_2S \cdot Bi_2S_3$)

X-ray fluorescence methods were used for minor element analysis and a number of specimens were totally analyzed by d.c. arc spectrographic methods. Differential thermal analysis was utilized under controlled atmosphere and vacuum conditions to isolate inversion temperatures and for study of structural changes.

A number of recent workers have indicated the diversity of the minerals comprising Dana's "Bournonite group" of the sulfosalts. Therefore, a rather extended discussion of sulfosalt classification is included in this paper.

Data from minor element analysis coupled with least squares refinement of lattice parameters of the study minerals has provided a fresh approach to better understanding the crystal chemistry of these complex structures. The several consistent minor elements found in the analyses of the study sulfosalts have been investigated from many directions utilizing various techniques. The use of such methods in this investigation has indicated chemical complexities not previously thought to exist in these mineral systems.

ACKNOWLEDGEMENTS

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Natural specimens were generously provided by the United States National Museum, the Chicago Museum of Natural History, the British Museum and the University of Cincinnati, Department of Geology. Additional fine specimens were received from Mr. Mario Arenas[1] and Mr. Reid Craig[2].

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[1]Mr. Arenas is associated with the Herminia Mine, Julcani District, Huancavelica, Peru.

[2]Mr. Craig is chief geologist for the Cerro Co. in LaOroya, Peru.

TABLE #2

LOCALITIES OF NATURAL SPECIMENS

Specimen	Name	X	N	M	S	D	P	C*	Locality	Obtained
									Foreign	
112640	bo	X		M	S				Ceilhes, France	U.S. Nat. Museum
R-12018	bo	X		M	S				Chichibu Mine, Mitsumine, Chichibugun, Saitama, Japan	" " "
R-6845	bo	X	N	M					Redruth, Cornwall, Eng.	" " "
C-764	bo	X	N	M			P		Machacamarca, Bolivia	" " "
R-10829 PB	bo	X	N	M					Pulacayo, Bolivia	" " "
C-767	bo	X	N	M					Wolfsberg, Harz, Germ.	" " "
81295	bo	X		M					Liskeard, Cornwall, England	" " "
78427	bo						P		Altai, Siberia, U.S.S.R.	" " "
R-8055	bo	X	N	M					Pulacaya Mine, Huanchaca, Bolivia	" " "
C-762	bo	X	N	M					Machacamarca, Bolivia	" " "
R-10829 FH	bo	X	N	M					Felsobanya, Hungary	" " "
18561	bo	X							Hatchimori, Samameto, Ugo, Japan	" " "
12998	bo	X							Freiberg, Saxony, Germ.	" " "
R-13491	bo	X		M					Oradna, Siebenburgen, Hungary	" " "
R-1048	bo	X							Welch Carinthia, Austria	" " "
R-6846	bo	X					P		Sannidal, Kragero, Norway	" " "
113077	berth	X		M					Djebal Slata, Tunisia	" " "

TABLE #2 (Cont'd)

Specimen	Name	X	N	M	S	D	P	C	Locality	Obtained
53234	bo	X		M					Zancudo Mines, Antioquia, Colombia	U.S. Nat. Museum
C-4963	bo	X					P		Pacoani Mine, Pata-camaya, Bolivia	" " "
M-8367	bo	X	N	M					Cornwall, England	Chicago Museum
M-704	bo	X	N	M	S				Cornwall, England	" "
M-13611	bo	X							Cornwall, England	" "
M-17539	berth	X		M					Djebal Slata, Tunisia	" "
B.M. 32909	bo	X		M	S				Neudorf, Harz, Germ.	British Museum
B.M. 43625	bo	X		M	S				Herodsfoot Mine, Liskeard, Cornwall, Eng.	" "
B.M. 54797	bo	X		M	S				Wolfsberg, Harz, Germ.	" "
B.M. 82782	bo	X		M					Hiendelaecina, Guadajara, Spain	" "
B.M. 1912,151	bo	X		M					Pranal Mine, Pontgibano, Puyde Dome, France	" "
A-862	bo	X		M					Kapnik, Hungary	U. of Cincinnati
A-864	bo	X		M			P		Felsobanya, Hungary	" " "
A-3920	bo	X	N	M					Kapnik, Hungary	" " "
A-4053	bo	X							Felsobanya, Hungary	" " "
A-863	bo	X							Braunsdorf, Saxony, Germany	" " "
J-1	bo	X	N	M					Julcani District, Huancavelica, Peru	Private Source[1]
J-2	bo	X	N	M					Julcani District, Huancavelica, Peru	" "

TABLE #2 (Cont'd)

Specimen	Name	X	N	M	S	D	P	C	Locality	Obtained
M-Bourn.	bo	X	N	M	S	D	P		Herminia Mine, Julcani District, Huancavelica, Peru	Private Source[1]
Cerro-1	bo	X					P		Morococha, Peru	Private Source[2]
W-1	bo							C	Pribram, Bohemia	Ward's Nat. Sci.
W-2	bo	X	N	M	S	D			Germany	" " "
94112	selig	X							Lengenbach Quarry, Binnental, Switzerland	U.S. Nat. Museum
C-771	ai	X	N	M	S	D			U.S.S.R.	" " "
106760	ai	X	N	M					Silver Miller Mine, Cobalt, Ontario	" " "
R-7902	ai	X							Beresov, Urals, U.S.S.R.	" " "
R-1026	diap	X							Broken Hill, New South Wales, Australia	" " "
R-1027	diap	X	N	M		D			Charichari, Potosi, Bolivia	" " "
C-755	diap	X	N						Colquechaca, Bolivia	" " "
B.M. 63514	diap	X	N	M					Felsobanya, Hungary (= Baia Sprie, Romania)	British Museum
B.M. 88839	diap	X	N	M		D	P		Potosi, Bolivia	" "
R-1034	freie	X	N	M	S				Hiendelencina, Spain	U.S. Nat. Museum
R-8243	freie	X		M	S				Delfina Mine, Chilpancingo, Guerrero, Mexico	" " "
R-11454	freie	X							Alte Hofnung-Gottes Mine, Voightsberg, Saxony, Germ.	" " "

TABLE #2 (Cont'd)

Specimen	Name	X	N	M	S	D	P	C	Locality	Obtained
						U. S.				
94977	bo	X		M			P		Park City, Utah	U.S. Nat. Museum
C-788	bo	X					P		Park City, Utah	" " "
R-1052	selig	X				D	P		Bingham, Utah	" " "
105571	ai	X		M			P		Balls Mine, Little Cottonwood District, Utah	" " "
R-12049	ai	X							Roadside Mine, Pima Co., Arizona	" " "
R-9192	freie	X	N	M					Lander Hill, Austin, Nevada	" " "

* X -x-ray diffraction studies
N -Nonius-Guinier camera studies
M -Minor element analysis
S -d.c. arc spectrographic analysis
D -differential thermal analysis
P -polished section study
C -single crystal investigation

[1] See acknowledgements

[2] See acknowledgements

ENVIRONMENT OF DEPOSITION

The environment of deposition characteristic of the five study minerals is typically that of moderate-to-low temperature hydrothermal veins. Bournonite, seligmannite and aikinite are generally of a higher temperature origin than diaphorite and freieslebenite. The latter two minerals are associated with such low temperature, silver-bearing sulfides as acanthite, pyrargyrite, miagyrite, as well as with native silver.

Bournonite is usually found as the cogwheel twinned crystals, typical of those mined at Felsobanya, Hungary, Cornwall, England, and many Bolivian localities (table #2). Occurrences of the prismatic variety of bournonite are much less common but include such areas as Harz, Germany and Pribram, Bohemia.

Very unique bournonite specimens were obtained by this writer from the Herminia Mine (Julcani District), Huancavelica, Peru. The size and unique character of these fine specimens is indeed worthy of special attention at this time. The bournonite from this mine consists of unusually large (up to 2½ cm) cogwheel crystals elongated parallel to the direction of twinning. The crystals (M-Bour., J-1 and J-2) were found to have a very high bismuth content of from 2-4

weight percent (see table # 8). The same specimens also showed a high lead content (48 weight percent) but low antimony percentage (20 weight percent).

The deposits in the area of the Herminia Mine are hydrothermal fracture-filling veins of moderate to medium-high temperatures and are related to a quartz monzanite intrusive which cuts tertiary volcanics. Associated minerals with the bournonite crystals are: tetrahedrite, chalcopyrite, pyrite, jamesonite, bismuthinite and quartz. The presence of chalcopyrite and bismuthinite in this deposit is taken as evidence that the temperature of deposition was considerably higher than any other where bournonite has been collected. Chalcopyrite is present as inclusions in many of the bournonite cogwheel crystals.

Many of the bournonite specimens show evident zoning thought to be related to a rather large, rapid, temperature change during deposition. The presence of high bismuth in these specimens and its relationship with temperature of deposition will be discussed later in this paper.

PREVIOUS WORK

A great portion of the previous work on the minerals of the "Bournonite Group" of the sulfosalts had been restricted to determination of stoichiometric formulas, physical, descriptive mineralogy and to basic clarification of the structure from single specimens. Prior to the publication of Dana's System of Mineralogy (Palache and others, 1944) only a few writers (Oftedal, 1932; Palache, 1928; Palache, Richmond and Winchell, 1938; Peacock, 1942; Solly, 1903 and Frondel, 1941) offered any paragenetic, structural or chemical data on these minerals. The minerals of the bournonite group were mentioned, however, by Ross (1957), Hellner (1958), Hiller (1953) and Strock (1936) in regard to the classification of the sulfosalts in some orderly scheme.

Recent advancements in the study of these minerals have come, primarily, from Germany where Hellner and Leineweber (1956, 1957, 1958) have investigated the structures of bournonite, seligmannite, diaphorite and freieslebenite. Wickman (1953) refined the aikinite lattice and proposed its similarity with the stibnite structure. Wernick (1960), working in the pseudo-binary $AgSbS_2$-PbS, outlined the high temperature phase-fields for synthetic preparations equivalent to diaphorite and freieslebenite.

The limits of substitution for various minor elements and their function in the lattices of these minerals have not been investigated prior to this study and since much of the early x-ray data has been found to be incomplete and erroneous, in part, a re-evaluation of such data has been undertaken.

Mineral synthesis is included in the present work on the bournonite group as an important part of the high temperature research since few previous workers (Doelter, 1885; Wernick, 1960) have reported synthetic studies in this regard.

Differential thermal analysis techniques have been utilized on the sulfides to some extent by many workers (Papaihau, 1958; Levy, 1958; Asensio, Isidoro and Sabatier, 1958; Kopp, 1948; Stone, 1960; Hiller and Probsthian, 1955, 1956a-b; Sabatier, 1956 and others) but the sulfosalt ores have been rather neglected. The corrosive nature of the sulfides and especially arsenic-containing sulfosalts at elevated temperatures has inhibited past workers from these minerals; however, with the new, evacuated and controlled, inert gas atmosphere furnaces and very accurate temperature control, feasible research can now be carried out in this field.

CHEMICAL ANALYSES AND STOICHIOMETRY

The accumulation of chemical analyses for the minerals of the bournonite group as listed in Dana's System, vol. I (Palache and others, 1944) indicate that many were made prior to 1900 and the rest in the first three decades of the present century. Aikinite, diaphorite and freieslebenite have no listed chemical analyses after 1900 with the earliest being in 1839 (tables #11-13).

Bournonite's stoichiometric formula of $PbCuSbS_3$ has remained as first presented by Bournon in 1804. The same is true for seligmannite, the arsenic isotype of bournonite, whose original stoichiometry of $PbCuAsS_3$ was given by Baumhauer in 1901. Aikinite, likewise, has retained its original formulation of $PbCuBiS_3$ since first being described by Nadelerz in 1804.

Diaphorite and freieslebenite have been given a number of formulas through the years. Earlier formulas proposed for diaphorite (in Dana, 1892) were based on the supposed chemical identity with freieslebenite. Winchell later (in Palache, 1938) showed that the older formula, $(Pb,Ag_2)_5Sb_4S_{11}$ for freieslebenite, as given in Dana (1892), was not consistent with the cell dimensions. More recently, Hellner

(1957) has proposed the "idealized" stoichiometry of freieslebenite to be $Pb_4Ag_4Sb_4S_{12}$ and gives the reduced cell of $PbAgSbS_3$.

This writer will later discuss proposals for new formula designations for these minerals as a result of minor element investigations.

CELL DIMENSIONS AND SPACE GROUPS

Oftedal (1932, p. 157) first attempted to delineate the structure of bournonite on crystals from Horhausen, Germany and Cornwall, England using the oscillation method. He was unable to furnish any structural data outside of the unit cell and space group information. He proposed the axes parameters of: $a_o = 8.10\text{Å}$, $b_o = 8.65\text{Å}$ and $c_o = 7.75\text{Å}$ (all $\pm$ 0.05Å) and a space group designation of D_{2h}^{13}Pnmm. No further evaluation of the structure of bournonite was attempted until Leineweber (1956, p. 161-184) recently initiated a rather complete structural examination of both bournonite and seligmannite, its arsenic isotype. He proposed a new space grouping of C_{2v}^{7}-$Pn2_1m$ for bournonite and reported, as a result of Nonius-Guinier camera data, the new axes of: $a_o = 8.162\text{Å}$, $b_o = 8.710\text{Å}$ and $c_o = 7.810\text{Å}$.

Seligmannite, which was first investigated structurally by Frondel (1941, p. 25) and given the space group D_{2h}^{13}Pnmm,

has also been re-evaluated by Leineweber (1956, p. 161-184). He gives seligmannite the same new space group as bournonite: C_{2v}^{7}-$Pn2_1m$ and the more accurate axes parameters of: a_o = 8.081Å, b_o = 8.747Å and c_o = 7.636Å. Leineweber found that apart from slight differences in parameters both bournonite and seligmannite have identical structures and show very close relationship to the analogous Bi-compound aikinite ($PbCuBiS_3$) and also to stibnite (Sb_2S_3).

Aikinite was investigated originally by Peacock, (1942, p. 63) and given the space group Pnam or Pna2 with axes of: a_o = 11.30Å, b_o = 11.64Å, and c_o = 4.00Å. Wickman (1953, p. 501) further refined the structure and was able to relate its structure as a derivative of the stibnite lattice. He suggested that the aikinite cell could be derived from the stibnite lattice by the insertion of Cu atoms in the tetrahedral voids of the stibnite (see figure # 1).

Diaphorite and freieslebenite was first investigated, in a structural manner, by Winchell (in Palache, 1938) and more recently studied by Hellner (1958, p. 169; 1957, p. 284). Winchell listed diaphorite as an orthorhombic mineral of the space group Cmma and with lattice parameters of: a_o = 15.83Å, b_o = 32.23Å, and c_o = 5.89Å. Hellner utilizing modern Guinier powder methods and Weissenberg single crystal techniques reported a monoclinic cell for diaphorite.

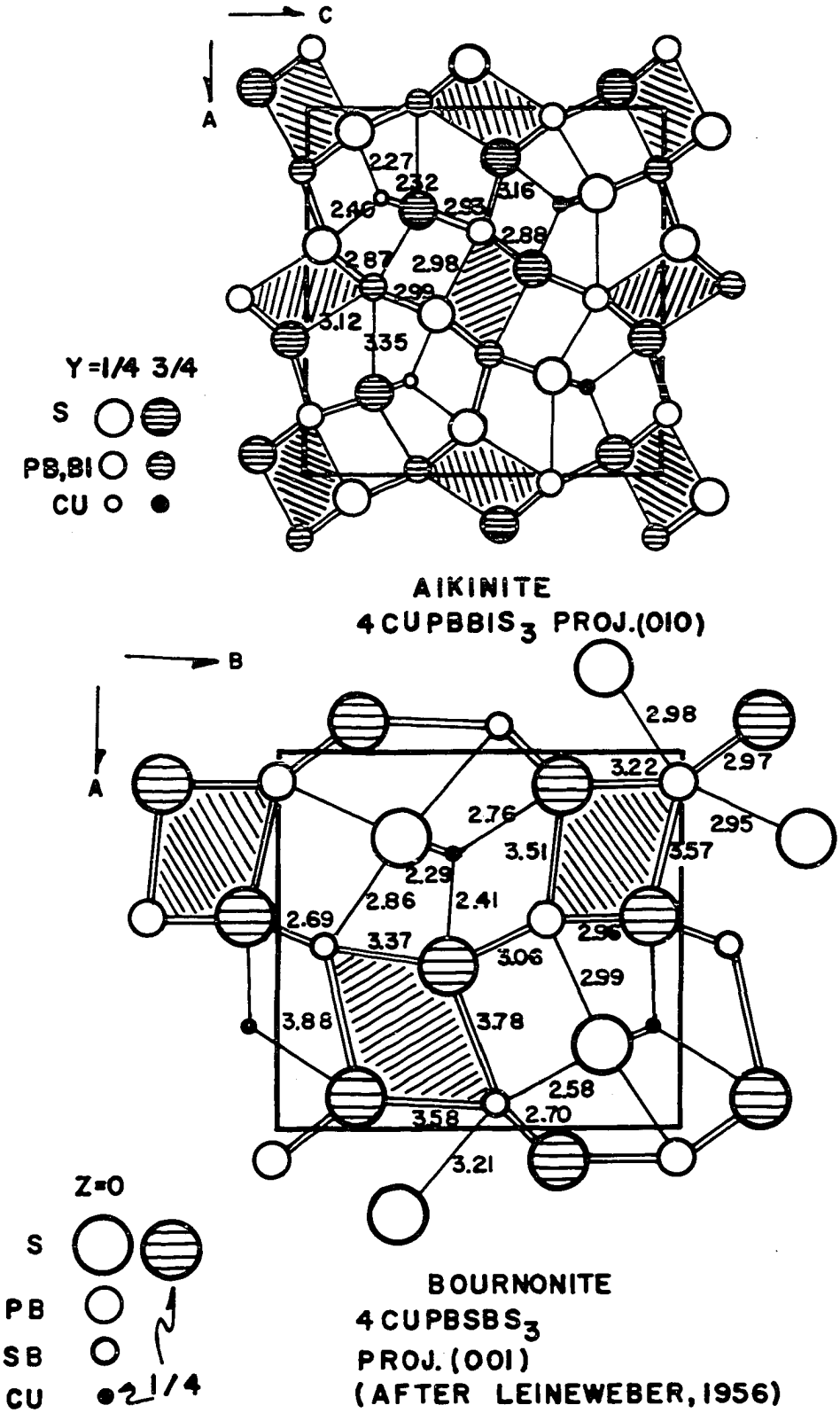


Figure 1. Structural projections of aikinite and bournonite

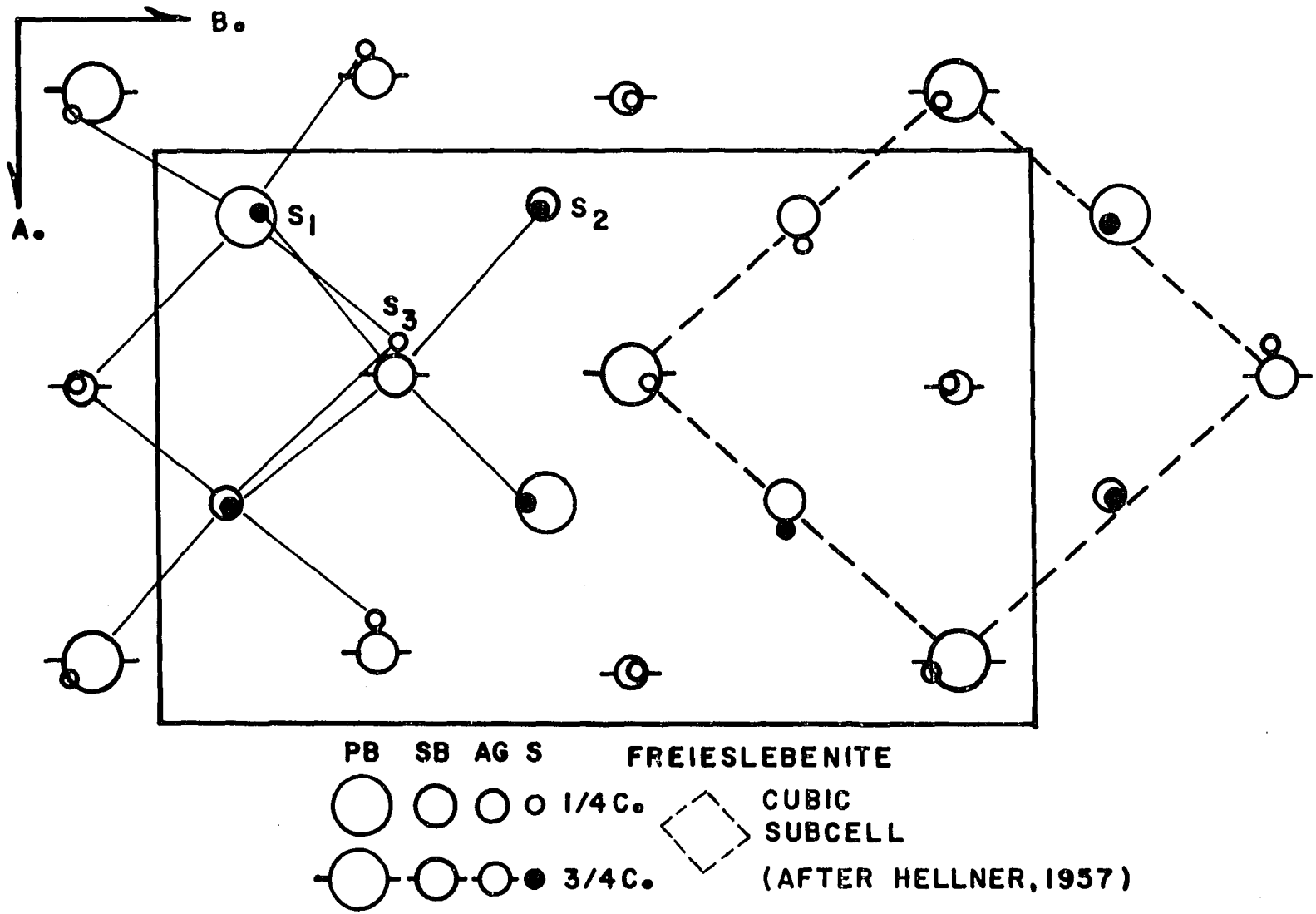


Figure 2. Structural projection of freieslebenite

PLATES A-E

BOURNONITE AND FREIESLEBENITE
STRUCTURAL MODELS(SCALE: 1Å = 2")

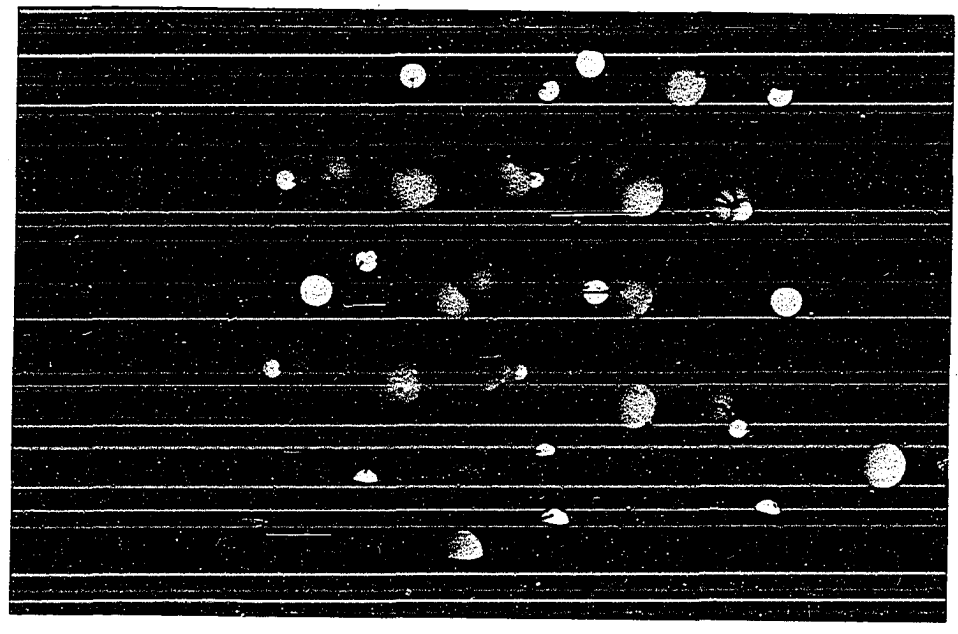
COLOR CODE

BOURNONITE - ORANGE ATOMS(LARGE) ---SULFUR
RED ATOMS ----------LEAD
GREENISH-WHITE ATOMS --ANTIMONY
GOLD ATOMS(SMALL) -----COPPER

FREIESLEBENITE - ORANGE ATOMS(LARGE)----SULFUR
RED ATOMS ----------LEAD
GREENISH-WHITE ATOMS --ANTIMONY
GOLD ATOMS(SMALL) -----SILVER

The models were constructed with cork spheres(painted with fluorescent spray paint) and wire coat hangers, mounted on a plywood board representing the unit cell, looking down the 001 of the mineral.

Photos were taken using long wavelength light with Ektachrome X color film. Exposures ranged from 3 to 20 minutes.



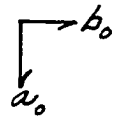


PLATE A - BOURNONITE MODEL
LOOKING DOWN A-AXIS
(SEE PRECEDING PAGE)

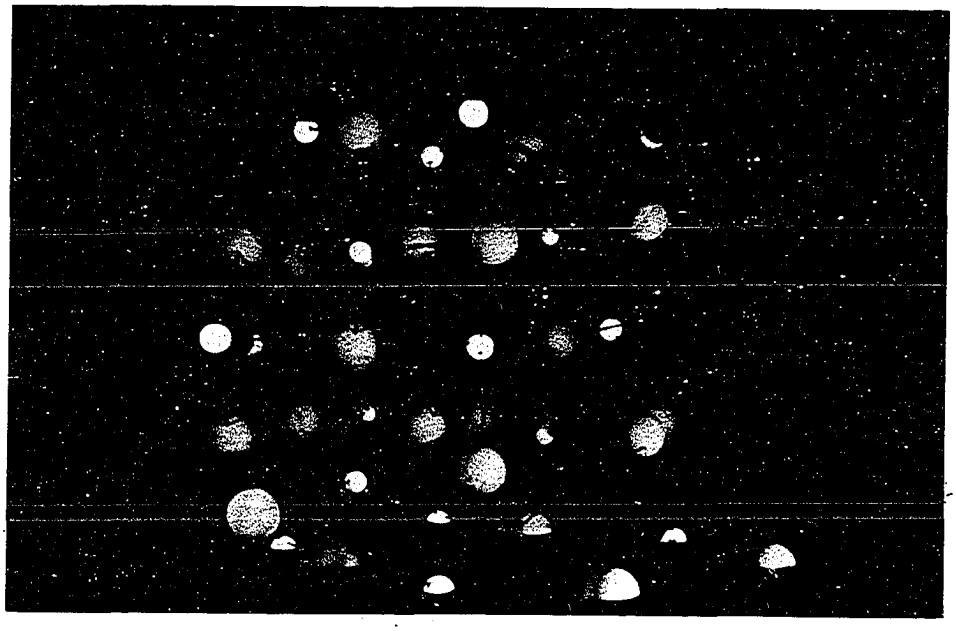


PLATE B - BOURNONITE MODEL
LOOKING DOWN B-AXIS
(SEE PRECEDING PAGE)

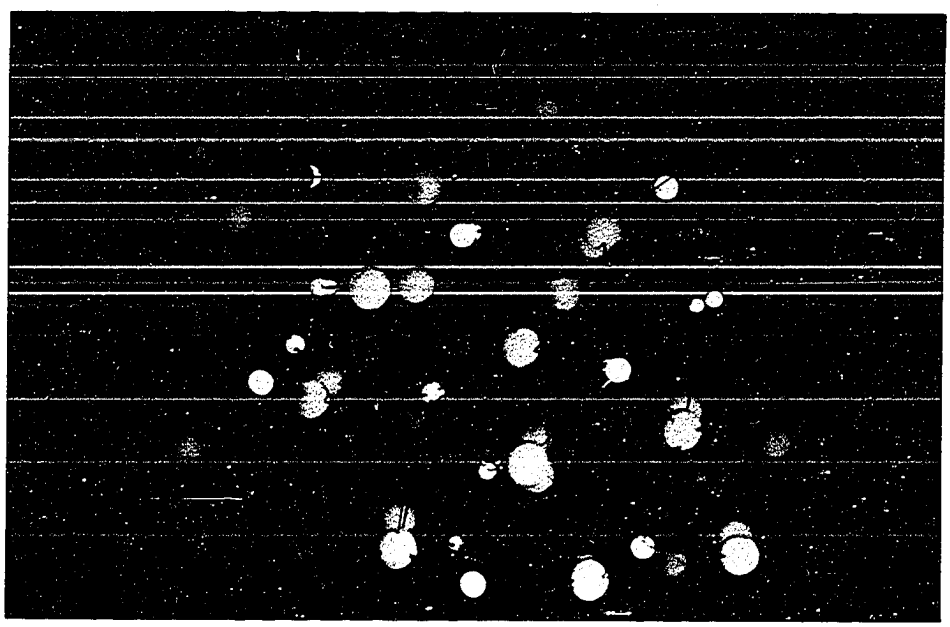
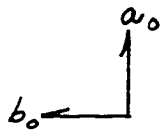
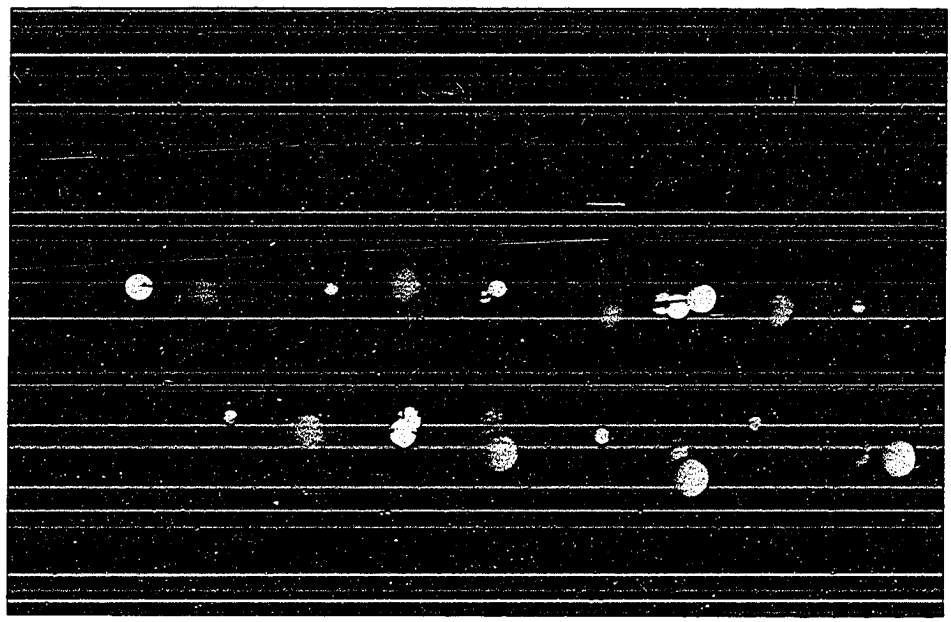


PLATE C - BOURNONITE MODEL
LOOKING DOWN THE C-AXIS





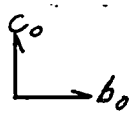
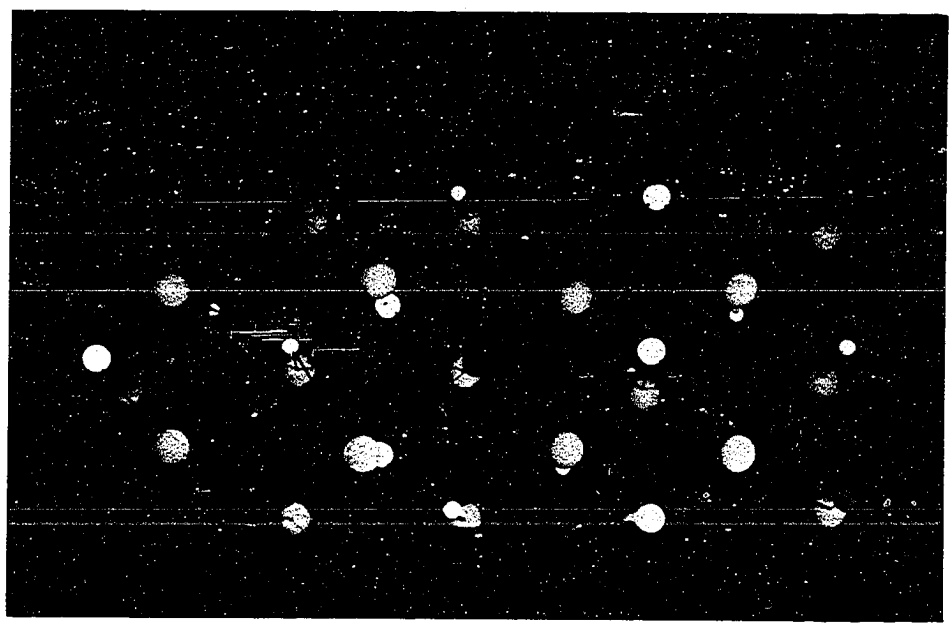


PLATE D- FRIESLEBENITE
LOOKING DOWN THE A-AXIS



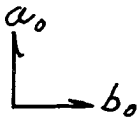


PLATE E- FRIESLEBENITE
LOOKING DOWN THE C-AXIS

TABLE # 3

SUMMARY OF STRUCTURAL DATA

****

BOURNONITE $PbCuSbS_3$ Orthorhombic

C_{2v}^7-$Pn2_1m$

$a_o = 8.145\text{Å} - 8.174\text{Å}$ $b_o = 8.685\text{Å} - 8.724\text{Å}$

$c_o = 7.802\text{Å} - 7.836\text{Å}$ (cell ranges from this paper)

$Z = 2$

The structure determined by Hellner and Leineweber (1956) required:

cell containing $4PbCuSbS_3$

2a) xyo *
-x, ½+y, ½

4b) xyz
xy-z
-x, ½+y, ½-z
-x, ½+y, ½+z

	X	Y	Z
2Pb in (2a)	0.079	0	0
2Pb in (2a)	0.560	0.170	0.500
2Sb in (2a)	0.073	0.050	0.500
2Sb in (2a)	0.515	0.125	0
4Cu in (4b)	0.269	0.440	0.249
2S in (2a)	0.225	0.310	0
2S in (2a)	0.225	0.310	0.500
4S in (4b)	0.084	0.706	0.248
4S in (4b)	0.564	0.425	0.267

* recalculated from those given in International Tables for X-ray Crystallography, vol. I (see Appendix C for complete set of atom positions calculated for construction of models)

TABLE # 3 CONT.

****

SELIGMANNITE $PbCuAsS_3$ Orthorhombic

C_{2v}^7-$Pn2_1m$

$a_o = 8.054\text{Å} - 8.088\text{Å}$ $b_o = 8.729\text{Å} - 8.747\text{Å}$

$c_o = 7.636\text{Å} - 7.647\text{Å}$ (cell ranges from this paper)

$Z = 2$

The structure determined by Hellner and Leineweber (1956) required:

cell containing $4PbCuAsS_3$

2a) xyo *
$-x, \frac{1}{2}+y, \frac{1}{2}$

4b) xyz
$x\bar{y}-z$
$-x, \frac{1}{2}+y, \frac{1}{2}-z$
$-x, \frac{1}{2}+y, \frac{1}{2}+z$

	X	Y	Z
2Pb in (2a)	0.080	0	0
2Pb in (2a)	0.550	0.175	0.500
2As in (2a)	0.067	0.110	0.500
2As in (2a)	0.510	0.110	0
4Cu in (4b)	0.272	0.440	0.247
2S in (2a)	0.236	0.300	0
2S in (2a)	0.223	0.310	0.500
4S in (4b)	0.096	0.695	0.238
4S in (4b)	0.550	0.440	0.266

* recalculated from those given in International Tables for X-ray Crystallography, vol. I

TABLE #3 CONT.

****

AIKINITE $PbCuBiS_3$ Orthorhombic

D_{2h}^{16} - Pnma

a_o = 11.310Å - 11.318Å b_o = 11.639Å - 11.666Å

c_o = 4.001Å - 4.017Å (cell ranges from this paper)

Z = 2

The cell determined by Wickman (1953) required:

cell containing $4PbCuBiS_3$ (c) $xy\frac{1}{4}$

	X	Y
4A (Pb or Bi) in (c)	0.685	0.017
4B (Pb or Bi) in (c)	0.013	0.832
4Cu in (c)	0.210	0.240
12S in (c) (three sets)	0.690	0.730
	0.135	0.060
	0.045	0.370

(see figure # 1)

TABLE #3 CONT.

****

DIAPHORITE $Pb_2Ag_3Sb_3S_8$ Monoclinic

C_{2h}^5 -$P2_1/a$

a_o = 15.849Å (+or-0.02) b_o = 17.914Å (+or-0.01)

c_o = 5.901Å (+or-0.001) Gamma = 116° 25.5' (+or-2')

Z = 2 = $4(Me_8S_8)$

The reduced cell determined by Hellner (1958) requires the following, approximate, metal positions:

		(4e) xyz		
		X	Y	Z
Me_I	in (4e)	0.219	0.062	0.250
Me_{II}	in (4e)	0.281	0.438	0.750
Me_{III}	in (4e)	0.156	0.188	0.750
Me_{IV}	in (4e)	0.344	0.312	0.250
Me_V	in (4e)	0.406	0.186	0.750
Me_{VI}	in (4e)	0.031	0.435	0.750
Me_{VII}	in (4e)	0.469	0.063	0.250
Me_{VIII}	in (4e)	0.094	0.312	0.250

The S atoms have similar x and y parameters as the metal atoms and are placed at c/2, above and below the metal positions.

TABLE #3 CONT.

****

FREIESLEBENITE $PbAgSbS_3$ Monoclinic

C_{2h}^5 -$P2_1/a$

$a_o = 7.53\text{Å}$ (+or-0.01) $b_o = 12.80\text{Å}$ (+or-0.02)

$c_o = 5.91\text{Å}$ (+or-0.03) Beta 92°15' (+or-1')

$Z = 1$

The structure determined by Hellner (1957) requires:

cell of $4PbAgSbS_3$	(4e) xyz		
	X	Y	Z
4Pb in (4e)	0.113	0.085	0.240
4Ag in (4e)	0.095	0.415	0.240
4Sb in (4e)	0.385	0.256	0.720
$4S_I$ in (4e)	0.100	0.100	0.740
$4S_{II}$ in (4e)	0.100	0.413	0.680
$4S_{III}$ in (4e)	0.340	0.260	0.140

(see Plates # D-E and Figure # 2)

He suggested the space group C_{2h}^5-$C2_1/a$ and the lattice constants: a_o = 15.849Å, b_o = 32.084Å, c_o = 5.901Å and Gamma = 90°10'. Hellner also proposed that the "ideal" structure for diaphorite can be derived in a simple way from the PbS(NaCl) cell type. He suggested that the "substructure" (Buerger, 1956) is a body-centered cell with $a \approx b \approx \frac{1}{2}a_{PbS}(2)^{\frac{1}{2}}$ and $c \approx a_{PbS}$ = 5.92Å.

Freieslebenite's space grouping of C_{2h}^5-$P2_1/a$ (monoclinic) (Winchell, in Palache, 1938) was verified by Hellner (1957, p. 284) and a new c_o axis of 5.95Å (± 0.01Å) was established by Weissenberg and Guinier camera methods. Hellner suggested that the freieslebenite cell, like diaphorite, can be deduced in a simple way from the PbS(NaCl) type lattice.

STRUCTURAL DETERMINATIONS

The cell structures used in the following discussions of the bournonite group minerals have been taken from Hellner (1957, 1958), Leineweber (1956) and Wickman (1953) (see figures#1-2 and table # 3).

The cell determinations of bournonite and seligmannite were deduced from Patterson diagrams by the "Superposition Method" with the x and z parameters being refined by Fourier syntheses and the y parameter corrected by trial

and error methods. Hellner (1957) indicated that for freieslebenite, however, Patterson diagrams show only maxima with special parameters and therefore explain only the "ideal" structure of the mineral. The Superposition Method, as a result, could not be used to find the "real" atom positions, especially deviations from the "ideal" structure.

Wickman (1953) found that discrimination between lead and bismuth atom positions in the aikinite structure was impossible because of their similar x-ray scattering power. Therefore, the exact relationship of these atoms in the cell is still uncertain (see figure # 1 and table # 3).

Hellner, Leineweber and Wickman utilized Weissenberg single crystal cameras and Nonius-Guinier (quartz crystal, monochromatized radiation) powder cameras for their basic x-ray investigations. Copper K alpha$_1$ (λ = 1.5405Å) was the most frequent radiation used in these studies.

Reference to tables#3-6 and figure #1-1 is suggested by this writer for a summary of structural parameters characteristic of the study sulfosalts.

CRYSTAL CHEMISTRY[1]

Bournonite, Seligmannite and Aikinite

Bourninite, seligmannite and aikinite are composed of a distorted, close-packed, orthorhombic, sulfur lattice containing a superlattice of the metal atoms: Pb,Cu,(Sb,As,Bi). (Author's note: the role of consistent minor elements in all study minerals will be discussed in a later section).

Hellner (1956) found the As-S atomic distances in the seligmannite structure to be short when compared to the Sb-S atomic distances in bournonite (table #4-5). Likewise, when considering only the nearest neighbors, the coordination of Cu and Sb(As) atoms in these minerals is definitely characteristic. The Cu atoms are situated in tetrahedral coordination with four surrounding sulfur atoms with the tetrahedrons being joined in the c-axis direction. Sb and As, on the other hand, are coordinated to three nearest neighbor sulfur atoms in a two-dimensional isosceles triangle, thereby forcing the metal and sulfur atoms to form a tetrahedron with the Sb or As atom forming the apex.

Hellner has proposed two lead coordinations (Pb_I and Pb_{II}), two antimony (arsenic) coordinations

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[1]Reference should be made to tables#3-6 and figures # 1 and # 2 .

TABLE# 4

ATOM DISTANCES IN BOURNONITE(after Leineweber,1956)
(given in Å)

	S_I	S_{II}	S_{III}	S_{IV}
Pb_I	2.95 (1)*	2.98 (1)	2.97 (2) 3.22 (2)	3.57 (2)
Pb_{II}	3.59 (1)	2.99 (1)	3.51 (2)	2.96 (2) 3.06 (2)
Sb_I	3.21 (1)	2.58 (1)	2.70 (2) 3.58 (2)	3.78 (2)
Sb_{II}	2.86 (1)	3.47 (1)	3.88 (2)	2.69 (2) 3.37 (2)
Cu	2.29 (1)	2.29 (1)	2.76 (1)	2.41 (1)
S_I		3.90 (1)	3.31 (2) 4.12 (2)	3.61 (2) 4.19 (2)
S_{II}	3.90 (1)		3.31 (2) 4.12 (2)	3.46 (2) 4.31 (2)
S_{III}			4.57 (2)	3.45 (2) 4.62 (2)
S_{IV}				4.49 (2)

* Distances measured between atoms in same plane(1)
~ or plane above or below(2)

TABLE# 5

(given in Å) ATOM DISTANCES IN SELIGMANNITE(after Leineweber,1956)

	S_I	S_{II}	S_{III}	S_{IV}
Pb_I	2.91 (1)*	2.96 (1)	2.99 (2) 3.23 (2)	3.52 (2)
Pb_{II}	3.71 (1)	2.89 (1)	3.39 (2)	2.93 (2) 3.00 (2)
As_I	3.65 (1)	2.16 (1)	2.36 (2) 4.15 (2)	3.99 (2)
As_{II}	2.77 (1)	3.40 (1)	3.83 (2)	2.37 (2) 3.54 (2)
Cu	2.27 (1)	2.28 (1)	2.65 (1)	2.25 (1)
S_I		3.82 (1)	3.47 (2) 4.06 (2)	3.47 (2) 4.01 (2)
S_{II}	3.82 (1)		3.31 (2) 4.05 (2)	3.39 (2) 4.24 (2)
S_{III}			4.64 (2)	3.57 (2) 4.30 (2)
S_{IV}				4.45 (2)

* Distances measured between atoms in same plane(1)
or plane above or below(2)

TABLE# 6

(given in Å) ATOM DISTANCES IN FREIESLEBENITE(after Hellner,1957)

	S_I	S_{II}	S_{III}
Pb	2.98	3.11	2.89
	2.99		2.97
	2.86		
Sb	2.94	2.72	3.45
	2.46	2.94	2.54
Ag	3.30	2.70	2.79
		3.33	2.99
		2.62	
S_I	4.08	4.02	4.55
	4.33	3.77	3.58
		4.18	4.38
		4.70	3.61
		3.80	4.43
S_{II}	3.77	3.40	4.31
	4.70	4.71	4.08
	4.18		4.58
	3.80		4.23
	4.02		3.77
S_{III}	4.55	4.23	3.77
	3.58	3.77	3.77
	4.39	4.58	
	3.61	4.31	
	4.43	4.08	

(Sb_I and Sb_{II}) and four sulfur coordinations (S_I, S_{II}, S_{III} and S_{IV}) for bournonite and seligmannite. Copper atoms are all of one coordination since they are situated only in the tetrahedral voids between the metal-sulfur tetrahedrons (see figure # 1). The Pb_I atoms are arranged in a distorted octahedral coordination with six sulfur atoms and is thus in six-fold coordination, while the Pb_{II} atoms have the unique five-fold coordination. The Pb_{II}, five-fold coordination can, however, be increased to six-fold by enlarging the atomic distances from 3.51Å to 3.59Å. A similar situation could allow an eight-fold coordination for the Pb_I atoms.

Hellner noted also that, aside from the slight variation in cell parameters, both bournonite and seligmannite show some very close relationships to the analogous Bi-compound, aikinite, and also to stibnite (Sb_2S_3). It was also assumed that the bournonite-seligmannite structures can, in some more complex manner, be derived from this Sb_2S_3 lattice. The plane diagonal (110) of bournonite and seligmannite does correspond to the a and b translations of stibnite; and with the doubling of the c-translation, the Sb point positions of stibnite are alternately filled with Pb and Sb. It becomes apparent upon study of the bournonite, seligmannite or aikinite models, that the stibnite-type pyramids determine the basic structural

units of these minerals. The work of Hellner, Leineweber and Wickman, therefore, pointed to placement of bournonite, seligmannite and aikinite in the same "group" because of their similarities.

Diaphorite and freieslebenite

Diaphorite and freieslebenite are composed of a distorted, close-packed, monoclinic sulfur lattice with "super-lattice" formed by the metal atoms: Pb, Ag, Sb. Diaphorite and freieslebenite are related by chemistry, lattice type and their sub-structures of the PbS(NaCl) form. Hellner (1957, 1958), in discussing these structures devotes primary interest in the derivation of the ordered structure from the PbS(NaCl) type subcell and says little about crystal chemistry (bond types, coordination, substitutional elements, etc.). He does mention in his "Strukturdiskussion" that the deformed, monoclinic structure of diaphorite can be derived from the PbS(NaCl) type by filling of the point position of Pb in the PbS structure with Pb, Ag and Sb atoms.

Hellner, (1957, p. 291), suggested that in the freieslebenite structure the metal atoms are in the distorted, octahedral arrangement with the antimony atoms forming the SbS_3 pyramid with three sulfur atoms of short distances (2.46, 2.58 and 2.70Å) (see figure # 2).

Details of the coordination and bond deformation is not clearly known in freieslebenite since Hellner's Patterson diagrams allowed only maxima with special parameters and therefore outlined only the "ideal" structure of this mineral.

The fact that all octahedral voids are filled in the structure of diaphorite and freieslebenite led Hellner to propose an f = 1 for these minerals in his "structure factor" classification scheme for the sulfides and sulfosalts (see discussion on page 52).

PHASE RELATIONSHIPS

Phase fields within the sulfide systems involving the metals: Pb, Ag, Sb, As, Bi and Cu with sulfur have been investigated, in part, by Van Hook (1960) and Wernick (1960). Van Hook investigated the terniary system Ag_2S-Bi_2S_3-PbS utilizing thermal analysis and quenching methods while Wernick, using similar methods discussed the constitution of the systems: $AgSbS_2$-PbS, $AgBiS_2$-PbS, and $AgBiS_2$-$AgBiSe_2$.

Van Hook's investigation of the Ag_2S-Bi_2S_3-PbS system resulted in confirmation of the high solubility of bismuth and silver in the synthetic, galena-type structures (see section on minor elements in this paper).

Wernick found that there exists a complete series of solid solutions with high temperature, disordered, NaCl-type structures in the pseudo-binaries: $AgBiS_2$-PbS and $AgSbS_2$-PbS. Working with synthetic components, as Van Hook had done, Wernick determined the system $AgSbS_2$-PbS up to 1100°C and 50 mol. percent PbS (see figure #20). He found that synthetic compositions corresponding to the natural minerals, diaphorite and freieslebenite, reverted to disordered, high temperature polymorphs of the cubic, NaCl type. Schermirite ($PbS \cdot 2Ag_2S \cdot 2Bi_2S_3$) was the only natural mineral composition which Wernick found to possess the cubic, high phase for the system $AgBiS_2$-PbS. He postulated complete solubility of PbS in $AgSbS_2$ to 100 percent PbS along with the existence of the disordered, isometric, Beta phase (see figure #20).

SULFIDE AND SULFOSALT CLASSIFICATION

Classification of the sulfide and sulfosalt minerals into an orderly, systematic scheme of reference has always lent itself to a great many problems. Early attempts at classification of the minerals based primarily on external characteristics and chemical similarities resulted in relatively useless arrangements. Later, crystallography was coupled with crystal chemistry as a basis for a new classification of crystalline substances. Advancements in the

study of bond types and bond strengths later led Dana to the isodesmic, mesodesmic and anisodesmic division into classes of the minerals. The A:X (positive and negative ion) ratios of Dana further subdivided the classes into "types", the idea being that the A_mX_n "types" in the various "classes" often show geometric and structural similarities when the A:X ratio is the same. However, it was realized at that time that, from a mineralogical point of view, it was not advisable to place such dissimilar minerals as galena (PbS) and Halite (NaCl) together in the classification just because they have the same A:X ratio.

Complex structures such as are found in the sulfosalt minerals have never lent themselves to such a simple scheme of classification. Although many of the A:X ratios of these minerals show some correspondence, they have been found to be totally unrelated from a structural point of view. A few decades ago it became very evident, with the increasing amount of structural data, that a true "structural" classification of these minerals was necessary.

Gruner (1929, p. 470-481) early outlined the various cell types represented in the sulfide and sulfosalt minerals although little was known at this time as to the character

of the bonds; and even the "ionic" or "atomic" nature of the constitutent atoms was in doubt. The existence of a sulfide "molecule" was discredited by Gruner. The sulfide structures outlined by Gruner included the: (1) NaCl type (PbS, MgS, CaS, SrS, BaS, etc.); (2) the zincblende structure type (ZnS, BeS, CdS and HgS); (3) the wurtzite type (MnS, CdS); (4) the NiAs structure type (FeS, CoS); (5) the fluorite structure type (Cu_2S, Na_2S and Li_2S); (6) the pyrite structure type (FeS_2, MnS_2, CoS_2 and NiS_2) and (7) the molybdenite structure type (MoS_2, WS_2). Among the sulfosalt structures, Gruner included discussion of: (1) chalcopyrite, (2) stannite, (3) magnetite, (4) bornite, (5) pentlandite, (6) sulvanite and (7) tetrahedrite.

Gruner's conclusions included:

1. Sulfosalts do not differ structurally from sulfides except the two or more metals in them occupy at least two structurally non-equivalent positions.

2. Structural radicals are not distinquishable except in the pyrite, pentlandite and sulvanite groups.

3. The most common arrangements of the S atoms in sulfides and sulfosalts seem to be those involving close packing of cubic face-centered and hexagonal types. (Author's note: Gruner here pointed out correctly that slightly disordered close packing of this nature may also be expected in the orthorhombic and monoclinic sulfosalts).

4. With the exception of the layer lattices of the molybdenite group, most sulfides and sulfosalts have their sulfur atoms arranged at the corners of regular or slightly distorted tetrahedrons.

Gruner's pioneering ideas opened the way for Strock (1935) and others to further outline and develop the crystal chemistry of the sulfides and sulfosalts.

Strock (1935, p. 285) outlined a classification of mineral structures with what he called "defect structures" which were to include all lattices which did not fit into the already prevalent "structure theory" (Niggli, 1919, p. 551). The "structure theory" required that each different atom type had to be assigned to a specific set of equivalent positions which these atoms filled, and filled "completely." Thus, any lattice which contained a solid solution scheme or other type of atom substitution or vacancy defect was labeled by Strock as a defect structure. Strock realized that in compounds which contain large anions such as sulfur, selenium, tellurium, etc., one sort of atom builds a very stable, rigid lattice while the metal atoms present can also build a well defined, complete lattice for themselves even though the anion lattice controls the position and symmetry of the secondary, cation lattice.

Strock stated (1935, p. 287), "It is therefore easy to understand that in such crystals where the nature of the solid state is largely determined by the rigid lattice of the large anion, that the lattice of either all, or part of the cations can exist in all stages of incompletion." Thus, it was understood at this time that in the case of the defect lattice, one can find various transitions from the "ideal" crystal to a very dispersed situation where the lattice of one atom type is eliminated.

The first true attempt to classify the sulfosalts in a more desirable, structural manner was proposed by Berry (1943, p. 9) who, realizing the very great complexity of sulfosalt structures, indicated that the only common parameter might be the frequently occurring cell dimensions of these minerals. He noted that the numbers: 4, 6, 8, 11, 15 and 19Å were found to occur over and over again in these structures. He arranged the sulfosalt minerals for which structural data was available in a series of "groups," principly based on similarities of cell dimensions and in order of increasing cell size and chemical complexity. He added some simple sulfides in the classification in order to bring out the structural connections of the sulfosalts with minerals of simpler composition.

For many of the "groups" proposed by Berry, however, it has been found that such a classification based on recurring cell dimensions has no actual structural significance since many of the minerals of a given group differ both in crystal system and chemical type. Berry realized this and stated that since these persistent lattice periods are probably associated with certain recurring styles of atomic arrangement, such a grouping of the sulfosalts with common cell dimensions may aid future structural classifications when more x-ray data from these minerals becomes available.

A classification of the sulfosalts by means of chemical bonding or coordination numbers and polyhedron arrangement was suggested by Hiller (1953). He pointed out that a crystal-chemical classification could be utilized in either of the following ways:

1. A classification based on the bonding types of the lattice atoms.
2. A classification based on the static geometry with a basis of coordination number and polyhedron arrangement.

Hiller's classification was based primarily on the sulfur lattice types and then subdivided on basis of metal atom coordination in the sulfur lattice.

Ross (1957, p. 755-774), in compiling a summary of the chemical and physical features of the sulfides and sulfosalts necessary to formulation of a workable classification, stressed the importance of packing geometry and bonding characteristics of the metal cations. Her system, being based primarily on cubic and hexagonal closest packing types was subdivided into "type structures" based on metal-sulfur coordination and further divided into "simple" and "complex" derivatives, the former having but one metal coordination and the latter derived by a general re-ordering of metal atoms into sites filled by only one atom in the simpler sulfide structures.

In a very timely discussion of substitution derivatives in the sulfosalts, Ross points out the few basic structures of these systems attributed to the constancy of the sulfur lattice packing and the varied possibilities of substitution of similar-sized metals into the structures. Ross, referring to Buerger's work (Buerger, 1947, p. 1) on substitutional derivatives mentions that the sulfosalts, which appear to be very complex chemically, are commonly "patterned" structurally after the simple sulfides and substitution of a single metal in the simple "substructure" can result in a distortion or suppression of the crystal symmetry.

Hofmann, (1935, p. 161-185), a number of years before, was able to show that various sulfosalt minerals (e.g. herzenbergite, teallite, wolfsbergite, stibnite, bismuthinite, enargite, miargyrite and others) have distorted Bl-galena type substructures. Hofmann also indicated that these structures contained SbS_3-pyramids (chains) as well as chains of copper-containing tetrahedrons. Therefore, Hofmann, thinking that the complex sulfosalts might be composed of octahedral rings of $(PbS)_6$ groups and of tetrahedral chains containing Cu and Fe, arranged these minerals according to the proportion of S to Sb(As, Bi) atoms in the structure.

Hellner, (1958, p. 503-525), taking up where Hofmann left off, utilized the Bl-galena type derivative lattice of the sulfosalt minerals in proposing his structural classification. Hellner showed that all the known structures of the complex sulfides can be derived in three ways from the (PbS) galena type:

1. Some of the Sb, Pb and Bi sulfides have one axis with an a_o value very near that of galena.
2. Other structures (many of the Sb and Bi sulfides) can be derived from the galena type when projected in the 110 direction. The length of one axis is nearly equal to $d_{110} = 4.20\text{Å}$, or a simple multiple of it.

3. A final sulfide group (primarily the As-sulfides) can be derived from the galena type when projected on (111).

Hellner's classification scheme, although adding a great deal to the present knowledge of sulfide mineralogy, does not fulfill the requirements for a workable, systematic arrangement of these minerals. Many of the known sulfide mineral structures do not fit well into his "formula factor" and "structure factor" classification.

Previous classification attempts for the sulfide minerals have undoubtedly contributed much to the better understanding of the problems to be faced in systematizing such a complex group. It is apparent to this writer, however, that no workable scheme can be devised until many more structural and crystal chemical investigations have been undertaken. The sub-lattice of the simple sulfide type which has been found to occur in many of the more complex sulfosalt minerals is likely to be the primary objective of any future classification but only when the chemical and physical factors controlling this pattern are understood.

ORDER - DISORDER

It has been known for many years that a great number of the sulfides and sulfosalts exhibit some type of order-disorder transitions upon elevation to high temperatures.

Very little work was done in this regard until Strock, (1936), Buerger, (1945, 1947, 1949), Ingerson, (1955) and Frueh, (1958) discussed derivative crystal structures and disorder relationships in non-metal systems.

The primary interest in the disorder characteristics of the sulfide ore minerals has been in determining geologic temperatures of vein formation and related processes of paragenesis. Buerger (1949) discussed some transitions of the "substitution disorder" type which occur in such minerals as chalcopyrite ($CuFeS_2$) and stannite (Cu_2FeSnS_4). Others such as chalcocite (Cu_2S) and argentite (Ag_2S) which exhibit the random, "interstitial disorder" were discussed by Rahlfs (1936). It has become evident in such studies that the disordered, high temperature forms are of a higher crystal symmetry than their low temperature, ordered forms; and when such a transition from one polymorph to another takes place, certain crystallographic symmetry relationships remain in common between the two phases. Buerger (1947) proposed the term, "basic structure" for the low temperature, ordered structure and "derivative structure" for the high, disordered, form.

Two of the types of disordering processes described by Buerger (1949) as "interchange (substitution) disorder" and "interstitial disorder" become important in the sulfide systems. For an example of the interchange disordering

we might consider two crystalline substances with the same composition, XYZ; one with all atoms in perfect order as described by the space group symmetry relationships forced upon the lattice, the other having the same structure with the exception of some X atoms having changed places with Y atoms. Thermodynamically, these crystals have diverse internal energies. The first, ordered variety, possesses the minimum energy, while the second, disordered form, has the higher energy. It is important, however, to realize that the disordering of a crystal has meaning only when it is stated with respect to what atom positions the structure is disordered. In the case discussed above, the disordered polymorph is so in respect to the X and Y atoms, the Z atoms not being considered.

Interstitial disorder occurs in such mineral systems as the sulfides and sulfosalts when there is one large atom (anion) and one or more small, cation metals which tend to fill in the interstices of the large anions. Since the packing of the anion (sulfur in the sulfides) dominates the structure and is very stable at elevated temperatures, when thermal energy is supplied to the lattice, some percentage of these metal atoms obtain sufficient energy to migrate from one interstice to another throughout the

crystal. Such a disordered polymorph inherits a higher energy as a result of these metal cations landing in interstices of greater than minimum energy.

High-low polymorphs related by disorder show many types of symmetry operations in common as mentioned above. When a high temperature form is cooled, there is a requirement for the structure to take on a reduced symmetry as the disordered form starts to order. Such an ordering does not involve the entire crystal at one time but is centered independently in a number of different areas. These little nuclei are thus enlarged by further ordering into "domains" and, as Frueh (1958) points out, since their orientation is controlled by the ordered form's structure, any alignment is possibly being controlled by the orientation of the so-called "short range order" at the point of nucleation. Freuh also mentions that in the cases where these domains of ordering bear a symmetrical relationship to one another, they have been referred to as "transformation twins" by Buerger (1945).

METHODS AND PROCEDURES

The primary objectives of this study can be summarized as follows:

(1) To indicate possible minor elements characteristic of the bournonite group sulfosalts and to delineate their role in the crystal chemistry of these complex systems.

(2) To outline the maximum and minimum limits reached by the axis parameters in these minerals and to relate any variations with atomic substitution (ordered and disordered) and temperature of vein formation.

(3) To investigate possible high temperature, disordered, polymorphs of the study minerals utilizing both synthetic and natural systems.

The procedure followed by the writer in this regard has been as follows:

(1) To obtain as many specimens from world-wide localities as possible.

(2) To carefully select the uncontaminated specimens for x-ray diffraction analysis.

(3) To choose from the x-ray data specimens for further study by polished section methods.

(4) To utilize differential thermal analysis techniques on natural and synthetic specimens for observation of polymorphic transformations and temperatures of melting.

(5) To index and refine by digital computer methods the lattice parameters of all natural and synthetic specimens as well as any high temperature phases quenched to room temperature.

(6) To analyze the relationships between crystal chemical processes by use of unit cell models.

NATURAL SPECIMENS

A total of 67 natural specimens was obtained for the purpose of this investigation (table # 2). The great majority of these specimens were correctly labeled but others were found to contain many more mineral species than indicated by the donor. The specimens consisted of euhedral crystals as well as massive sulfide and gangue. The collection of study specimens included 60 foreign and 7 United States occurrences. The majority of the collection was obtained from the United States National Museum while

other fine specimens were donated by the Chicago Museum of Natural History, the British Museum and the University of Cincinnati, Department of Geology. The remaining specimens were received from private individuals (see table # 2).

SEPARATORY TECHNIQUES

The desire to obtain uncontaminated, x-ray patterns of these minerals necessitated the utilization of a standard separatory procedure involving use of the Franz Isodynamic Separator and a heavy liquid such as Bromoform to remove the sulfide ore from its gangue material. Although many of the more contaminated specimens were not used because of the large collection of relatively pure specimens, some were crushed, sized and separated from their gangue by the Bromoform and Franz Separator methods. All minerals so separated were then hand picked under the binocular microscope to thus insure a clean, uncontaminated sulfide.

POLISHED SECTIONS

A suite of 27 specimens were chosen for polished section study. Mountings were prepared from lucite thermoplastic[1] by means of the Buehler Press and grinding-polishing was carried out in the standard manner on the Sampson-Patmore (Sampson, 1949) polisher. Some difficulty was

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[1]Requires heating specimen to 150°C.

encountered in section preparation due to porous textures and brittleness of many of the synthetics and some natural specimens. Final polish scratching also proved to be common as a result of the extreme softness of the Ag and Pb-bearing sulfosalts. Photomicrographs of selected sections were taken utilizing the Zeiss attachment camera for photomicrographs which was used on a Baush and Lomb reflecting, ore microscope. Photos were taken with 35mm Panatomic X film and printed on Varigam AL paper.

SYNTHETICS

A total of 61 synthetics (primary and re-heated runs) were prepared during the course of this investigation. These represented either the stoichiometry of one of the five minerals of the study group or were mixed to some unique composition for purposes of element substitution experimentation.

The synthetic specimens were mixed from reagent grade (dry chemicals) lead sulfide powder, copper sulfide powder, silver powder (precipitated), antimony powder, arsenic powder, bismuth powder, iron powder and flowers of sulfur. Each synthetic charge was mixed to a total of 2.5000 grams utilizing a Sartorius analytical balance accurate to 0.00001 grams. The mixtures were then compressed into pellets (all 2.5000 grams in one pellet) utilizing drill bushings, dowell

pins and the Buelher Press. The pellets were sealed in evacuated silica glass (Vycor) tubing and heated to various temperature levels in a Kanthal wire furnace with a Barber-Colman, proportioning controller.

All synthetic charges were heated to melting for purposes of homogenization and then lowered to experimental temperature at furnace rate. High temperature phases were quenched in cold water. X-ray diffraction and polished section techniques were used to verify the presence of one mineral phase (see Appendix A).

X-RAY DIFFRACTOMETER

All natural and synthetic samples were x-rayed by the powder method on a General Electric XRD-5 diffractometer. Samples were ground to a very fine powder in an agate mortar then placed on thin glass slides with dope thinner and a very small amount of dope as a bonding agent. No pattern was observed resulting from the dope.

Samples were scanned with nickel-filtered, copper radiation (K $alpha_1$ λ = 1.5405) at 16 ma and 40 KV. Recordings were made through 70 degrees 2-theta at a rate of 2 degrees per minute. A slow scan of 0.2 degrees per minute was used over certain peaks of poor resolution.

A slit system of 3 degrees MR/MR/⊖.1 degrees was found to be the best combination for good resolution and intensity of the study sulfosalts.

Intensity of peaks from the diffractometer patterns were calculated by means of a straight peak height measurement above background with the highest peak in the scan given a numerical value of 100 and the others scaled accordingly. (The d-spacings were taken from the "Tables for Conversion of X-ray Diffraction Angles to Interplanar Spacing," Applied Mathematics Series 10, published by the National Bureau of Standards).

NONIUS - GUINIER CAMERA

A large number of single crystal specimens were used to determine lattice parameters and re-evaluate line indexing on the four sample Guinier camera. These specimens (table # 2) were finely powdered in an agate mortar, after which they were re-ground in a dope thinner solution. The sample was then placed on Scotch "Magic Tape" in the sample holder of the Guinier camera. Since the sample holder could accommodate four samples, a standard of reagent grade lead sulfide was always added.

The camera was mounted on a Picker (Model 795) x-ray unit with cobalt radiation and operated at 15 ma and 40 KV.

Exposures were made for various lengths of time ranging from 15 to 48 hours depending on the amount and composition of the sample. Measurements of lines from the Guinier films were made on a single crystal measuring device manufactured by Charles Supper of Massachusetts.

A great number of very weak lines were recorded with the Guinier camera that have never been observed in previous x-ray studies of these minerals. These were indexed and used to re-evaluate the known lattice parameters of the minerals under study (see tables #17-21).

X-RAY FLUORESCENCE ANALYSIS

A great deal of difficulty was encountered in attempts to obtain satisfactory major element analysis on lead, copper and antimony by x-ray fluorescence techniques. The problem was one of excessive matrix absorption resulting from the high concentration of these heavy elements in the sulfosalt structures. Analyses of natural bournonite, for example, when plotted against standard, synthetic samples, indicated up to 10 weight percent higher lead, 4 to 5 weight percent lower copper and completely diverse antimony values from those expected. Eleven natural specimens were analyzed by d.c. arc spectrographic methods[1] (see table # 7) in

[1]Analyses by Dr. Oiva Joensuu of the Institute of Marine Science, Miami, Florida.

hopes of obtaining some suitable standards for the fluorescence techniques. However, no satisfactory standard curves could be drawn. Matrix absorption effects were found to be impossible to eliminate completely although many diverse approaches to the problem were tried. Barium sulfate-borax fusion and acid solution methods[2] were investigated but were dismissed as unsatisfactory for this study since they destroyed the samples, which were small, and thus eliminated future study.

Arsenic, silver and bismuth in minor percentages were found to be little affected by matrix absorption and repeatable analyses of at least semi-quantitative order were obtained (see table # 8).

A General Electric XRD-5 omission spectrograph unit with full pulse height discrimination was used with a scintillation counting tube and operated at 40 KV and 30 ma. Both chromium and platinum radiations were utilized in the present investigation. Bismuth was analyzed on the platinum tube while silver and arsenic were done on the chromium radiation. A lithium fluoride analyzing crystal was used for silver and bismuth while ADP was found

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[2]Highly dilute solutions run in liquid cells gave the best results.

necessary for arsenic. The K alpha (1) line at 16.01 degrees 2-theta was measured for silver and the LAl (1) line at 33.01 degrees 2-theta was found best for bismuth. The only line free of contamination from other element wavelengths for arsenic analysis was found to be the L beta 1 (1) at 124.41 degrees 2-theta in the ADP spectrum.

The samples were ground in a Spex grinding mill to a very fine mesh and then placed on thin glass slides with dope thinner and a very small amount of dope as a bonding agent.

Standard curves for silver and bismuth were drawn from the eleven spectrographically analyzed natural specimens while the curve for arsenic was drawn from a number of synthetic standards.

All peak intensities were measured by hand from the recorder charts owing to the low intensity of the minor element lines.

COMPUTER TECHNIQUES

An IBM 1620 digital computer with Monitor I disk feed was utilized in the present study for purposes of rapid indexing and least squares refinement of lattice parameters.[3]

[3]The least squares program was written by Dr. Hans Jaffe of the Department of Chemistry, University of Cincinnati.

$1/d^2_{hkl}$ was chosen as the refinement parameter and the higher angle spacings were given added weight in the refinement owing to their greater accuracy. All indices were refined from 3-place d-values.

DIFFERENTIAL THERMAL ANALYSIS

A Stone model KA-W inert gas, differential thermal analysis apparatus was utilized for the purpose of isolating exact temperatures of melting, disorder polymorphism and for general investigations of enthalpy. Samples were used in alloy S-46, liquid-type cells and sintered Al_2O_3 was used as the inert standard. Nitrogen gas was flushed through the furnace chamber during runs to prevent oxidation reactions. Temperature rates of increase varied from 7 degrees per minute to 11 degrees per minute.

CHEMISTRY

MAJOR ELEMENTS

Major element, quantitative analyses for the study sulfosalts is limited to the eleven natural specimens analyzed by d.c. arc spectrographic means and the literature analyses which are all of very early date (see tables #9-12 and #13). The spectrographically analyzed specimens were investigated for Pb, Sb, Ag, Bi, Cu, Fe, Zn,

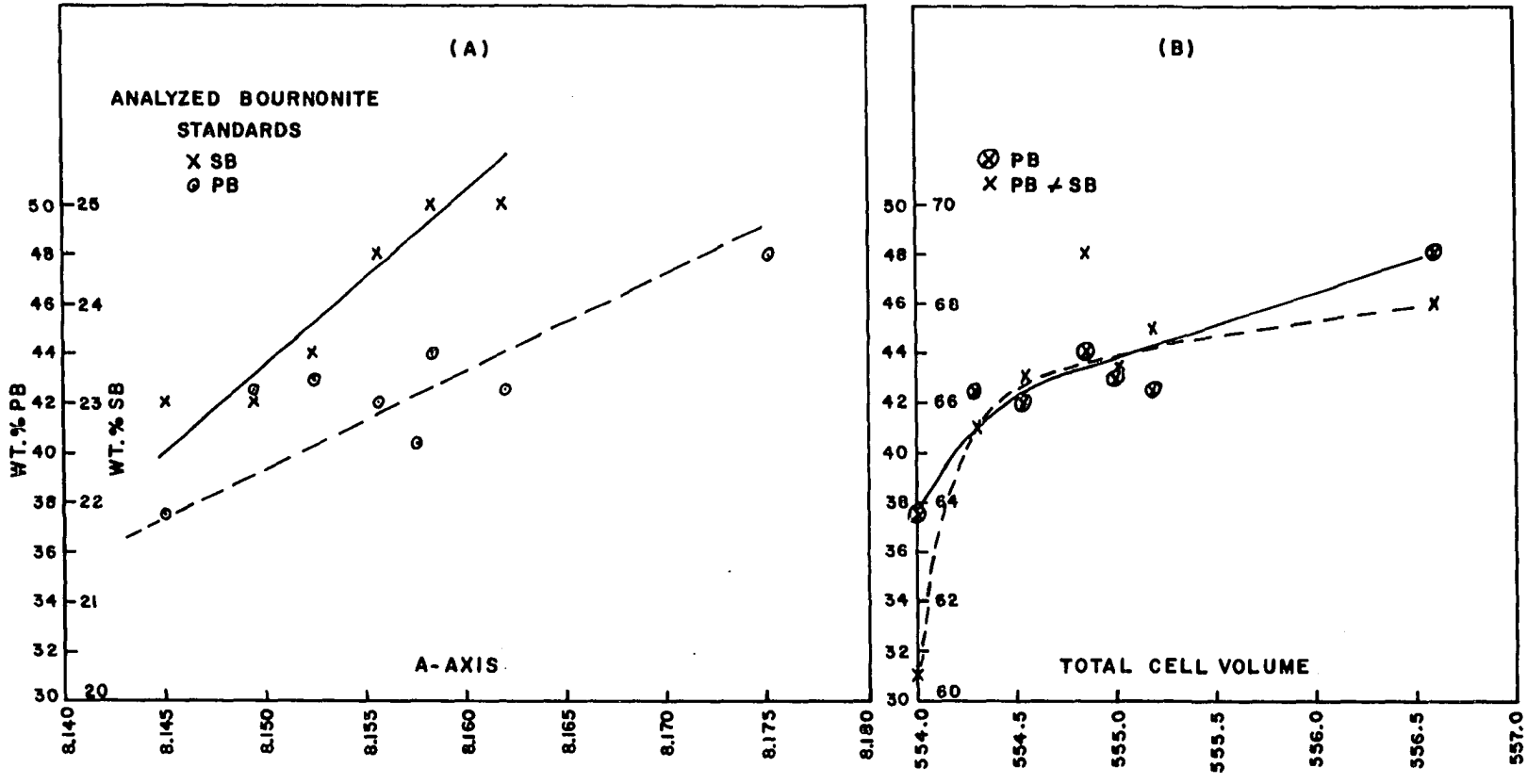

Figure 3. Plots of refined a_o-axis and total cell volume of bournonite verses weight percent lead antimony

Ge, Ga, Tl, In, Ni, Co, Cr, Mn and Cd. Arsenic was not determined by this method but was undertaken in a semi-quantitative manner by x-ray fluorescence analysis.

The lead and antimony weight percentages given for the spectrographically analyzed specimens of bournonite were plotted against various axes of this mineral for indication of cell-size relationships with major element chemistry. Figure #3 clearly suggests a linear correlation of weight percent lead and weight percent antimony with the a-axis of bournonite. Antimony also showed a rather good linearity with the b-axis; however, the c-axis was found to be little affected by such chemical variation.

Total cell volume of bournonite was also found to be a rather acceptable parameter to indicate lead and antimony content as can be seen in figure #3 . Weight percentages of lead plus antimony plotted against total cell volume suggest an exponential relationship (see figure #3).

The analytical data for bournonite gathered from this paper and older literature values indicates that lead can range from around 37.5 weight percent to a maximum of 48 weight percent.[1] Copper is by far the most consistent

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[1] Upper limit possibly influenced by submicroscopic, exsolved, secondary sulfosalts of lead.

element varying only 2.0 weight percent as a maximum. Antimony can apparently range about 6.5 weight percent and sulfur in the range of 2 to 3 weight percent. It therefore becomes clear that minor element substitution is concerned primarily with the lead and antimony in this structure (see section on minor elements).

Similar relationships can be seen for the other minerals under investigation but because of the scarcity of satisfactory samples, such extensive relations with refined lattice parameters, as shown above for bournonite, were not attempted.

MINOR ELEMENTS

The elements represented in minor amounts within the lattices of bournonite, seligmannite, aikinite, diaphorite and freieslebenite were found to be: silver, arsenic, bismuth, copper, antimony and less frequently, iron and zinc (table # 8). Bournonite was studied in much greater detail because of the number of specimens collected.

Analysis of minor elements: silver, arsenic and bismuth was accomplished by x-ray fluorescense techniques and is reported in a semi-quantitative manner (table # 8).

TABLE # 7

ARC SPECTROGRAPHICALLY
ANALYZED SPECIMENS*

BOURNONITES:

	(1)BM-43625 wt. %	(2)BM-32909 wt. %	(3)BM-54797 wt. %	(4)M-Bourn. wt. %	(5)112640 wt. %	(6)W-2 wt. %
Ag	0.19	0.25	0.30	0.10	0.08	0.02
As	.....	.....	.....	.....	.....	.....
Bi	0.01	0.01	0.01	3.3	0.01	0.95
Fe	.....	.....	.....	.....	.....	.....
Zn	.....	.....	.....	.....	.....	.....
Sb	23.0	23.0	25.0	20.0	25.0	23.5
Cu	12.0	13.0	13.5	12.0	14.0	13.5
Pb	37.5	42.5	44.0	48.0	42.5	43.0
Contam.	.....	.....	.....	.....	.....	.....

AIKINITE: DIAPHORITES:

	(7)R-12018 wt. %	(8)M-704 wt. %	(1)C-771 wt. %	(1)R-1034 wt. %	(2)R-8243 wt. %
Ag	0.35	0.02	0.025	24.0	15.0
As	.....	.....	.....	.....	.....
Bi	0.20	0.30	37.0	0.01	0.01
Fe	2.8	.....	.....	.....	.....
Zn	1.5	.....	.....	.....	.....
Sb	22.0	24.5	0.25	25.0	28.0
Cu	13.0	13.0	13.0	0.16	0.78
Pb	40.0	42.0	29.0	30.0	35.0
Contam.	sp	.....	.....	.....	.....

*Analyses by Dr. Oiva Joensuu of the Institute of Marine Science, Miami, Florida

TABLE # 8

TRACE ELEMENT ANALYSES*

BOURNONITES:

	(1)BM-43625 wt. %	(2)W-2 wt. %	(3)M-704 wt. %	(4)R-12018 wt. %	(5)BM-32909 wt. %	(6)112640 wt. %
Ag	.....	.....	See Table #	.....	.....	.....
As	3.00	2.75	3.50	3.00	2.75	2.75
Bi	.....	.....	See Table #	.....	.....	.....
Fe	.....	.....	.....	2.8	.....	.....
Zn	.....	.....	.....	1.5	.....	.....
Sb	.....	.....	.....	.....	.....	.....
Cu	.....	.....	.....	.....	.....	.....
Contam.	.....	.....	.....	sp	.....	.....

	(7)BM-54797 wt. %	(8)M-Bourn wt.%	(9)C-762 wt. %	(10)C-767 wt. %	(11)R-13491 wt. %	(12)M-8367 wt. %
Ag	...See Table #	.....	0.33	0.30	0.26	0.18
As	3.50	3.25	1.25	3.50	2.50	2.50
Bi	...See Table #	.....	0.60	0.08	0.25	0.05
Fe	.....	.....	Trace	.....	.....	.....
Zn	.....	.....	.....	.....	.....	.....
Sb	.....	.....	.....	.....	.....	.....
Cu	.....	.....	.....	.....	.....	.....
Contam.	.....	.....	.....	.....	.....	.....

	(13)R-10829FH wt. %	(14)3411 wt. %	(15)R-6845 wt. %	(16)113077 wt. %	(17)A-2891 wt. %	(18)A-3920 wt. %
Ag	0.03	0.46	0.26	0.30	0.42	0.15
As	3.25	2.50	3.00	2.00	2.50	3.52
Bi	0.05	0.10	0.07	0.30	0.25	0.03
Fe	.....	Trace	.....	.....	.....	.....

* See Table #2 For Identification and Localities of Specimens

TABLE # 8
(Continued)

BOURNONITES:

	(13)R-10829FH wt. %	(14)3411 wt. %	(15)R-6845 wt. %	(16)113077 wt. %	(17)A-2891 wt. %	(18)A-3920 wt. %
Zn	.....	.....	.....	.....	.....	.....
Sb	.....	.....	.....	.....	.....	.....
Cu	.....	.....	.....	.....	.....	.....
Contam.	.....	.....	.....	.....	.....	.....

	(19)A-86[illegible] wt. %	(20)53234 wt. %	(21)82782 wt. %	(22)81295 wt. %	(23)J-2 wt. %	(24)1912,151 wt. %
Ag	0.6 IM	0.30	0.31	0.40	0.25	0.31
As	2.00	2.75	2.75	2.75	3.25	3.25
Bi	0.21	0.08	0.33	0.22	2.02	0.10
Fe	Trace	.....	Trace	.....	.....	.....
Zn	.....	.....	.....	.....	.....	.....
Sb	.....	.....	.....	.....	.....	.....
Cu	.....	.....	.....	.....	.....	.....
Contam.	sp td	.....	.....	.....	.....	.....

	(25)A-861 wt. %	(26)A-862 wt. %	(27)R-8055 wt. %	(28)J-1 wt. %	(29)M-17539 wt. %
Ag	0.40	0.41	0.025	0.18	0.12
As	3.50	2.25	3.50	2.77	3.25
Bi	0.32	0.08	0.43	4.05	0.05
Fe	.....	Trace	.....	Trace	Trace
Zn	.....	.....	.....	.....	.....
Sb	.....	.....	.....	.....	.....
Cu	.....	.....	.....	.....	.....
Contam.	.....	.....	.....	.....	.....

TABLE # 8
Continued

AIKINITES:

	(1)C-771	(2)105571	(3)106760
	wt. %	wt. %	wt. %
Ag	0.02	0.65	0.01
As	1.10	1.00	1.00
Bi	37.0	40.0	39.2
Fe	Trace	Trace	Trace
Zn	.....	.....	.....
Sb	.....	Trace	.....
Cu	.....	.....	.....
Contam.	.....	py,td	Au

DIAPHORITES:

	(1)BM-63514	(2)BM-88839	(3)R-1027
	Wt. %	wt. %	wt. %
Ag	.....	.....	.....
As	2.25	2.50	2.75
Bi	0.14	0.08	0.10
Fe	.....	Trace	Trace
Zn	.....	Trace	Trace
Sb	.....	.....	.....
Cu	Trace	Trace	Trace
Contam.	.....	gn	gn

FREIESLEBENITES:

	(1)R-8243	(2)R-9192
	wt. %	wt. %
Ag	.....	.....
As	3.00	2.00
Bi	0.01	0.08
Fe	.....	.....
Zn	.....	.....
Sb	.....	.....
Cu	.....	.....
Contam.	mn	qtz,cp,gn,sp

TABLE# 9

LITERATURE ANALYSES OF
BOURNONITE
(Dana's System of Mineralogy, vol. I,1944)

	1	2	3	4	5	6	7	8	9
Pb	42.40	43.18	42.34	42.75	43.25	43.62	39.37	40.21	43.85
Fe	-----	-----	0.27	-----	-----	0.74	0.31	0.35	0.51
Ag	-----	-----	-----	trace	-----	-----	1.69	-----	-----
Zn	-----	-----	0.04	-----	-----	-----	0.09	0.35	0.20
Cu	13.01	13.14	12.80	12.77	12.86	12.95	13.52	15.12	12.87
Sb	24.91	25.03	24.44	24.76	24.53	22.22	24.74	18.99	18.42
As	-----	-----	-----	-----	-----	0.03	-----	2.81	3.18
S	19.68	19.59	19.58	19.40	19.17	20.40	19.94	20.04	20.22
Rem.	-----	-----	0.37	-----	-----	0.38	-----	1.67	0.26
S.G.	5.93	5.83	-----	5.85	5.81	5.77	-----	5.84	5.77

1. $PbCuSbS_3$ 6. Rem. is Mn(0.38),Ni trace 8. Rem. is insoluble 9. Rem. is Mn(0.26)

TABLE# 10

LITERATURE ANALYSES OF
SELIGMANNITE
(Dana's System of Mineralogy, vol. I, 1944)

	1	2
Pb	46.89	46.34
Fe	-----	0.06
Zn	-----	0.27
Ag	-----	0.11
Cu	14.38	13.09
Sb	-----	0.64
As	16.99	16.88
S	21.74	21.73
Total	100.00	99.12
S.G.	-----	5.44

1. $PbCuAsS_3$ 2. Binnental

TABLE#11

LITERATURE ANALYSES OF
AIKINITE
(Dana's System of Mineralogy, vol. I,1944)
(Peacock,1942)

	1	2	3	4	5	6
Pb	35.98	35.15	36.01	35.69	36.05	36.31
Cu	11.03	11.11	10.90	11.79	10.59	10.97
Bi	36.29	36.25	36.20	34.62	36.45	34.87
Ni	-----	-----	-----	-----	-----	0.36
Au	-----	-----	-----	-----	-----	0.09
S	16.70	16.56	16.60	16.05	16.61	16.50
Total	100.00	99.07	99.71	98.15	99.70	99.10

1. $PbCuBiS_3$ 2-6. Beresovok, Ekaterinburg, Urals

TABLE#12

LITERATURE ANALYSES OF
DIAPHORITE
(Dana's System of Mineralogy, vol. I,1944)

	1	2	3
Pb	30.48	28.67	31.06
Ag	23.78	23.44	23.36
Sb	26.87	26.43	25.92
Fe	-----	0.67	-----
Cu	-----	0.73	-----
S	18.87	20.18	18.51
S.G.	-----	5.73?	6.04

1. $Pb_2Ag_3Sb_3S_8$ 2-3 Pribram

TABLE# 13

LITERATURE ANALYSES OF
FREIESLEBENITE
(Dana's System of Mineralogy, vol. I,1944)

	1	2	3	4	5	6
Pb	28.85	31.90	31.38	30.77	30.08	30.00
Ag	25.03	22.45	23.31	23.08	23.76	22.18
Sb	28.26	26.83	25.64	27.11	27.05	27.72
Fe	-----	-----	-----	0.63	-----	0.11
Cu	-----	-----	0.13	-----	-----	1.22
S	17.86	17.60	18.90	18.41	18.71	18.77
S.G.	6.27	-----	6.040	6.230	-----	-----

1. $Pb_3Ag_5Sb_5S_{12}$ (old formula given to freieslebenite)

2-3 Spain

4. Pribram

5-6. Freiberg

The eleven spectrographically analyzed natural specimens (table # 7) plus a number of synthetic specimens were used as standards in this analysis.

BOURNONITE

The bournonite structure was found to consistently reveal the presence of three minor elements: silver, arsenic and bismuth (table # 8). Arsenic is present in the greatest amount, ranging in the semi-quantitative analyses given in this study from 2.0 to 3.5 weight percent. One specimen (C 762) contains less arsenic (1.25 weight percent) while another specimen (94977) revealed 7 weight percent. Both of these specimens are known to contain more than one mineral species (see Appendix B).

Earlier analyses (see table # 9) have shown a maximum of 4 : 1 ratio for Sb : As substitution in bournonite. The present study has confirmed a $3\frac{1}{2}$: 1 ratio maximum and thereby leaves little doubt that the natural solid solution series between bournonite and seligmannite does not exist.

Silver and bismuth also appear quite regularly in the bournonite lattice (table # 8). Bismuth weight percentages were found to be well under 0.3 weight percent for most of the specimens analyzed but reached 4.05 weight percent in

some crystals from Julcani, Peru. Silver percentages did not rise above 0.5 weight percent in all bournonite specimens analyzed but averaged approximately 0.3 weight percent (tables # 7 and 8).

The x-ray patterns for nearly all bournonite specimens analyzed show a number of odd lines most of which are just visible as ledges on indexable, bournonite peaks. Two distinct lines at 3.13Å (28.5 degrees 2-theta) and 3.03Å (29.5 degrees 2-theta) were observed in a great percentage of the diffractograms and appeared to be related directly to bismuth minor element content in the lattice. Another distinct, odd line was recorded in a somewhat smaller number of specimens, at 3.43Å (26.0 degrees 2-theta). This line is thought to represent the (111) spacing of galena (intensity of 9 in galena structure) which is present as contamination or as an exsolved phase (see "discussion" of minor elements). The other major lines of galena are very close to some in the bournonite pattern, and thus the intensities of peaks at 2.98Å, 2.10Å, 1.79Å, 1.71Å, 1.48Å, 1.36Å, etc. in the bournonite diffractograms can be somewhat influenced by presence of galena as a secondary phase (~~table #~~). Several of the bournonite specimens showing a high silver content (0.3 - 0.4 weight percent) were also observed to contain galena either as an

exsolved phase or contamination. The high solubility of silver and bismuth in the PbS structure will be discussed later in this section.

Difficulty was encountered by this writer in trying to assign most of the recurrent, odd lines of the bournonite diffractograms to a single sulfide or sulfosalt structure containing arsenic, silver or bismuth (observed as minors in bournonite). The primary reason for this is that a great many of the sulfides and sulfosalts of similar composition have related structures and therefore exhibit many common lines in their x-ray patterns (see table #14).

The lines observed at 3.03Å and 3.13Å in many bournonite patterns, for example, could belong to any one or more of the following minerals (see table #14):

Bismuthinite	Bi_2S_3
Schirmerite	$PbS \cdot 2Ag_2S \cdot 2Bi_2S_3$
Emplectite	$Cu_2S \cdot Bi_2S_3$
Galenobismutite	$PbS \cdot Bi_2S_3$

Similarly, the lines appearing consistently as ledges on good bournonite peaks are obviously the result of the presence of a mineral structure very like that of bournonite. It is suggested that these lines could be related to one or more of the following minerals:

Cosalite	$2PbS \cdot Bi_2S_3$
Dufrenoysite	$2PbS \cdot As_2S_3$
Rathite I	$13PbS \cdot 9As_2S_3$
Baumhauerite	$3PbS \cdot 2As_2S_3$
Semseyite	$9PbS \cdot 4Sb_2S_3$
Boulangerite	$5PbS \cdot 2Sb_2S_3$
Stibnite	Sb_2S_3
Bismuthinite	Bi_2S_3

The secondary sulfide or sulfosalt phases contained within the bournonite lattice are submicroscopic in nature and in polished section appear to be revealed only by the unique, pitted texture shown by a great many specimens (see Appendix B).

X-ray diffraction of oriented, polished section specimens from Julcani, Peru,[2] resulted in evidence of a two-dimensional nature for the exsolved, secondary sulfosalts; possibly similar to the case found for the micro-perthites in the feldspars.

The literature analyses for bournonite show arsenic in only three of the eight listed with maximum weight percentage as 3.18. Bismuth is not even listed as a minor

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[2]See "Environments of Deposition" for discussion of Julcani specimens.

TABLE#14

X-RAY DATA* SHOWING STRUCTURAL SIMILARITIES BETWEEN VARIOUS SULFIDES AND SULFOSALTS
(Data after Berry and Thompson,1962)

MINERAL	THETA	d	I	MINERAL	THETA	d	I
Stibnite	7.85	5.64	3	Bismuthinite	7.8	5.68	2
Sb_2S_3	8.75	5.07	4	Bi_2S_3	8.7	5.10	2
	11.1	4.00	2		11.1	4.00	3
	12.45	3.58	10		11.8	3.77	1½
	14.2	3.14	2		12.45	3.58	10
	14.6	3.06	2		13.7	3.25	1½
	16.2	2.76	3		14.2	3.14	5
	16.75	2.67	1		15.85	2.82	2
	17.2	2.61	½		16.4	2.73	1
	17.8	2.52	4		16.85	2.66	½
	18.5	2.43	1		17.85	2.51	6
	19.9	2.26	1		18.25	2.46	½
	20.3	2.22	2		19.45	2.32	1
	21.55	2.10	3		19.95	2.26	3
	22.75	1.994	1½		20.6	2.19	1½
	23.5	1.933	5		21.25	2.13	½
	24.2	1.881	½		21.65	2.09	1
	24.6	1.852	½		22.8	1.989	1
	25.65	1.781	½		23.25	1.953	2
	26.5	1.728	3		23.5	1.933	2
					24.05	1.892	1

* Data is not complete as given in Berry and Thompson(1962)

TABLE#14 (cont'd)

MINERAL	THETA	d	I	MINERAL	THETA	d	I
Baumhauerite	10.8	4.11	8	Jamesonite	7.35	6.03	½
$3PbS \cdot 2As_2S_3$	11.3	3.93	1	$4PbS \cdot FeS \cdot 3Sb_2S_3$	8.7	5.10	½
	11.5	3.87	2		10.85	4.10	3
	11.7	3.80	2		11.5	3.87	4
	11.9	3.74	3		11.95	3.72	2
	12.1	3.68	2		12.40	3.59	3
	12.3	3.62	2		12.95	3.44	10
	12.5	3.56	6		13.35	3.34	1
	13.0	3.43	8		14.04	3.18	5
	13.2	3.38	1		14.45	3.09	5
	13.7	3.25	8		15.15	2.95	2
	14.2	3.14	3		15.75	2.84	9
	14.9	3.00	10		16.3	2.75	8
	15.2	2.94	10		17.0	2.63	1
	15.7	2.85	5		19.0	2.36	1
	16.2	2.76	10		19.55	2.30	3
	16.6	2.70	5		20.1	2.24	4
	17.0	2.64	½		20.8	2.16	1
	17.6	2.55	½		21.35	2.11	½
	18.1	2.48	½		21.95	2.06	5
	19.3	2.33	6		22.4	2.02	4
	19.6	2.30	½		23.1	1.965	1
	20.0	2.25	½		23.85	1.907	1
	20.5	2.20	4		24.4	1.866	1
	20.8	2.17	½				
	21.1	2.14	½				
21.7	21.7	2.08	6				

TABLE# 14 (cont'd)

MINERAL	THETA	d	I
Emplectite $Cu_2S.Bi_2S_3$	6.0	7.38	5
	9.4	4.72	2
	12.2	3.65	½
	13.8	3.23	9
	14.25	3.13	7
	14.65	3.05	10
	15.8	2.83	½
	16.4	2.73	½
	17.2	2.61	½
	18.55	2.42	½
	19.2	2.34	5
	20.0	2.25	1
	20.85	2.17	4
	23.1	1.965	2
	24.45	1.863	3
	25.3	1.804	3
	25.6	1.784	2
	26.0	1.759	2
	26.7	1.716	½
	27.7	1.658	3
	28.5	1.616	½
	29.6	1.561	2
	31.5	1.475	½
	32.05	1.453	2

MINERAL	THETA	d	I
Chalcostibnite $Cu_2S \cdot Sb_2S_3$	6.0	7.38	2
	9.5	4.67	1
	12.2	3.65	1
	14.24	3.13	10
	14.9	3.00	9
	16.05	2.79	½
	17.55	2.56	1
	19.5	2.31	4
	20.1	2.24	2
	21.3	2.12	3
	24.0	1.895	3
	24.9	1.831	4
	25.1	1.817	½
	25.95	1.762	5
	26.25	1.743	½
	27.2	1.687	1
	28.4	1.621	2
	28.75	1.603	1
	29.75	1.554	1
	32.35	1.441	3

element and silver is given in only two of the eight analyses (table # 9). Analysis #7 of table # 9 shows 1.69 weight percent silver along with iron and zinc. It is the opinion of this writer that the #7 analysis was contaminated. Two of the analyses give manganese as a minor element and one gives nickel. The writer did not observe manganese in any specimen analyzed. However, it will be admitted that the K-alpha line of this element is hidden by chromium K-beta (1) and K-beta (5) which results from the tube target metal. Nickel was identified in one specimen labeled "bournonite and wolchite"[3] from Wolch Carinthia, Austria (table # 2). Wolchite is a supposed alteration product of bournonite.

Iron was found in only eight of the natural bournonite specimens analyzed during this study and in at least four of these, contaminants are known to exist. Zinc was identified in only one specimen (R 12018) and can definitely be attributed to sphalerite contamination. A small amount of cadmium associated with this specimen also is very likely present in the sphalerite.

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[3]Wolchite is thought to be an alteration product of bournonite.

SELIGMANNITE

No seligmannite specimens collected for this study were found to be suitable for even a semi-quantitative analysis and therefore investigations of this mineral were limited to study of synthetics and polished section observation of available natural samples.

AIKINITE

Five specimens of aikinite were obtained for study but only three were of sufficient quantity to be analyzed for minor element content by x-ray fluorescence methods (see table # 7). One specimen (#C771) was analyzed by d.c. arc spectrographic methods.

The minor elements found to be present were: silver, arsenic, antimony, iron and gold. Arsenic is notably less abundant than in the bournonite lattice, averaging approximately 1.0 weight percent. Silver was found in small quantities of 0.01 weight percent and 0.02 weight percent in the two specimens (106760) and (C 771) respectively. A higher silver content of 0.65 weight percent observed for sample (105571) is thought to be influenced by tetrahedrite noted in the polished section of this sample (Appendix B, plate # 7). Iron was found in minor amounts

in all samples analyzed and the gold listed for specimen (106760) is thought to be inclusions of the native metal.

The seven published analyses listed (table # //) are all from Beresovok, Ekaterinburg, Urals, and in all but one case, no minor elements are given as belonging to this mineral. The gold and nickel shown for analysis #6 are thought to be inclusions.

DIAPHORITE

Seven diaphorite specimens (5 labeled "brongniardite," one labeled "freieslebenite") were collected for this study with only one found to be entirely free of contamination (BM 63514). The others were invariably associated with galena, with some silver, miargyrite, pyrargyrite, pyrite and sphalerite. The presence of associated galena is clearly revealed in the diffraction patterns of (BM 88839) and (BM 63514) (figure #15) since many of the lines of the galena pattern are superimposed on the diaphorite lines thereby causing an evident intensity variation. Polished section study of the diaphorite specimens confirmed the close relationship with galena (Appendix B).

It is not certain just how much of the minor quantities of arsenic and bismuth recorded for the diaphorite samples was contributed from the galena. Specimens (BM 63514),

(BM 88839) and (R-1027) contained 2.25, 2.50 and 2.75 weight percent arsenic and 0.14, 0.08 and 0.10 weight percent bismuth, respectively. All three samples showed copper minors and two of them, iron and zinc. The iron and zinc are thought to be sphalerite contamination.

Again, as in the bournonite discussion, the copper and bismuth minor elements appear to be related to one or more submicroscopic inclusions of copper and bismuth-bearing sulfosalts. Specimens (BM 63514), (BM 88839) and (R-1027) all exhibited the same odd diffraction lines at 3.03Å and 3.13Å that were seen in bournonite.

Previous analyses given for diaphorite in the literature indicate no minor elements in the mineral except 0.67 weight percent iron and 0.73 weight percent copper for an analysis from Pribram (table #/2). No arsenic or bismuth was reported.

FREIESLEBENITE

Four specimens containing freieslebenite were obtained for this study and three of these were of suitable size to separate from contaminants for a semi-quantitative analysis. Arsenic, bismuth and copper were the only minor elements observed with a possibility of manganese in specimen (R 8243) (table # 8). Two of the samples (R-1034) and

(R 8243) were analyzed by d.c. arc spectrograph (table # 7) and indicated 0.16 and 0.78 weight percent copper, respectively. Two of the literature analyses (table # 13) give copper and iron as minor elements.

It is obvious that these elements are very common minors in freieslebenite and are possibly needed in the structure to fulfill a valency or other crystal chemical compensation. Synthetic studies in this investigation further bore out this conclusion.

DISCUSSION

Minor element analysis is a basic tool in the understanding of sulfosalt crystal chemistry. The complex, distorted structures of these minerals, with their substitutional and omission defect characters, utilize foreign atoms to help achieve thermodynamic equilibrium. Of course, even the low temperature, ordered structures of the sulfosalts never quite reach lowest internal energy as would be realized in the "ideal" crystal.

Substitution of foreign atoms in the sulfosalts during the high temperature phases of growth generates valency and coordination disturbances which in turn result in atom

omission sites, suppression of symmetry relations within the lattice (distortion) and tendency toward exsolution upon lowering of the temperature.

Previous workers have focused their attention on structural determination of the Bournonite Group sulfosalts but have neglected quantitative evaluation of atom substitution limitations. However, related sulfosalts such as those of the "Tetrahedrite Series" have been recently investigated in this regard (Bohmer, 1964).

It has long been known that only certain atoms are "allowed" to substitute for other atoms or to fill tetrahedral and octahedral voids in a mineral structure owing to radius ratio and valency considerations. In the geometrical packing of atoms it is a rule that the size of the center atom is restricted by the size and number of surrounding, coordinating atoms. Thus, the ratio of the size of the center atom to the size of the coordination atoms is expressed by the ratio of their respective radii, the "radius ratio." In sulfide systems such radius ratios are based on the S^{-2} atom with which the metal atoms coordinate (table #14A). For example, the radius ratio limits for the 4:4 coordination (tetrahedral) are 0.225 - 0.414 while the limits for the 6:6 coordination are 0.414 - 0.732 (Azaroff, 1960). Such a designation means

that the 4:4 or 6:6 coordinations have maximum stability when the cation-anion ratio stays within these ranges.

Atomic radii of the elements have been approximated from substances of diverse bond character including ionic, covalent and metallic. However, in the sulfosalts we are dealing with a complex system of all three bond types, i.e. the ionic and covalent nature of the metal-sulfur bonds imparts a partial metallic, metal-metal bond.

The size of an individual atom radii depends on its coordination number and the electrostatic forces between atoms, both of which are complicated in the sulfosalt structures. The radii shown in table #14A, therefore, are approximate values but illustrate suitably the possible combinations for atom substitution in the study sulfosalts.

It can be seen from table #14A that divalent Cu, Fe and Zn are closely similar in size and differ only by 3 percent in radii. The small amounts of iron and zinc found in several analyses of this study could well be substituting for copper in its tetrahedral void position (see figure # 1). Trivalent As, as seen in table #14A is 25 percent smaller than trivalent Sb for which it is thought to substitute in bournonite, diaphorite and freieslebenite. Monovalent Ag and divalent Pb show good substitution possibilities in these structures and differ in size

TABLE # 14A

RADIUS RATIOS FOR CONSTITUENT ELEMENTS OF THE BOURNONITE SERIES

element	valence	*r/S^{-2} within range 0.225 - 0.414 radius	radius ratio
As	+5	0.46	0.250
As	+3	0.58	0.315
Sb	+5	0.62	0.336
Fe	+3	0.64	0.347
Cu	+2	0.72	0.391
Fe	+2	0.74	0.402
Bi	+5	0.74	0.402
Zn	+2	0.74	0.402
Sb	+3	0.76	0.413

element	Valence	*r/S^{-2} exceeds 0.414 radius	radius ratio
Pb	+4	0.84	0.456
Ag	+2	0.89	0.483
Cu	+1	0.96	0.521
Bi	+3	0.96	0.521
Hg	+2	1.10	0.597
Pb	+2	1.20	0.652
Ag	+1	1.26	0.684

* S^{-2} taken as 1.84

(after Pauling, 1948, p. 346, Azaroff, 1960 p. 438)

by only 5 percent while trivalent Bi is 20 percent smaller in radius than divalent Pb and 7 percent larger than divalent Ag. However, substitution of trivalent Bi for either Pb or Ag requires some form of "coupled substitution" perhaps with As or generation of omission sites for purposes of charge balance.

Atoms which are found to substitute in a mineral structure may be disordered or ordered in equivalent sites. In the structures of sphalerite and chalcopyrite, for example, the zinc atoms of the sphalerite are replaced by regularly alternating copper and iron to form chalcopyrite. This, then, is an example of an orderly distribution in equivalent sites of a substituting atom. As a consequence of such an orderly substitution, changes in the symmetry of the affected structure are imposed. Chalcopyrite has the same original, basic close-packing of sulfur atoms with all metal atoms occupying tetrahedral sites, however, the chalcopyrite unit cell has inherited a new, tetragonal, body-centered symmetry as a result of the ordered arrangements of the substitution metals in a so called "superlattice." X-ray diffraction techniques can be used to reveal these superlattices by the appearance of new lines or reflections.

On the other hand, atoms substituted in a disordered manner do not affect a change in the symmetry of the mineral structure. Intensity of reflections from atom planes affected by such substitution should, however, vary in a systematic manner.

Measurement of diffraction peak intensities for a number of bournonite patterns (~~table #~~) showed no obvious, systematic variations with increase of silver, arsenic or bismuth minor elements. This was taken as additional evidence that these minor elements are not disordered in this mineral lattice but are in ordered equivalent sites, associated, for the most part, with the submicroscopic, exsolved, secondary sulfosalt phases (see section on minor elements in bournonite). Tetrahedrite (Bohmer, 1964), on the other hand, shows disordering substitution of Ag, Cu, Fe, Zn, etc. in much greater range than the minors in the present study and exhibits noticeable fluctuation in diffraction lines representing atom planes affected by such substitutions.

Linear plots of minor element weight percents versus variation in the a-axis of bournonite were drawn by the writer utilizing the least square refined axis values. Figure # 5 is a plot of weight percent Bi against the

a-axis of bournonite and illustrates readily the concentration of specimens bearing less than 0.6 weight percent Bi between 8.145Å and 8.174Å for the a-axis. Also apparent is the value of approximately 8.159Å for the maximum Bi content. Note also that the specimens of higher Bi weight percentages (W-2, J-2 and M-Bourn.) also peak at about the same a-axis value of 8.159Å, indicating a possible second phase relationship in regard to Bi substitution in the lattice.

In figure #6 weight percent Ag ± Bi is plotted against the same parameter of bournonite. Here, however, the maximum is skewed toward lower a-axis values to about 8.152Å.

A plot of weight percent As versus weight percent Ag in the bournonite and aikinite specimens shows some interesting relationships as seen in figure #4 . Bournonite analyses show an evident, rapid decrease in weight percent Ag with rise of the As content toward the maximum of 3.5 weight percent. The two aikinite specimens plotted very close together and appear to accept As and Ag in a very different manner than bournonite.

The semi-quantitative As minor analyses given in this study for the minerals bournonite, diaphorite and freieslebenite revealed some unexpected relationships with Sb.

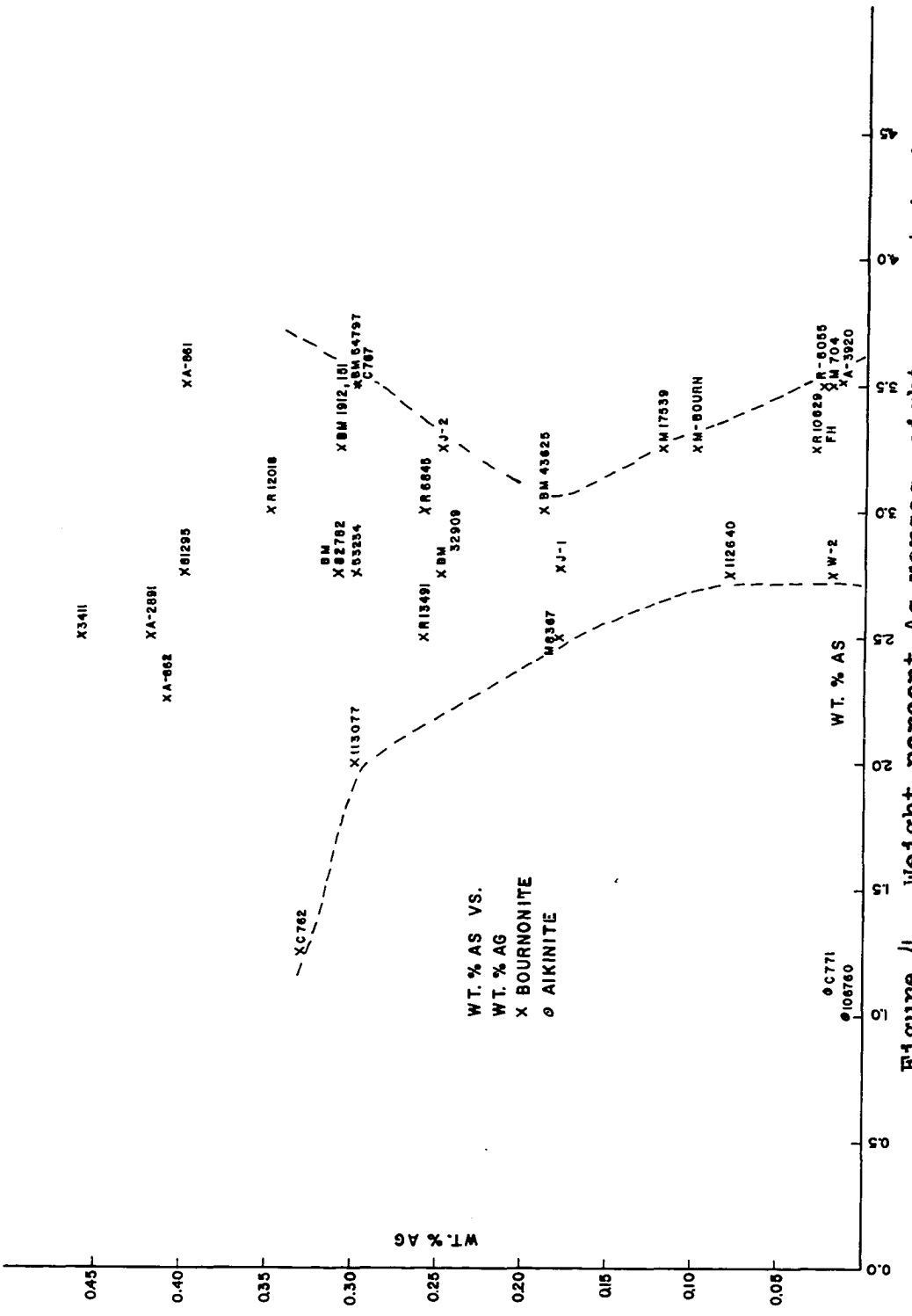

Figure 4. Weight percent As verses weight percent Ag in bournonite and aikinite

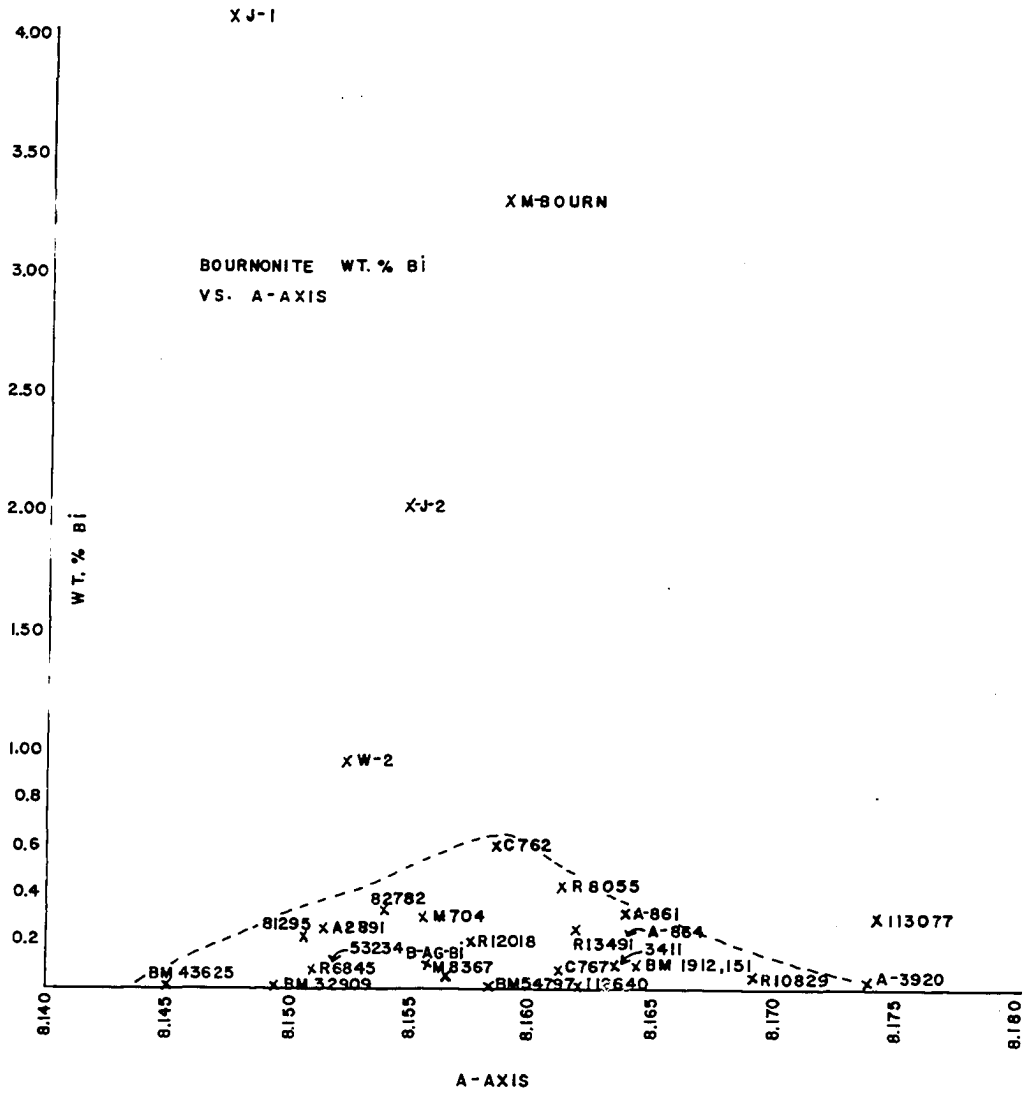

Figure 5. Weight percent Bi verses the a_o-axis of bournonite

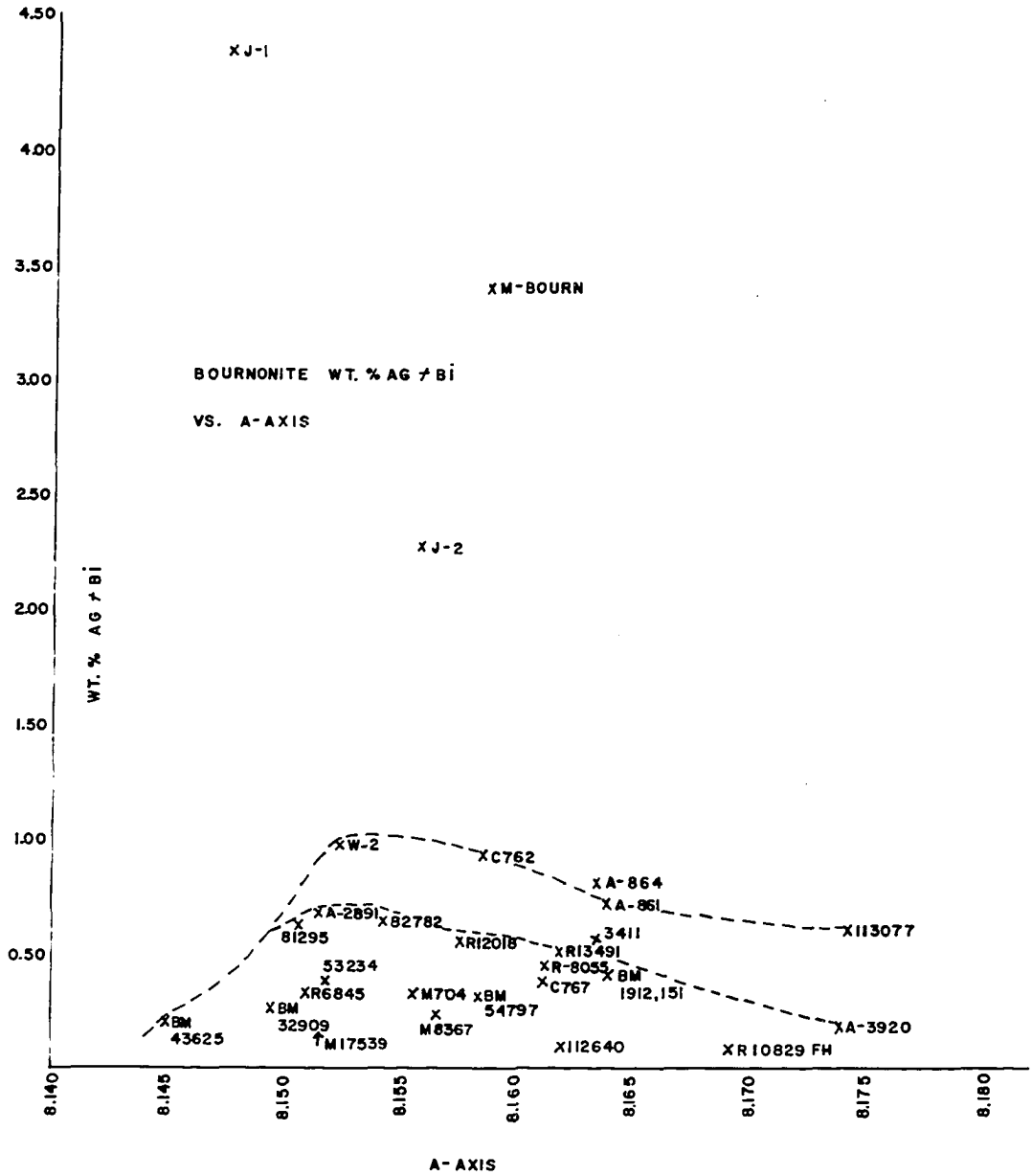

Figure 6. Weight percent Bi plus Ag verses the a_o-axis of bournonite

Although reliable quantitative Sb analyses could not be obtained with x-ray fluorescence techniques, comparisons with obviously high or low Sb samples with As were attempted. Unexpectedly, the specimens of lowest Sb peak intensity (K-alpha and K-beta (1)) also showed the lowest As content as well. Similarly, specimens of highest Sb peak intensity seemed to contain more As. This same relation was found for bournonite, diaphorite and freieslebenite specimens. If As is substituting for Sb in these structures one would expect the reverse condition of high Sb-low As and vice versa. The literature analyses for these minerals (especially bournonite) shows the expected relationship. If, however, the relation shown in this study is correct, the question might be asked, what then replaces Sb in a low Sb specimen if it is not As? Presence of As-bearing sulfosalts (see page 81), previously discussed as exsolved, submicroscopic phases in these minerals, could possibly account for such a relationship.

This writer previously mentioned the high solubility of Ag and Bi in the galena-type structure. Van Hook (1960) has suggested a possible coupled substitution of $Ag^{+} + Bi^{+3}$ for $2\ Pb^{+2}$ in derivation of alpha matildite ($AgBiS_2$) from the galena lattice. He prefers the Ag and Bi to be

randomly distributed in the octahedral sites and mentions also that large amounts of either Bi_2S_3 or Ag_2S in excess of the 1:1 composition can be held in the structure at high temperatures, possibly as substitutional solid solution of the atomic constituents in the same octahedral positions. Oftedahl (1943) found that solid solutions containing Ag and Bi in equal molecular proportions in galena are indistinguishable from normal galena in polished section but that samples containing more Bi than Ag are distinctly anisotropic and reveal an octahedral parting in contrast to the usual (001) cleavage. This parting has been thought by Oftedal to result from charge imbalance due to atomic substitution of Bi^{+3} for Pb^{+2}. Wahlstrom (1937) attributed it to oriented exsolution intergrowths in the galena. This is thought by this writer to be a very similar situation to that encountered for the sulfosalt minerals of the present investigation.

Argentite (= acanthite, Ag_2S), previously thought to be the common inclusion in galena-type minerals, was found by Ramdohr (1955) to be only slightly soluble in galena (less than 1 mol. percent). He further identified the inclusions as sulfosalts of Ag, not argentite.

Fleischer (1955) reported Sb, Bi and Ag as being the most recurrent minor constituents in galena and Oftedahl

(1940) suggested an increase in percentage of these elements with higher temperature deposits.

The possibilities for utilization of the bismuth-silver solubility in these sulfosalt structures in regard to geothermometry appears rather good. Van Hook's (1960) investigation of the system PbS-Bi_2S_3 indicated a definite correlation between formation temperatures and Bi content in galena. He postulated that the change in cell dimensions with solubility of Bi_2S_3 may be used as an indicator on minimum formation temperatures only if a second, lead sulfosalt phase is present. Van Hook (1960) showed that a very small amount of Ag has a marked effect on cell dimensions in the system PbS-Bi_2S_3.

It has been said that the presence of Ag in galena favorably influences the presence of Bi (or Sb, As, etc.) and vice versa. A similar but obviously more complicated relationship of Ag and Bi as minor elements is thought by this writer to be the case in the sulfosalts under investigation.

LEAST SQUARES REFINEMENT

Least squares refinement of lattice parameters of the five study sulfosalts proved to be a very useful technique for better understanding cell variation within these complex mineral systems. Figures# 7 and # 8 show plots of the a_o-axis of bournonite verses the b_o-axis and c_o-axis. Note that in figure# 7, the c_o-axis is little affected by variation of the a_o-axis. On the other hand, the b_o-axis is altered in some linear manner with the a_o-axis as shown in figure# 8 . This relationship corresponds well with the linearity of bournonite's weight percent Pb and Sb with both the a_o and b_o-axes(see page 66). The c_o-axis, as would be expected, is little affected by such variation of lead and antimony(refer to figure# 7).

It is suggested by this writer that such plots of computer refined lattice parameters could well be utilized in other sulfosalt systems under investigation. A hint can be obtained in regard to cell variation with elemental substitution by use of such techniques; even prior to actual chemical analysis.

Appendix D contains all least squares refinements of the study minerals discussed in the text.

TABLE # 15

LEAST SQUARED REFINED LATTICE

PARAMETERS OF STUDY SPECIMENS

SPECIMEN	A-AXIS(Å)	B-AXIS(Å)	C-AXIS(Å)	TOTAL CELL VOLUME
	SPECTROGRAPHICALLY ANALYZED BOURNONITES (See table # 2)			
BM-43625	8.145	8.703	7.816	554.003
BM-32909	8.150	8.704	7.815	554.290
BM-54797	8.158	8.705	7.813	554.848
M-Bourn.	8.159	8.685	7.808	553.272
112640	8.162	8.694	7.824	555.181
W-2	8.152	8.709	7.818	555.074
R-12018	8.158	8.705	7.810	554.627
M-704	8.156	8.706	7.810	554.530
	BOURNONITES CONT.			
A-861 D-136	8.164	8.725	7.820	557.008
82782	8.154	8.713	7.836	556.741
R-10829 PB	8.165	8.718	7.821	556.713
J-1	8.147	8.712	7.823	555.298
J-2	8.155	8.709	7.806	554.354
A-3920	8.174	8.714	7.807	556.096
M-8367	8.157	8.703	7.810	554.380
81295	8.151	8.709	7.802	553.874

BOURNONITES CONT.

A-2891 D-3411	8.152	8.700	7.810	553.877
R-13491	8.162	8.703	7.818	555.370
R-6845	8.151	8.706	7.814	554.476
R-8055	8.161	8.708	7.812	555.127
C-764	8.164	8.716	7.813	555.919
C-762	8.159	8.713	7.817	555.670
BM-1912,151	8.164	8.712	7.818	556.063
78894	8.146	8.704	7.812	553.113
C-767	8.161	8.709	7.814	555.364
94977	8.150	8.686	7.829	554.264
4073 d-3411	8.164	8.711	7.812	555.578
53234	8.152	8.711	7.814	554.914
R-10829 FH	8.169	8.712	7.810	555.870

BERTHONITES

113077	8.174	8.708	7.820	556.620
M-17539	8.152	8.678	7.809	552.467
S-19-Bourn.	8.171	8.689	7.846	557.017

SYNTHETICS

$S14-B_3$	8.157	8.700	7.796	553.264
B-Ag-Bi	8.156	8.706	7.817	555.054

TABLE #15
Continued

SPECIMEN	A-AXIS(Å)	B-AXIS(Å)	C-AXIS(Å)
		SELIGMANNITE SYNTHETICS	
S2-SX	8.054	8.714	7.613
S-4 (Reheat)	8.076	8.729	7.645
S-5 (Reheat)	8.088	8.733	7.647
		AIKINITES	
C-771	11.318	11.646	4.015
106760	11.310	11.666	4.017
		AIKINITE SYNTHETICS	
S-5A (Reheat)	11.317	11.639	4.024
A-6	11.341	11.656	4.001
		DIAPHORITES	
BM-88839	15.819	17.907 Gamma = 116° 32'	5.902
		DIAPHORITE SYNTHETICS	
S7-D (High Phase)	5.727		
		FREIESLEBENITES	
R-1034	12.787	5.953 Beta 92° 16'	7.532

TABLE # 15
Continued

SPECIMEN	A-AXIS(Å)	B-AXIS(Å)	C-AXIS(Å)
	FREIESLEBENITE SYNTHETICS		
S-F2 (High Phase)	5.836		
S-F3 (High Phase)	5.780		

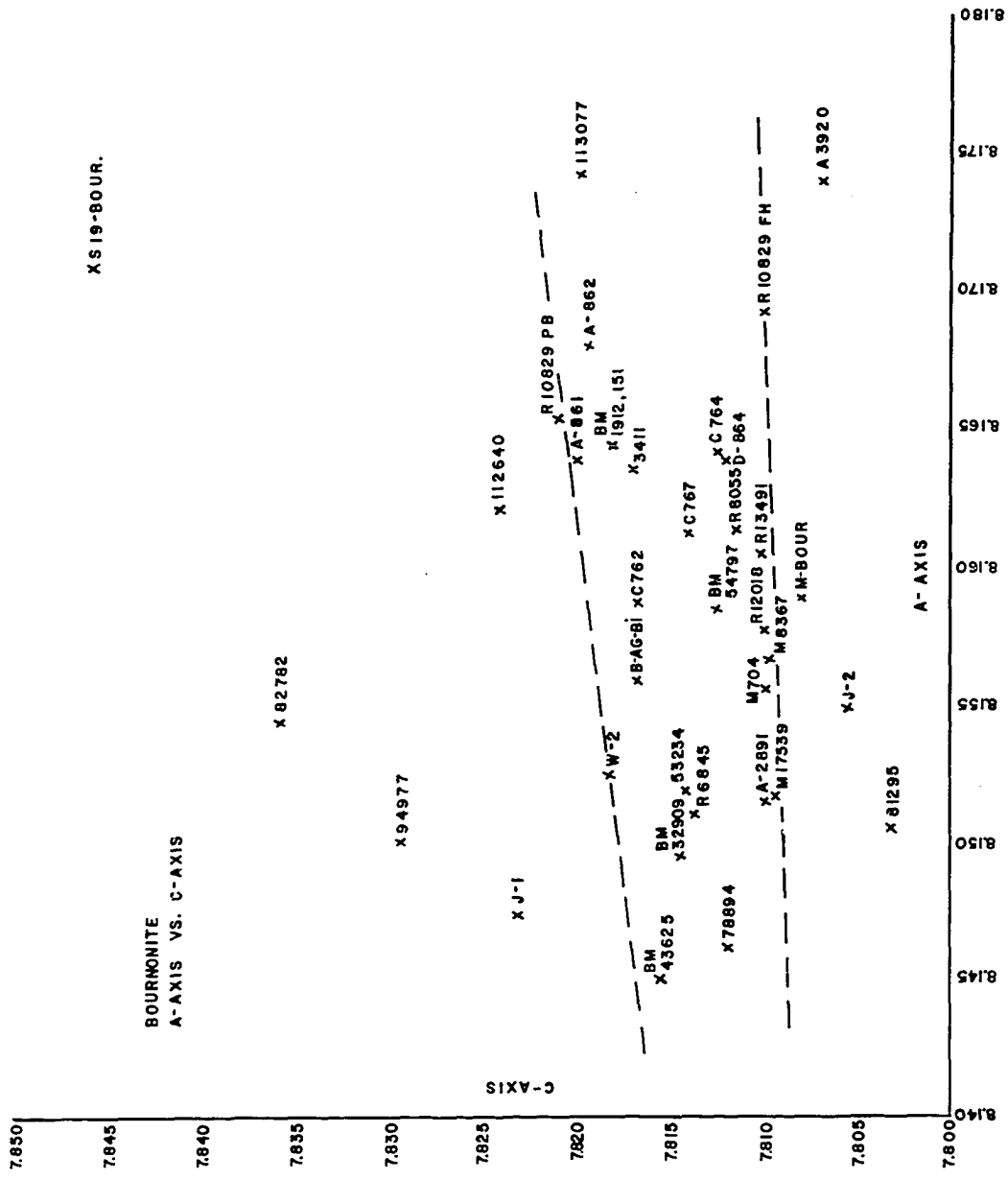

Figure 7. Plot of refined a_o verses refined c_o-axis of bournonite

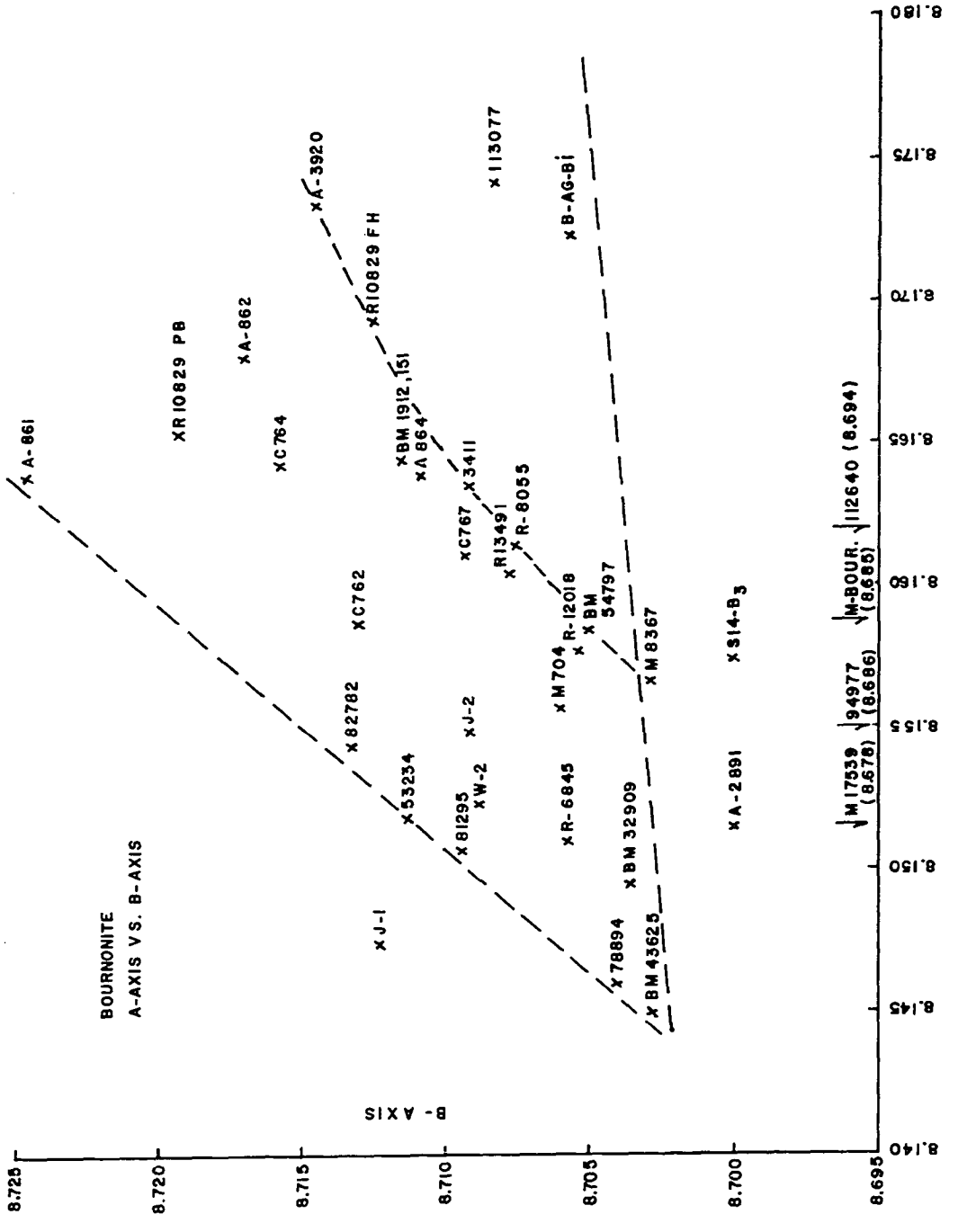

Figure 8. Plot of refined a_o-axis verses refined b_o-axis of bournonite

NONIUS-GUINIER CAMERA STUDIES

Utilization of the four sample, Nonius-Guinier powder camera resulted in the observation of a great many "new" lines in the diffraction patterns of the five study sulfosalts(tables #17-21). Twenty-eight new lines were observed in the bournonite pattern that were not seen by Leineweber (1956)(table#16). Similarly, sixteen new lines were observed for seligmannite, seventeen for aikinite(low phase), eleven for diaphorite and twenty-one for freieslebenite(tables#17-21).

It is suggested by this writer that these new lines be added to those already listed in the most recent publication on x-ray powder patterns of the ore minerals by Berry and Thompson(1962).

TABLE# 16

NONIUS CAMERA BOURNONITE LINES
(After Leineweber, 1956)
(Cu K-alpha$_1$ $\lambda = 1.5405$)

HKL	$I_{obs.}$	$I_{calc.}$	HKL	$I_{obs.}$	$I_{calc.}$
100		9	031	109	96
110	42	12	300		23
011	147	201	212	554	554
101	90	90	310	317	352
111	61	75	131	112	78
020	186	207	301	86	76
200	250	226	013		22
002	368	356	103		12
120	454	289	311		6
210	250	353	113	38	25
201		7	222	138	267
102		0.1	230		40
121		3	320	90	46
211	45	42	231	38	37
112	218	166	132	93	189
220	310	433	302	45	44
022	218	339	321		5
202	323	328	203		0.7
221	144	157	040	45	30
122	1213	947	312	51	20

TABLE#16 (Cont'd)

HKL	$I_{obs.}$	$I_{calc.}$	HKL	$I_{obs.}$	$I_{calc.}$
130		118	123		2
213		9	313		2
140	144	252	402		0.1
400		8	421	109	93
141	58	29	024	112	58
232		4	412	630	429
410		109	332		188
322	384	41	204	128	67
330		217			
401		7			
223	186	86			
004	378	331			
033	61	45			
411		9			
331	61	15			
240		6			
042	54	36			
104		0.4			
133	61	55			
303		32			
241		45			
114		0.7			
142	387	278			
420		2			

TABLE# 17

"NEW" BOURNONITE LINES
FROM NONIUS-GUINIER CAMERA

Cobalt K-alpha$_1$ radiation($\lambda = 1.7889$)

	HKL	d-SPACING(Å)		HKL	d-SPACING(Å)		HKL	d-SPACING(Å)
(6)*	100?	8.15-8.23		420			341	
(2)	201	3.631	(7)	050	1.740-1.746	(5)	143	1.636
(4)	013	2.496-2.500		124		(1)	034	1.621
(1)	311?	2.454	(5)	323?	1.727-1.729	(4)	510	1.602-1.604
(2)	023	2.234-2.239	(4)	242	1.723-1.725		250	
	302			214		(3)	052	1.591-1.592
(3)	123	2.158-2.162	(5)	150	1.701-1.705	(2)	304	1.587-1.589
	312			051			134	
(1)	232	2.020		340		(1)	511	1.571
(2)	114	1.854-1.856	(5)	043	1.670-1.674		251	
(3)	014	1.903-1.905		430		(3)	152	1.560-1.563
	042			422			314	
(2)	313	1.834-1.841	(7)	151	1.661-1.667	(3)	423	1.507-1.508

TABLE#17 (cont'd)

	HKL	d-SPACING
	502	
	234	
(3)	324	1.490-1.492
(5)	252	1.481-1.485
	512	
(4)	144	1.431-1.434
(2)	343	1.422-1.423

* Number of times line appeared in 10 randomly selected Nonius films.

TABLE #18

"NEW" SELIGMANNITE LINES
FROM NONIUS-GUINIER CAMERA

Cobalt K-alpha$_1$
radiation (λ =1.7889)

HKL	d-SPACING(Å)
110	5.900
101	5.516
002	3.805
121	3.418
211	3.293
030	2.945
202	2.842
221	2.762
212	2.638
320	2.285
231	2.253
132	2.218
041	2.089
330	1.972
223	1.926
421	1.774
402	
233	

TABLE#19

"NEW" AIKINITE LINES
FROM NONIUS-GUINIER CAMERA

Cobalt K-alpha$_1$ radiation(λ =1.7889)

$I_{obs.}$ on scale of 100

HKL	d-SPACING(Å)	$I_{obs.}$	HKL	d-SPACING(Å)	$I_{obs.}$
110	8.119	0.6	052		
020	5.798	1.3	641	1.471	----
120	5.156	1.8	560		
021	3.297	---	252		
201	3.283	1.9	080	1.459	----
321	2.489	1.6	522		
510	2.226	---	470	1.438	----
520	2.095	0.5			
501	1.970	3.3			
102					
012					
620	1.793	0.8			
222					
061	1.744	1.2			
541	1.627	0.5			
550					
640	1.579	0.9			
422					
342	1.515	1.3			

TABLE# 20

"NEW" DIAPHORITE LINES
FROM NONIUS-GUINIER CAMERA

Cobalt K-alpha$_1$
radiation($\lambda = 1.7889$)

HKL	d-SPACING	HKL	d-SPACING
001	16.47	131	
002	7.977	225	
-113	4.233	-708	
-304	4.092		
-313	3.697		
302	3.436(gn?)		
-206	2.976(gn?)		
312			
120	2.894		
021			
-118	2.005		
-711			
008			
-624	1.952		
031			
-622			
-509			
-802	1.920		
-132			

TABLE# 21

"NEW" FREIESLEBENITE LINES
FROM NONIUS-GUINIER CAMERA

Cobalt K-alpha$_1$
radiation(λ = 1.7889)

HKL	d-SPACING	HKL	d-SPACING
110	6.487	-222	
011	5.405	-321	2.201
120	4.889	161	1.927
-111	4.463	-113	
-121	3.820	410	1.861
121	3.723	242	
210	3.611	312	
211	3.042	033	1.798
012	2.894	-411	
-221		133	1.736
022	2.696	-412	1.604
-123	2.576	080	
-202	2.382		
320	2.335		
-212			
-124	2.275		
301			
151	2/232		
241			

SINGLE CRYSTAL STUDIES

A large number of single crystal films were taken during the course of this investigation utilizing the Buerger Precession Camera. The camera was operated with silver K-alpha$_1$ radiation($\lambda = 0.5594$) and was filtered with palladium foil.

Zero, first and second level pictures were taken of several bournonite specimens, including (W-1) and (M-bourn.) (see table# 2 for localities). Specimen (W-1) was selected for single crystal study since it contained many, very fine, small, prismatic crystals with no cogwheel twinning. Specimen (M-bourn.) was studied, on the other hand, due to its unusually high Bi content and typical cogwheel character(see page 17).

Several small octahedrons of unknown composition were removed from specimens (C-755) and (R-1027) for single crystal investigation with the hope of finding a natural occurence of the diaphorite, cubic, high phase. All crystals studied were found to be simple sulfides or oxides. An acicular, semi-metallic crystal associated with the unique bournonite crystals in the Julcani District(Peru) (see page 17) was oriented on the precession camera and investigated through the zero, first and second levels. The mineral was identified as bismuthinite(Bi_2S_3).

Double spotting was found to be a problem with bournonite single crystal films, owing to the common polysynthetic twinning of the mineral. Excessive x-ray absorption also proved to be a major problem in these high lead sulfosalts. It was eliminated, however, by choosing very small crystals and allowing long exposures. Exposure times for the first and second level pictures ranged from 12 to 60 hours.

There was two major objectives in the single crystal investigation of bournonite: (1) the first was to check the systematic extinctions with those inferred by the space group C_{2v}^{7}-$Pn2_1m$ which was given to bournonite by Hellner and Leineweber(1956); (2) the second was to search for odd reflection spots or streaks which could correspond to the consistent, odd peaks seen in many of the bournonite diffractometer patterns. No odd, un-indexable spots or streaks were seen in any of the pictures taken of specimens (W-1) and (M-bourn.). The 8.2Å line, seen repeatably in the diffractometer patterns was not resolved in the single crystal films with the silver radiation(see table#/7).

Lattice parameter measurements of specimens (W-1) and (M-bourn.) gave the following results:

	W-1	M-bourn.
a_o	8.159Å	8.161Å
b_o	8.710Å	8.718Å
c_o	7.794Å	7.804Å

Table#22 contains the extinct and strong lines that were observed from the bournonite single crystal films. The systematic extinctions agree well with those inferred by the given space group C_{2v}^{7}-$Pn2_1m$ and include the following conditions:

HOL: H plus L = 2n

HOO: H = 2n

OOL: L = 2n

TABLE # 22

EXTINCTIONS AND STRONG LINES FROM BOURNONITE SINGLE CRYSTAL FILMS

SPECIMEN	EXTINCTIONS			STRONG LINES	
	ZERO LEVEL				
W-1	300	830		200	620
	500	640		400	130
	700	840		210	230
	900	650		310	330
	610	360		410	140
	910	370		020	350
	320	570		040	860
	820			120	
	920			220	
M-Bourn.	300	830	670	020	410
	500	730		050	620
	700	340		060	350
	900	640		200	120
	610	840		400	
	910	450		600	
	320	650		210	
	820	560		220	
	920	370		330	
	720	570		310	
	FIRST LEVEL				
M-Bourn.	102	217	545	212	433
	104	219	547	214	544
	106	324	650	216	432
	108	326	654	2•1•10	546
	1•0•10	327		210	548
	211	438?		431	439
	213	541		540	
	215	543		542	

MINERAL SYNTHESIS

Sixty-six mineral synthesis runs were completed in this study with a number of second and third re-heats undertaken for purposes of homogenization and observation of disordering and reordering phenomena.[1] All five minerals of the study suite were synthesized a number of times and were identified by Nonius-Guinier powder and x-ray diffractometer techniques. Polished section methods were used for visible phase identification and evidence of twinning and reordering.

BOURNONITE

Bournonite was found to be the most difficult species of the group to synthesize according to its given stoichiometry of $PbCuSbS_3$. Early attempts (sample S14-B_3) by the writer to crystallize this mineral resulted in explosion of the charge under cooling furnace conditions. X-ray investigation of the oxidized fragments revealed the bournonite structure with some rather strong, odd lines (primarily at 3.13Å and 3.03Å) previously discussed as appearing consistently in the natural specimens. In this case, however, the writer believes the lines to belong to

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[1] All synthetic charges were taken to melting for homogenization.

TABLE # 23

SYNTHETIC PREPARATION DATA

SAMPLE	HEATING	PHASE	COMMENTS
S_{14}-B_3	to 700°C, furnace cooled	bournonite	exploded in furnace on cooling (sulfur vapor pressure?) hard, metallic pellet
B-Ag-Bi	to 690°C for 3 hours, lowered to 260° for 3 days water quenched	bournonite plus chalcostibnite? (emplectite)?	0.1 wt.% Ag; 0.1 wt.% Bi hard, metallic pellet; acicular needles present (chalcostibnite?)
S2-S_x	second heating, to 700°C lowered to 250° for 3 days water quenched	seligmannite (trace of other arsenic sulfosalts possibly baumhauerite	sulfur ppt. at end of tube; pellet metallic but not real hard sulfur vapor pressure
S5-A reheat	second heating, to 700°C lowered to 260° for 4 days water quenched	aikinite (low phase)	no sulfur residue, no sulfur vapor pressure; box-work crystalline pellet; metallic feathery, needle-like crystals (aikinite)

TABLE # 23
CONTINUED

SAMPLE	HEATING	PHASE	COMMENTS
S5-A reheat(2)	third heating, to 700°C for 2 days; water quenched	high aikinite (then reverted to low aikinite	no sulfur residue or vapor, metallic; brittle pellet
A-6	heated to 758°C for 3 hours lowered to 204° for 2 days water quenched	aikinite (low phase)	no sulfur in tube; feathery, needle-like crystals (aikinite)
S-4	to 700° overnight; lowered to 300° for 5 days water quenched	multiple phases (seligmannite, baumhauerite, etc.)	pungent sulfur odor on breaking of tube;
S-4 reheat	second heating; to 741°C for 1 hour, lowered to 150° for 3 days; water quenched	seligmannite plus galena	no sulfur residue or odor
S-5	to 700°overnight; lowered to 300° for 5 days water quenched	multiple phases	0.5 at.% Sb, 0.5 at.% As sulfur residue; feathery crystals; dendritic-like also

TABLE # 23
CONTINUED

SAMPLE	HEATING	PHASE	COMMENTS
S-5	second heating; to 741°C for 1 hour, lowered to 150° for 3 days; water quenched	seligmannite plus galena	no sulfur residue; pellet hard, metallic; acicular crystals in vugs
S7-D	to 600°C for 10 days water quenched	high diaphorite (cubic phase)	all sulfur reacted, residue; pellet very metallic and hard
S7-D reheat (1)	to 500°C for 2 days; lowered to 180° for 3 days water quenched	high diaphorite starting to order to low phase	very metallic; hard no sulfur residue
S7-D reheat (2)	to 182° for 9 days water quenched	further ordering to low diaphorite	very metallic; no sulfur residue; hard; slight odor of S
S7-D reheat (3)	to 234°C for 10 days quenched in water	low diaphorite	metallic; hard pellet; slight sulfur odor

TABLE # 23
CONTINUED

SAMPLE	HEATING	PHASE	COMMENTS
S4-F	to 700°C for 2 days then lowered to 275° for 5 days; water quenched	multiple phases (no freieslebenite)	mixed to $Pb_3Ag_5Sb_5S_{12}$ abundant sulfur residue; extremely viscicular; porous pellet; much sulfur vapor
S11-F	to 735°C for 1 hour; lowered to 275° for 2 days; cooled at furnace rate	poorly crystallized but closer to freieslebenite than S4-F	mixed as S4-F but with 0.25 at.% Cu and 0.25 at.% Fe some sulfur residue Fe and Cu seemed to have aided crystallization of freieslebenite phase
S15-F	to 700°C for 2 hours; lowered to 200° for 2 days; cooled at furnace rate	freieslebenite but poorly crystallized	mixed as S4-F but with o.1 at.% Fe and o.1 at.% Cu pungent odor of sulfur; pellet very metallic and hard. Definitely aided by lowered percentage of Fe and Cu

TABLE # 23
CONTINUED

SAMPLE	HEATING	PHASE	COMMENTS
SF-2	to 603° for overnight; lowered to 150° for 4 days; water quenched	freieslebenite (not totally ordered as yet)	mixed to $PbAgSbS_2$ (one atom sulfur deficient) pellet vesicular but metallic and hard; small needle-like crystals on pellet (freieslebenite)
SF-2 reheat	to 670°C for 6 hours; lowered to 504° for 1 day; water quenched	freieslebenite high phase (cubic)	no sulfur residue; no needle-like crystals as before
SF-3	to 662° for 1 day; lowered to 520° for 1 day	freieslebenite high phase (cubic)	mixed to $PbAgAbS_3$ no sulfur residue; pellet very metallic but brittle
SF-4	to 662° for 1 day; lowered to 520° for 1 day; water quenched	freieslebenite high phase(cubic)	mixed to PbAgSbS (excessive sulfur) extreme sulfur residue in tube

TABLE # 23
CONTINUED

HEATING OF NATURAL SAMPLES

SAMPLE	HEATING	PHASE	COMMENTS
S18-M-bourn Bournonite Julcani, Peru	to 575°C for 2 hours then lowered to 550° for 4 days; water quenched	bournonite but poorly crystallized	sulfur vapor; frags were hard and very metallic
S19-M-bourn same specimen as S18	second heating; to 450°C for 7 days water quenched	bournonite with bification of many peaks (exsolving second phase) baumhauerite?	very slight sulfur odor; drusy crystals on surface; frags are not hard but rather soft and brittle
W-2 bournonite Germany	to 450°C for 14 days; water quenched	bournonite (no change noticed from unheated form)	twinned crystals (polysynthetic) but not cog wheel crystals; after heating crystal surfaces show etched appearance
M-B-2 bournonite Julcani, Peru	to 700°C melted then quenched in ice after 15 days	bournonite structure but poorly crystallized	sulfur vapor present in tube; material very metallic

TABLE # 23
CONTINUED

SAMPLE	HEATING	PHASE	COMMENTS
106760 aikinite silver Miller Mine, Cobalt, Ontario	to 640°C for 2 days; water quenched (did not melt)	high aikinite	slight sulfur odor tube broken; frags appeared to have re-crystallized (much twinning)
R-1027 diaphorite plus galena Charichari, Potosi Bolivia	to 416°C for 6 days; water quenched	high diaphorite (cubic phase)	no sulfur residue or odor; not quite totally disordered

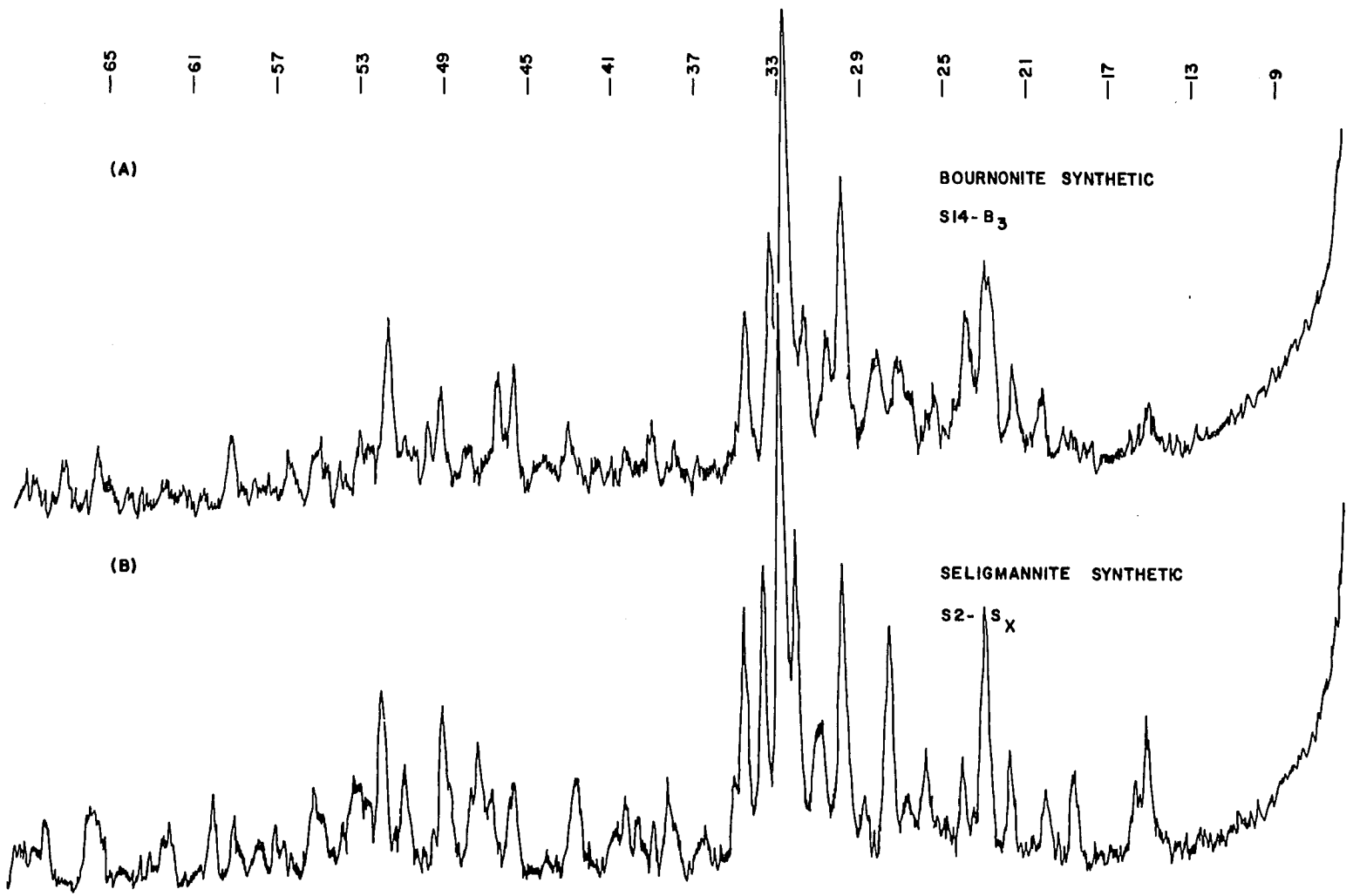


Figure 9. X-ray diffractogram of bournonite and seligmannite synthetics

chalcostibnite ($Cu_2S \cdot Sb_2S_3$) (figure # 9). Polished section study of this synthetic indicated abundant, polysynthetic twinning typical of bournonite and no evidence of a second mineral phase was observed. Least square refinement of the axes for synthetic ($S14\text{-}B_3$) indicated a somewhat shortened b- and c-axis (Appendix D and figures 7-8).

The second bournonite synthesized (sample B-Ag-Bi) was mixed to contain 0.1 weight percent Bi and 0.1 weight percent Ag in order to shed some light on the nature of these elements as consistent minors in the natural specimens. The charge appeared to be much easier to crystallize than the previous attempt without Ag and Bi. The charge did not explode as before. Again, as in $S14\text{-}B_3$, the odd lines at 3.13Å and 3.03Å appeared in the x-ray pattern. Synthetic (B-Ag-Bi) was examined immediately after quenching and was found to contain abundant, acicular, metallic, crystals filling the vugs and coating the surface of the pellet. These needles gave x-ray diffraction lines characteristic of many Sb_2S_3 and Bi_2S_3 sulfosalts but are thought to have been chalcostibnite or its isotype, emplectite. The question arises then as to whether these acicular crystals were simply a second mineral species which crystallized along with the bournonite or instead represent an exsolved phase

(containing Bi?) which was soluble in the bournonite lattice at the high temperature.

Refinement of the lattice parameters for synthetic (B-Ag-Bi) definitely revealed a fit into the average range of natural bournonite specimens (table #15 and figure # 7), thus indicating something of the importance Ag and Bi plays in this structure.

SELIGMANNITE

Three seligmannite synthetics were crystallized after reheating for homogenization. Samples ($S2-S_x$)and (S-4) were mixed to the ideal formulation $PbCuAsS_3$ and (S-5) was made to $PbCuAs_{0.5}Sb_{0.5}S_3$. Primary heating of all three resulted in multiple phases consisting of seligmannite plus one or more Pb-As sulfosalts all of similar structure. A second heating of these synthetics homogenized the charges and seligmannite was the only sulfosalt phase indicated in the x-ray patterns. However, very intense lines of galena were observed in samples (S-4) and (S-5). They were present in ($S2-S_x$) as well but of much less intensity. An excess of PbS was theoretically present in the charge, and upon homogenization to the seligmannite phase, it was exsolved out. Polished section study of specimen (R-1052)(Appendix B) confirmed the association of galena with seligmannite but indicated no visible exsolution lamellae.

Refinement of the lattice parameters of synthetics (S-4) and (S-5) show an increase of 0.1Å for the a-axis and 0.03Å for the c-axis with addition of 0.5 atomic percent antimony with 0.5 atomic percent arsenic. The b-axis appears to be little affected by such substitution.

AIKINITE

Two aikinite synthetics were successfully crystallized after many attempts. Samples (S5-A reheat) and(A-6) both contained the 2.98Å line of galena but few other lines not indexable for aikinite.

Polished section study of (S5-A reheat) failed due to the frothy, boxwork-like nature of the synthetic. Both synthetic aikinites were taken to a high temperature polymorph which will be discussed in a later section.

The refined lattice parameters of these aikinites agree quite well with both the literature values for the mineral and the natural specimens analyzed by this writer (table #15).

DIAPHORITE AND FREIESLEBENITE

Diaphorite and freieslebenite were synthesized by means of slow, low temperature, ordering from their high cubic phases. Figure #17 illustrates nicely the progressive

ordering in this system with figure #17 D representing the final stage with the low diaphorite pattern.

The two synthetic charges (S4-F) and (S16-F) were mixed to the old formulation of $Pb_3Ag_5Sb_5S_{12}$ for freieslebenite and to (S15-F) was added 0.1 atomic percent Fe and 0.1 atomic percent Cu. Sample (S11-F) was given additional Fe and Cu to 0.25 atomic percent. None of these charges resulted in well crystallized freieslebenite. It was apparent, however, that (S15-F), with the lower percentages of Fe and Cu, more closely approached the correct structure. Three freieslebenite synthetics were prepared according to the ideal formulation suggested by Hellner (1957) of $PbAgSbS_3$. The effect of sulfur excess and deficiency on the mineral system was also examined in these samples as they were mixed to: $PbAgSbS_2$, $PbAgSbS_3$ and $PbAgSbS_4$, respectively for (SF-2),(SF-3) and(SF-4). The affect of the sulfur atom excess or deficiency was best observed on the a_o of the cubic, high phase of freieslebenite which will be discussed later (see Appendix D).

HIGH TEMPERATURE PHASE RELATIONS

One of the primary objectives of the present study was concerned with the discovery and synthesis of high temperature polymorphs within these mineral systems. Although comparatively little work of this type has as yet

been done on the sulfosalt minerals, such work is of paramount importance for a better systematic, classification scheme as well as a basic understanding of derivative structures and the crystal chemical processes which they entail.

BOURNONITE AND SELIGMANNITE

Bournonite and seligmannite were found to have the most stable lattice structures of the five minerals observed at high temperature. Repeated attempts to crystallize a high polymorph of bournonite and seligmannite utilizing both synthetic formulations as well as natural specimens, resulted in failure. However, a bournonite specimen from Julcani, Peru (S19-Bourn.) after heating at 450°C for a period of 7 days, exsolved out many lines not belonging to the bournonite pattern but which were present in the unheated specimen only as slight shoulders on indexable main lines. These new lines are thought by this writer to belong to the mineral baumhauerite $3PbS \cdot 2As_2S_3$ or a related, arsenic sulfosalt. It is therefore, possible that the submicroscopic, inclusions in these mineral structures can be further exsolved by heating at rather high temperatures over a long period of time. In specimen (S19-Bourn.), however, it might well have been the presence of excess Bi (3.3 weight percent) that caused the exsolution (?) of the second phase.

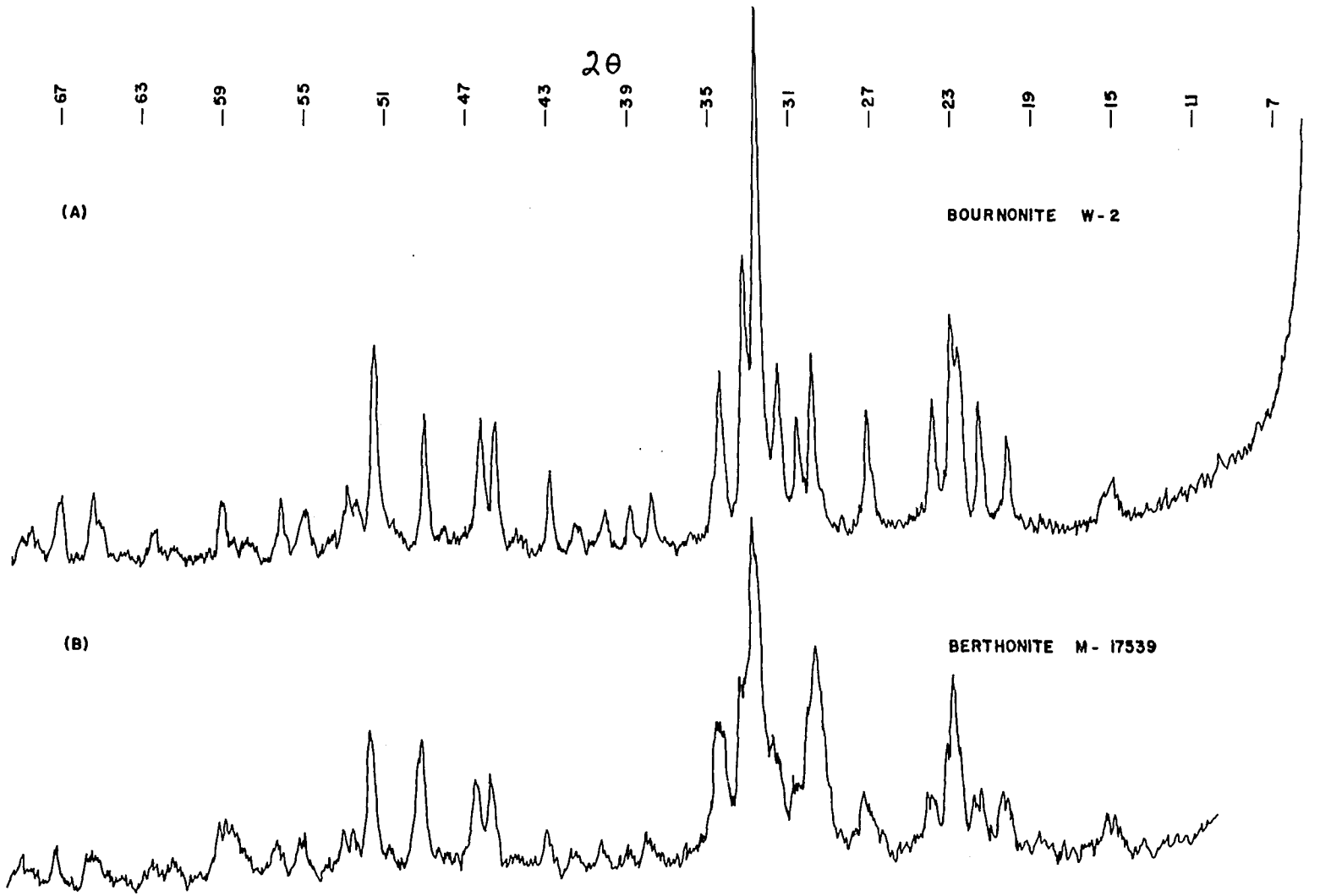


Figure 10. X-ray diffractogram of natural bournonite and berthonite. Note poor crystallization of berthonite

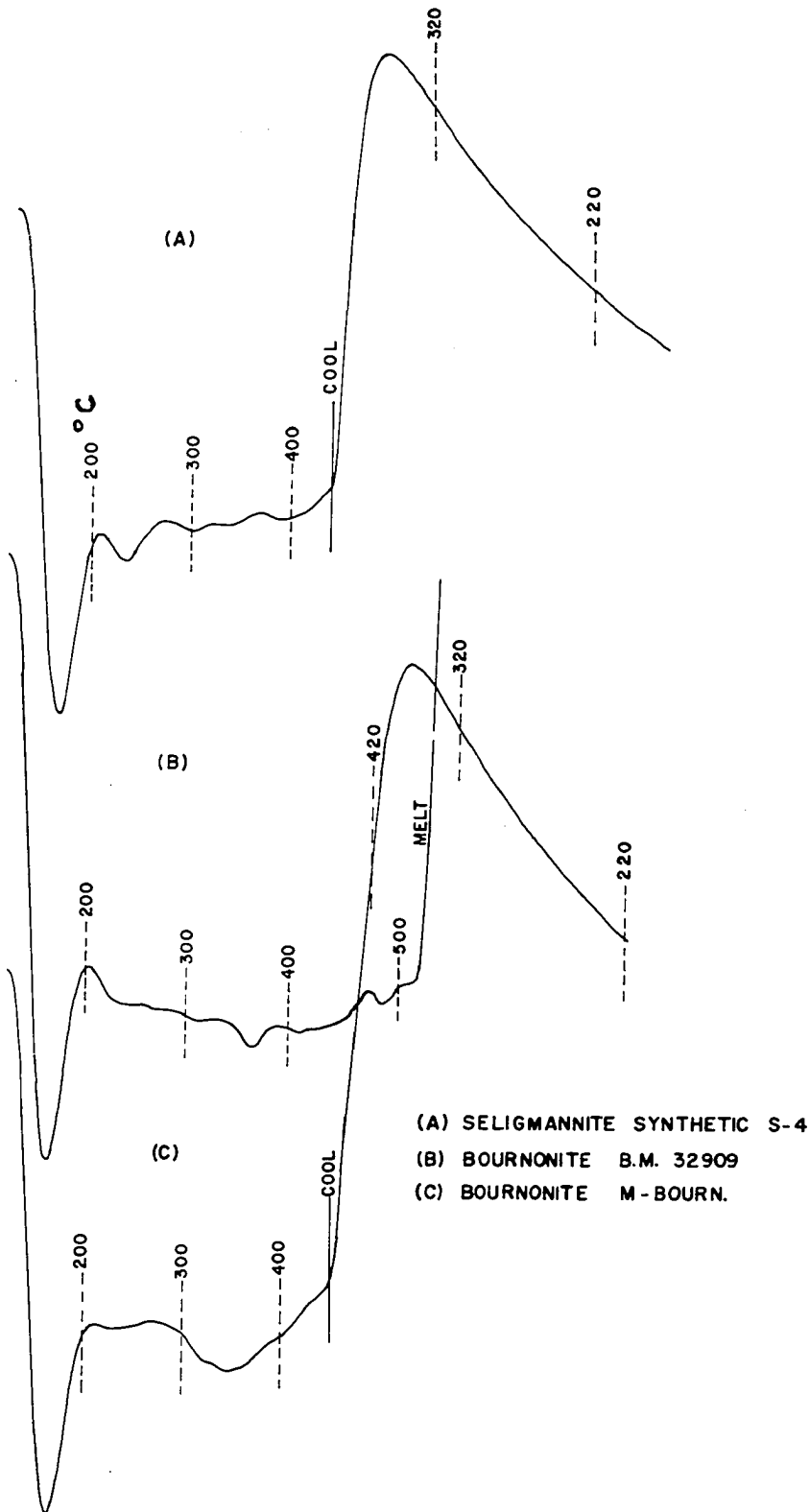


Figure 11. DTA patterns (heating and cooling) of a synthetic seligmannite and two natural bournonites

Differential thermal analysis of many bournonite specimens, both synthetic and natural, indicated no enthalpy changes of consequence at the heating rates used of 7-10 degrees/min. (figure$ # //).

Polished section studies revealed extensive polysynthetic twinning in many natural and synthetic specimens along with a persistent, unique textural appearance (see Appendix B). The constant presence of the polysynthetic twinning in bournonite might possibly be an attempt by the lattice to obtain "room" and can very likely be related to an unquenchable, order-disorder phenomenon.

The rarity of suitable seligmannite ores necessitated the use of synthetic specimens for the major portion of the high temperature phase studies. The one natural specimen (R-1052) heated to near the melting point and then quenched, in hopes of finding a high polymorph, was not entirely free of contaminants. However, no distinct variation from the low seligmannite was seen.

Synthetics (S2-S_x), (S-4) and (S-5) contained multiple phases after their primary heating but homogenized into seligmannite after reheating (table #23). Attempts at high temperature quenching of these samples resulted in galena exsolving out of a poorly crystallized seligmannite

lattice. Similarly, differential thermal analysis of these samples revealed only a pattern analogous to that of bournonite with no evidence of thermal reaction (figure # //).

AIKINITE

Aikinite was successfully converted to an apparent, high polymorph both from crystallized synthetic and natural specimens (figures # /2 -/3). The high polymorph is thought to have undergone a transformation from the primative, orthorhombic space group of low aikinite (D_{2h}^{16}-Pbnm) to a body-centered, orthorhombic, configuration. Figure # /2 clearly illustrates the simplification of the diffraction pattern and the increased symmetry of the cell. Final indexing and refinement of the high polymorph is not as yet completed but a basic study was made of the phase utilizing the indexing methods suggested by Ito (1950, Hesse (1948), Lipsom (1949) and Bunn (1946). The cell is evidently pseudo-tetragonal, but repeated attempts at computer refinement have indicated an orthorhombic indexing. The lattice parameters suggested for the high aikinite after preliminary investigation would be: $a_o \approx 6.5\text{Å}$, $b_o \approx 5.7\text{Å}$ and $c_o \approx 12.2\text{Å}$.

A polished section made of the synthetic, high aikinite (S5-A reheat(2)) was found to have almost completely

TABLE# 24

AIKINITE HIGH PHASE
X-RAY DATA

Cu K-alpha radiation
(1.5405 λ)[1]

SPECIMEN	2 THETA	D(Å)	I_{obs}	SPECIMEN	2-THETA	D(Å)	I_{obs}
S5-A	13.6	6.500	----	106760	13.7	6.459	----
reheat(2)	15.6	5.676	5.80		15.6	5.676	9.18
(syn.)	19.4	4.752	6.98		19.6	4.525	12.58
	21.9	4.055	11.43		22.0	4.037	7.82
	23.0	3.864	5.71		23.1	3.847	10.20
	24.3	3.660	37.46		24.5	3.630	42.18
	25.5	3.490	100.00		25.5	3.490	100.00
	26.4	3.373	46.98		26.3	3.386	29.93
	27.2	3.276	5.71		27.2	3.276	21.77
	27.7	3.218	6.03		27.7	3.218	8.16
	29.9	2.986	33.97		30.0	2.976	31.97
	31.4	2.851	40.32		30.7	2.910	29.93
	32.4	2.761	13.97		31.3	2.855	50.34
	33.4	2.680	7.30		32.4	2.761	12.24
	39.2	2.296	18.73		33.6	2.665	8.16
	42.4	2.130	34.28		39.4	2.285	30.27
	44.0	2.056	26.98		42.5	2.125	27.89
	44.4	2.039	33.65		44.0	2.056	18.37
	46.3	1.959	11.43		44.8	2.021	34.01
	48.6	1.872	6.35		46.0	1.971	13.60
					48.5	1.875	11.22

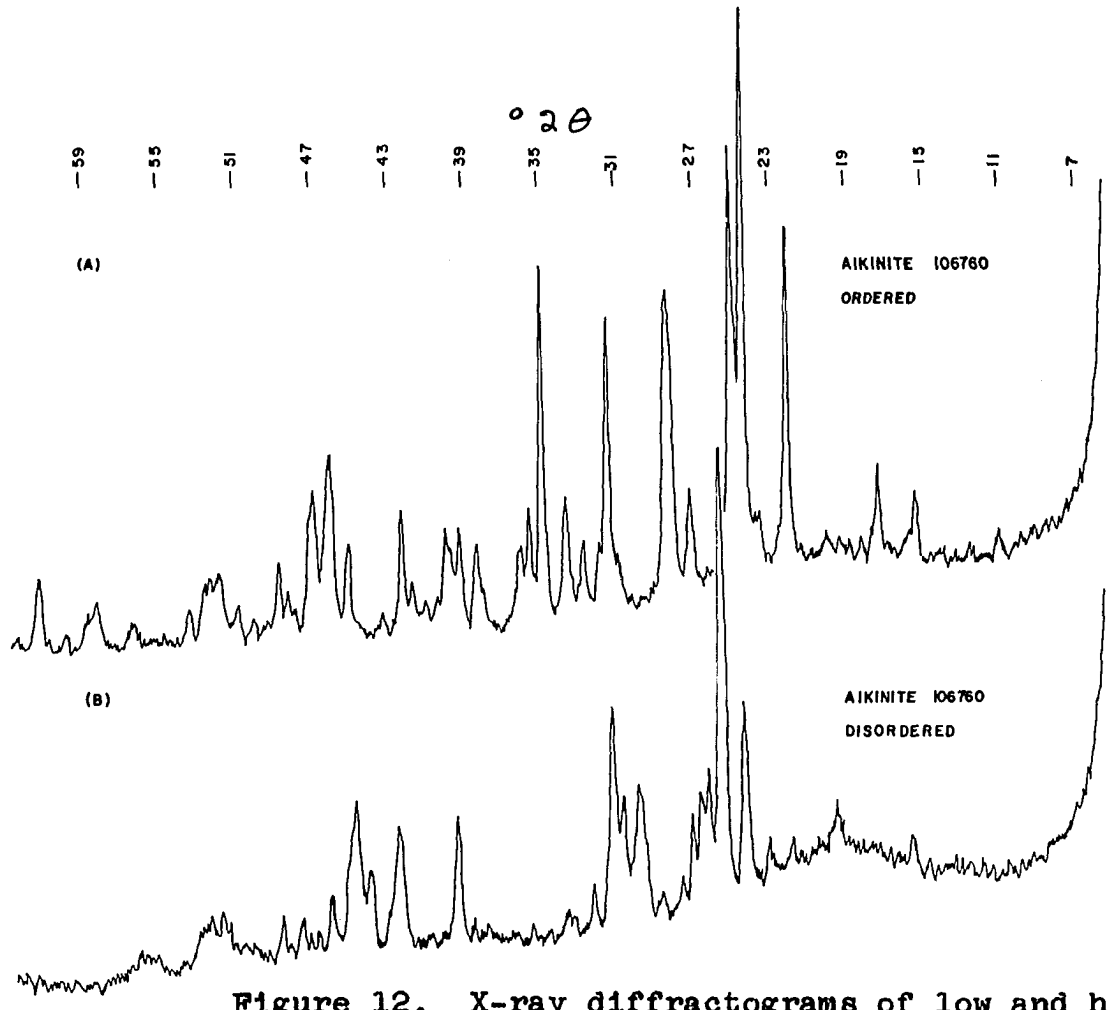


Figure 12. X-ray diffractograms of low and high polymorphs of a natural aikinite

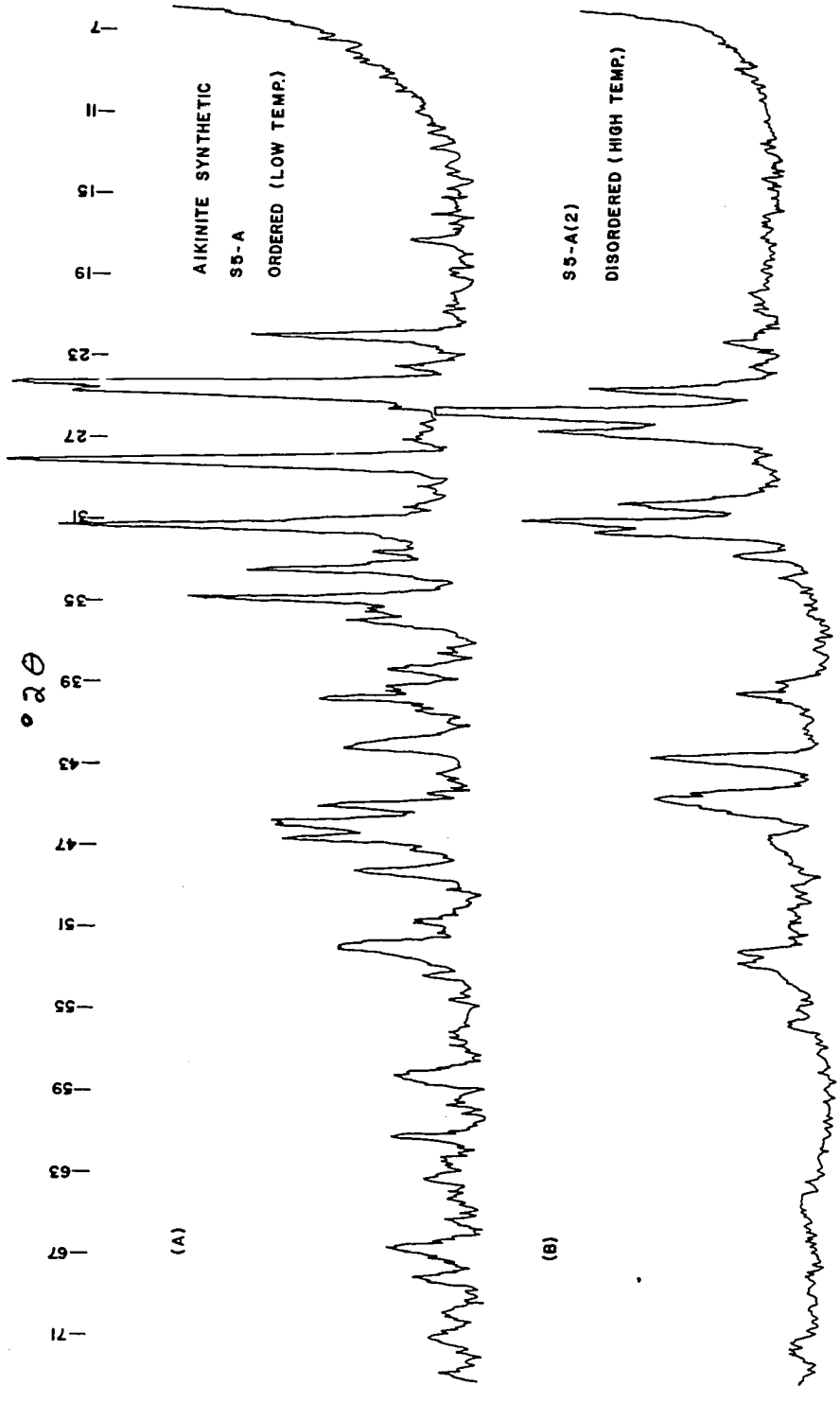


Figure 13. X-ray diffractograms of low and high polymorphs of a synthetic aikinite

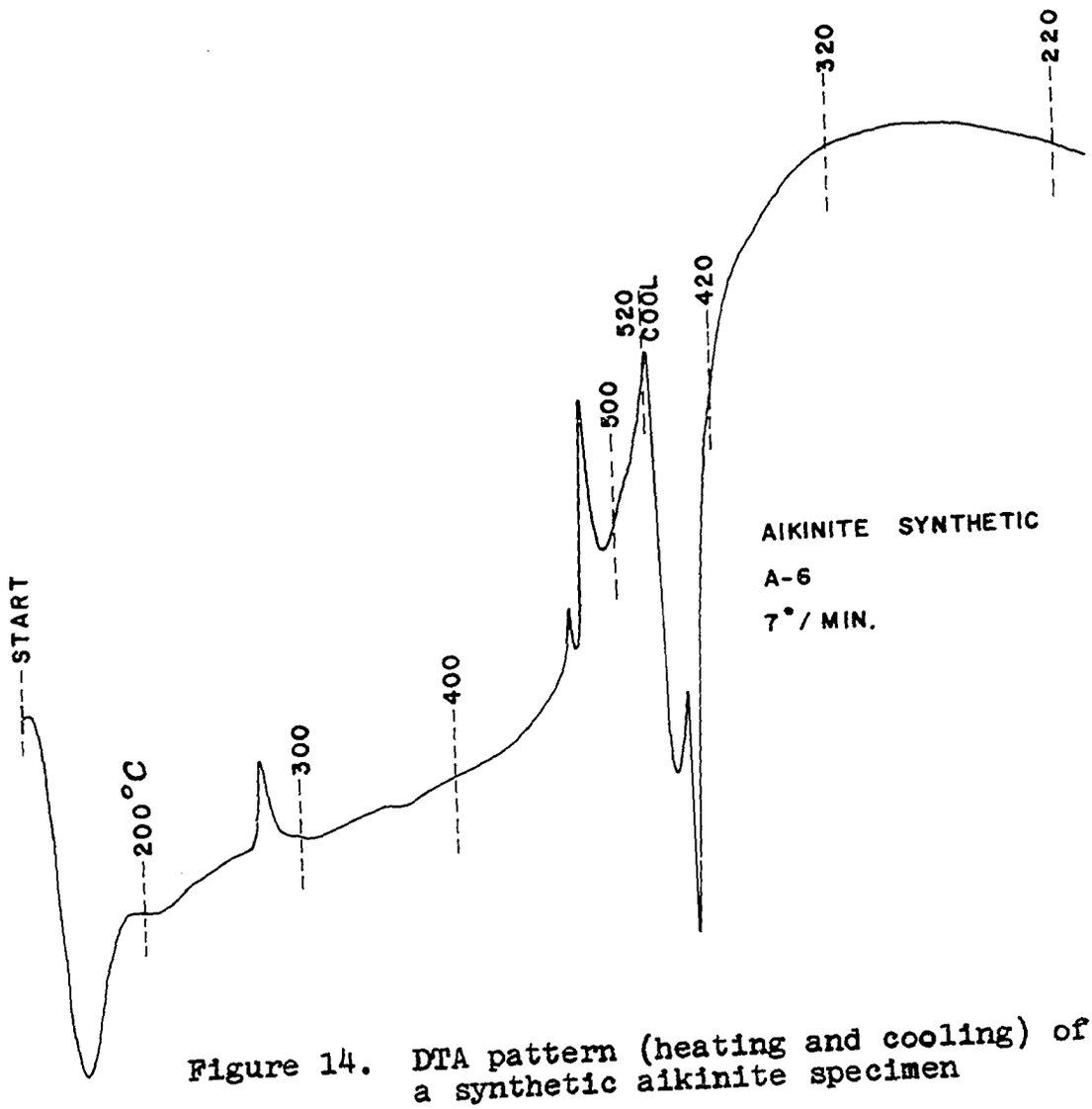


Figure 14. DTA pattern (heating and cooling) of a synthetic aikinite specimen

ordered back to low aikinite after less than two months (Appendix B, plate #10).

Differential thermal analysis of synthetic (A-6) starting from the low phase is shown in figure #14. Disordering is seen to commence at about 270 degrees C and to peak at approximately 273 degrees C. The energy involved here is many orders lower than that seen for the cubic high phases of diaphorite and freieslebenite to be discussed. Two possible fusion reactions can also be observed in figure #14 starting at 465 degrees C and 475 degrees C. It is possible that these last reactions might mark a second or even third disordering phenomenon just prior to fusion of the sample. Continuous recording after initiation of cooling in the DTA run revealed a very sharp, exothermic peak at 460 degrees C (figure #14). No further evidence of reordering can be seen in the remainder of the cooling phase.

DIAPHORITE AND FREIESLEBENITE

Diaphorite and freieslebenite were found to have a high temperature, disordered, cubic phase by this writer, independent of the knowledge of Wernick's study of the $AgSbS_2$-PbS pseudo-binary in 1960. However, the phase relationships suggested by Wernick were totally confirmed by this writer's investigation and most temperatures of

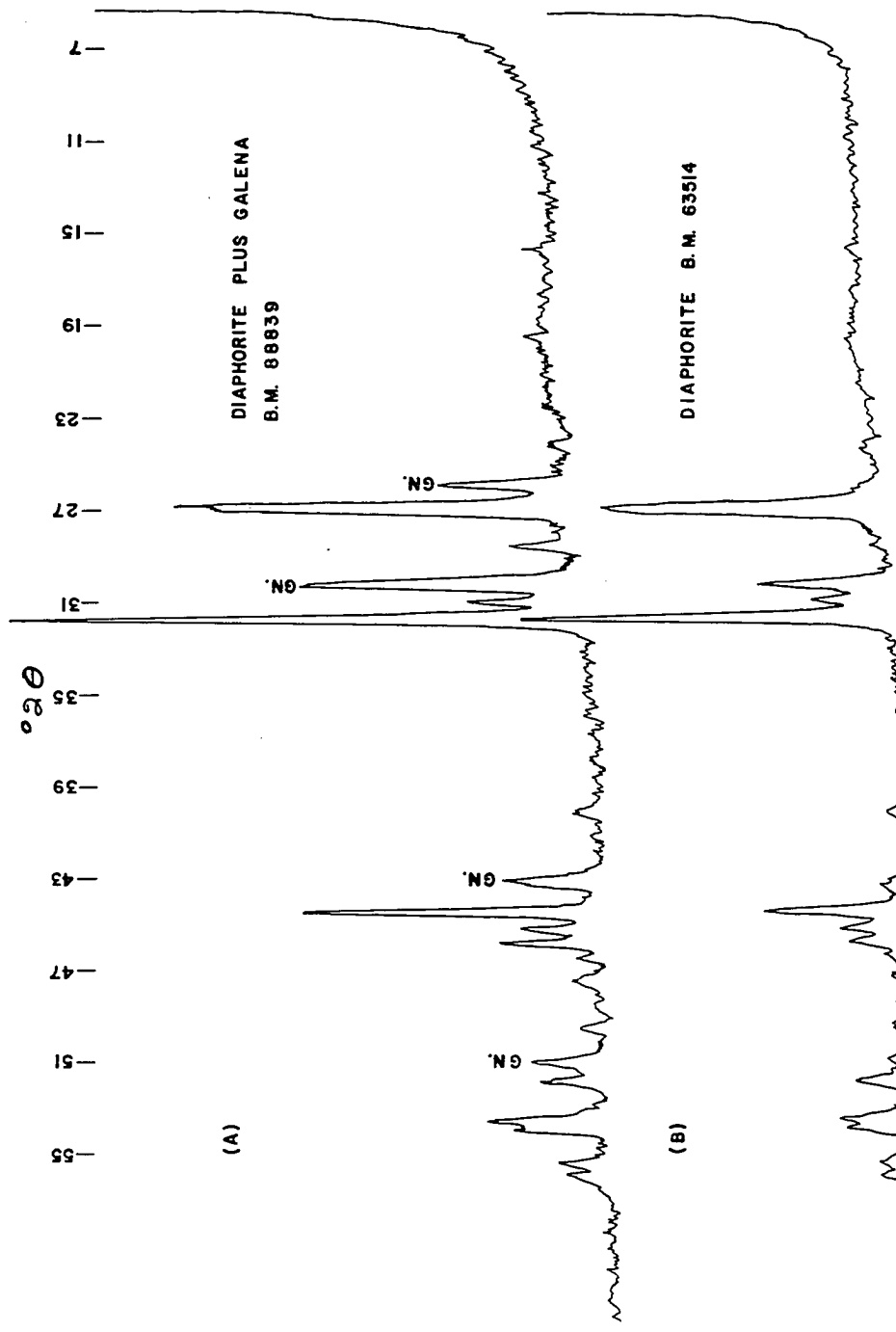


Figure 15. X-ray diffractograms of two natural diaphorite specimens. Note gn influenced lines.

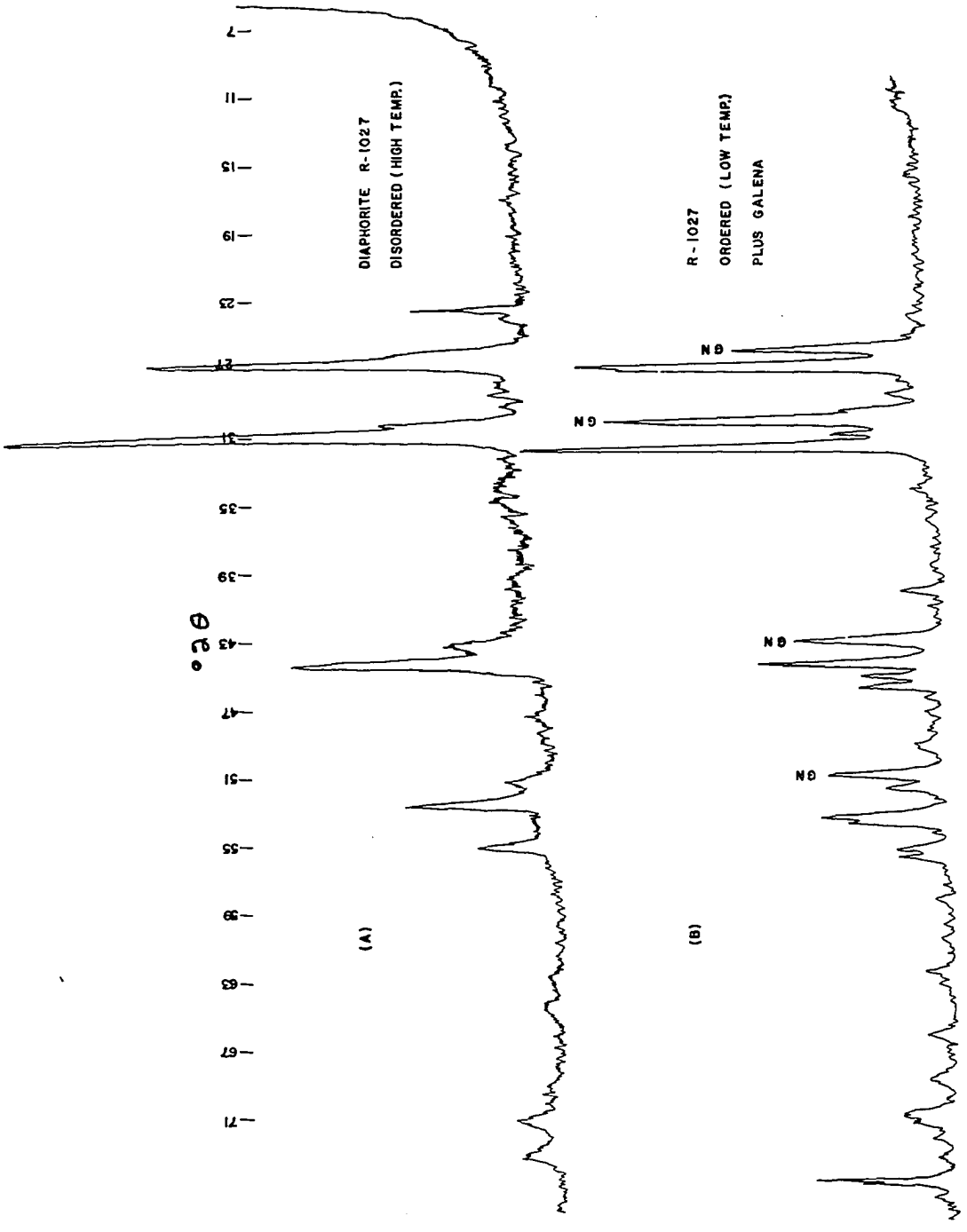


Figure 16. X-ray diffractograms of the low and high polymorphs of a natural diaphorite specimen.

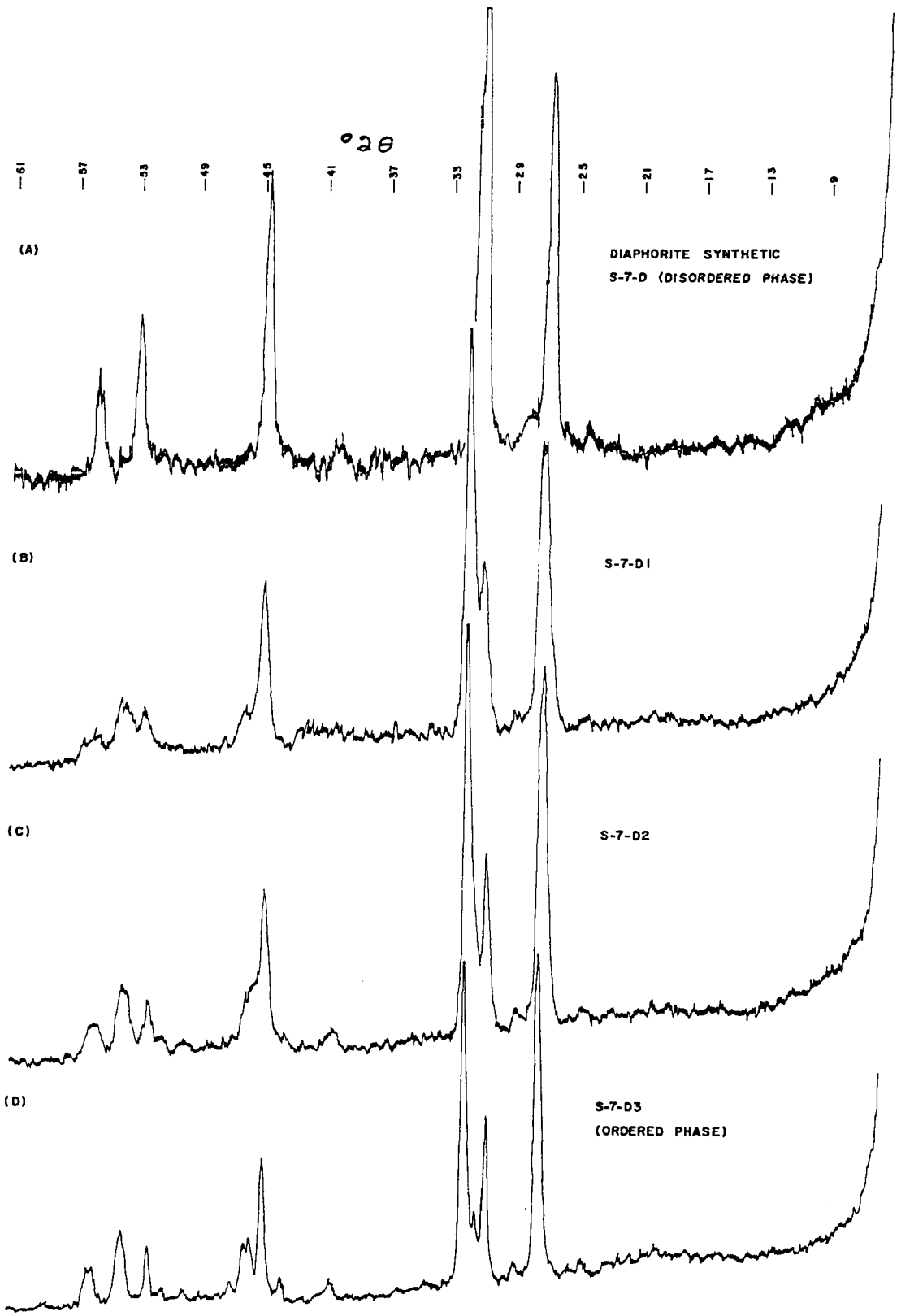


Figure 17. X-ray diffractograms showing reheating stages of a synthetic diaphorite

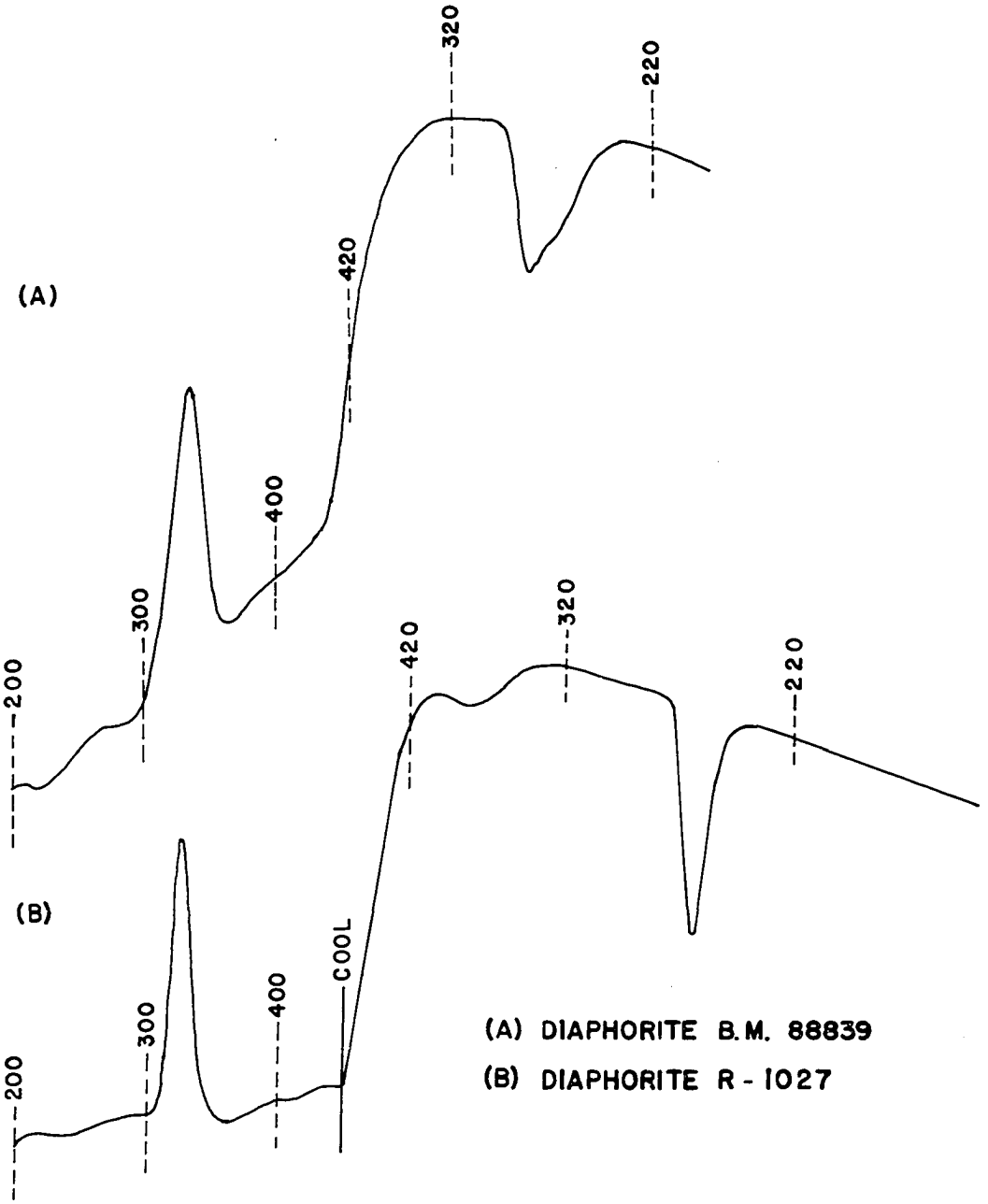


Figure 18. DTA patterns (heating and cooling) of two natural diaphorite specimens. Temperature in degrees C.

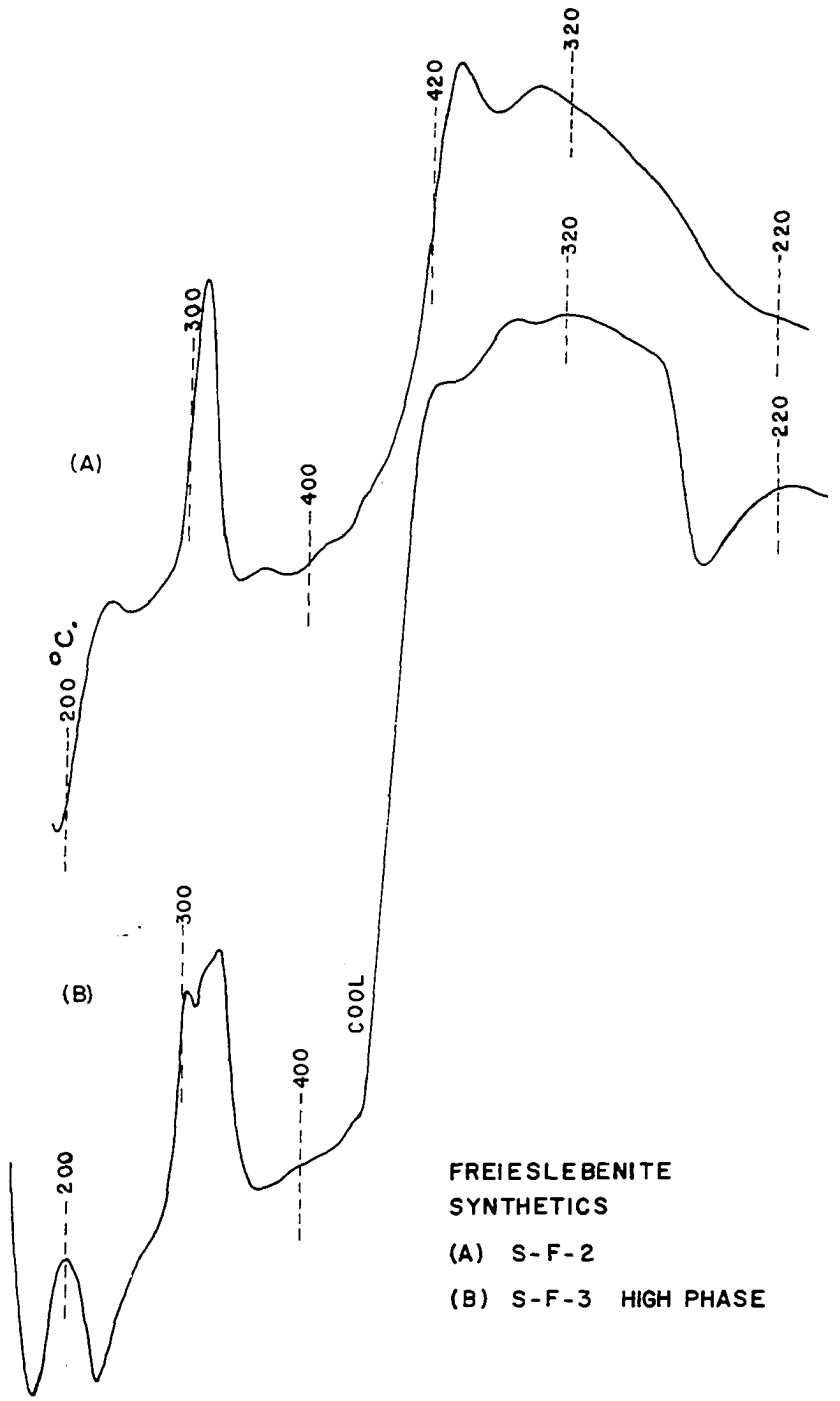


Figure 19. DTA patterns (heating and cooling) of two synthetic freieslebenite specimens. (B) was at the high phase when heated.

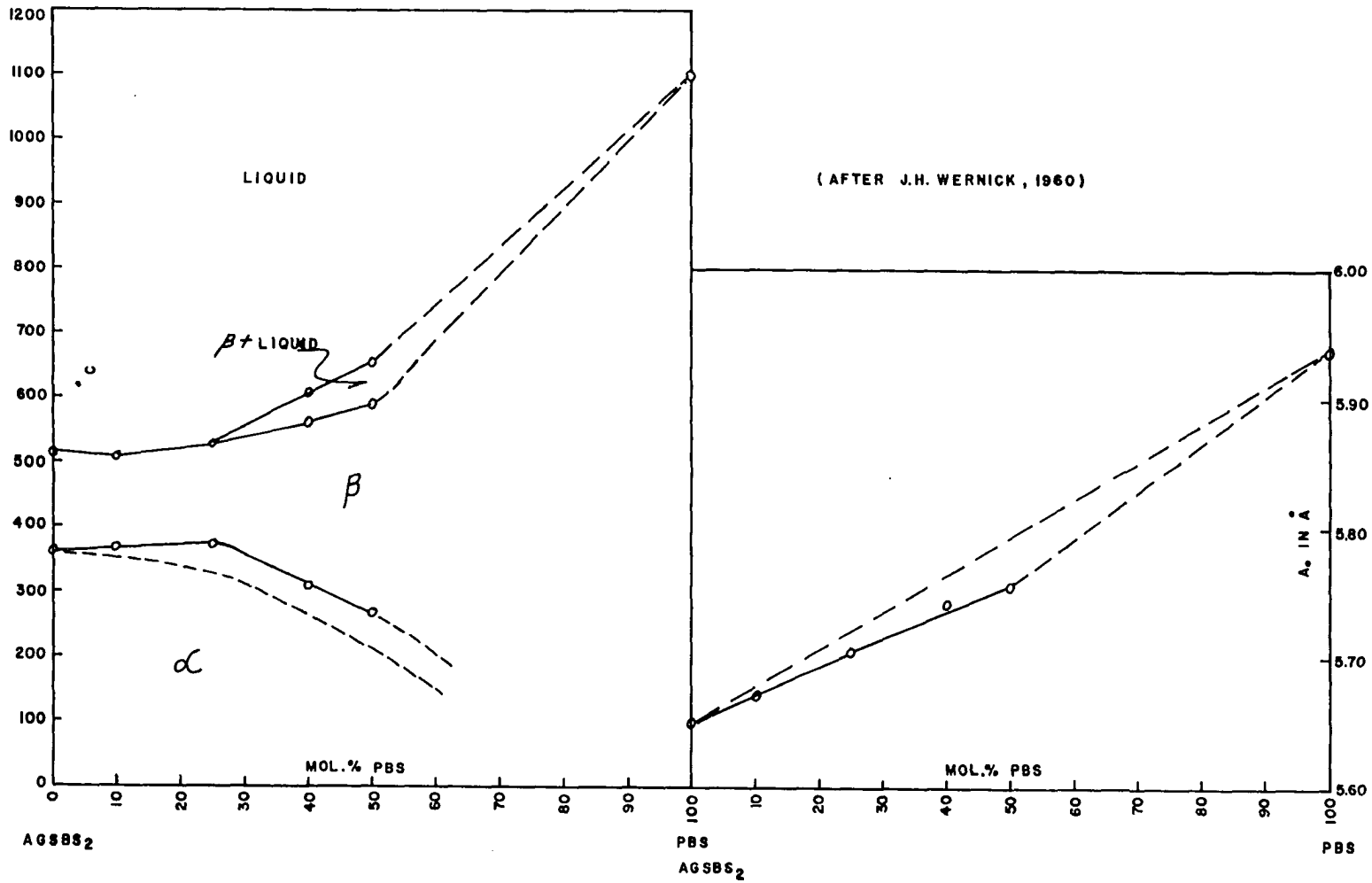


Figure 20. Pseudo-binary $AgSbS_2$-PbS phase diagram showing stability ranges of alpha and beta polymorphs. Diagram on right relates a_o of beta phase with mol.% PbS

high-low conversion plotted very close to his published phase diagram for the system $AgSbS_2$-PbS (figure #20). Deviations were found, however, from his plot of lattice constant a_o of the cubic, beta phase versus the mol. percent PbS (figure #20). This writer found that a synthetic of the composition equivalent to diaphorite ($Pb_2Sb_3Ag_3S_8$) gave a refined a_o of 5.727Å as compared to the value taken from figure #20 of 5.74Å. Likewise, synthetics of the freieslebenite composition ($PbAgSbS_3$) gave a refined a_o of 5.780Å instead of the 5.76Å indicated from Wernick's curve. It is very likely that sulfur loss during this writer's synthesis can account for this discrepancy.

Natural diaphorite specimens (BM-88839) and (R-1027) were heated in the DTA furnace to near melting and then cooled at furnace rate while plotting enthalpy changes (figure #18). The shape and intensity of the reordering reactions were apparently altered considerably by the presence of impurities in the specimens. Both (BM-88839) and (R-1027) have galena as major impurities and sphalerite is present in (BM-88839).

Two synthetic freieslebenite specimens were run on the DTA apparatus; one (SF-2) with a one atom sulfur deficiency ($PbAgSbS_2$), the other (SF-3) being already in

the high, cubic phase. The results can be seen in figure #19. The sulfur deficient sample starts reordering at the high temperature of 400 degrees C, while the normal freieslebenite should start at about 220 degrees. The reordering reaction for this sample is noticeably smaller than normal also, indicating that reversion to the monoclinic form had been inhibited from proceeding to completion.

CONCLUSIONS

From the results of work presented in this paper, the following conclusions are drawn:

1. Owing to the diversity of structure and crystal chemistry of the minerals of the "bournonite group", the following classification grouping is proposed:

Group A	Bournonite Seligmannite
Subgroup	Aikinite
Group B	Diaphorite Freieslebenite

2. Evidence from minor element analyses suggests the constant presence of several elements in the minerals of the study group. Therefore, this writer proposes the addition of constant minor elements in published, stoichiometric formulations, as follows:

1) Bournonite: $PbCuSb(As_x, Ag_y, Bi_z)S_3$
2) Seligmannite: $PbCuAsS_3$ (minor elements not determined)
3) Aikinite: $PbCuBi(As_x, Sb_y, Ag_z)S_3$
4) Diaphorite: $Pb_2Sb_3Ag_3(As_x, Cu_y, Bi_z)S_8$
5) Freieslebenite: $PbAgSb(As_x, Cu_y, Fe_z, Bi_{zz})S_3$

where the calculated number of atoms per $\frac{1}{4}$ cell and weight

percent ranges are:

1) Bournonite: x = 0.13 to 0.23(2.0-3.5 wt.%)
y = 0.005 to 0.021(0.10-0.46 wt.%)
z = 0.0002 to 0.094(0.01-4.0 wt.%)

2) Seligmannite: Not determined

3) Aikinite: x = in the range 0.08(1.0 wt.%)
y = in the range 0.012(0.25 wt.%)
z = less than 0.001(0.02 wt.%)

4) Diaphorite: x = 0.43 to 0.55(2.25-2.75 wt.%)
y = small but not determined
z = 0.006 to 0.01(0.08-0.14 wt.%)

5) Freieslebenite
x = 0.14 to 0.21(2.0-3.0 wt.%)
y = 0.013 to 0.065(0.16-0.78 wt.%)
z = not determined
zz = in the range of 0.0003(0.01 wt.%)

3. Chemical analyses suggests a maximum of $3\frac{1}{2}$:1 ratio for Sb:As in the bournonite lattice and therefore confirms the non-existence of a complete solid solution series between bournonite and seligmannite, at least at low temperature.

4. X-ray data, coupled with minor element analyses and polished section studies, indicates possible, submicroscopic, chain-like layers of exsolved, secondary sulfosalts as

inclusions in the five study minerals. The minor elements discussed are thought to be very soluble in the bournonite group minerals at high temperature, but upon cooling are forced out of the lattice as the submicroscopic sulfide or sulfosalt inclusions.

The common polysynthetic twinning in bournonite, for example, is thought to be a "room getting" process resulting from the exsolution of As, Ag and Bi which are present as minor elements.

5. It is apparent that the presence of Ag as a minor element in bournonite favorably influences the presence of Bi and vice versa. Little evidence was found, however, to indicate the compensatory substitution of $Ag^{+} + Bi^{+3} = 2Pb^{+2}$ suggested by Van Hook(1960) for the matildite ($AgBiS_2$) derivation from the galena structure.

6. The weight percent of Ag in the bournonite lattice was found(figure#4) to fall rapidly with slight increase in weight percent As.

7. A linear plot of weight percent Bi verses the refined a_o-axis of bournonite suggests a maximum Bi content at approximately 8.159Å. A similar plot of weight percent Ag + Bi verses the bournonite a_o-axis indicates the maximum skewed toward lower a_o-axis values to 8.152Å.

8. The weight percent Pb in bournonite is directly related to increase of the a_o and b_o-axes while Sb exhibits good linearity with the a_o-axis only. The c_o-axis of bournonite is not noticeably affected by the variation in these elements. Total cell volume can also be a usable parameter for relation to Pb and Pb plus Sb weight percentages in the bournonite structure. The cell volume increases nearly linear with Pb and exponentially with the combination of Pb plus Sb.

Such relationships can possibly be utilized in other sulfosalt systems for semi-quantitative chemical analysis, free of the matrix absorption problems faced in instrumental analysis.

9. The disordered, cubic, beta phases of diaphorite and freieslebenite(Wernick,1960), although showing a rather constant temperature of disordering, exhibit a premature reordering with the presence of impurities. Diaphorite (natural) commences disordering at approximately 310 degrees C and peaks at 320 degrees(figures#17 and #18). Reordering, which ordinarily starts at 280 degrees C and peaks at 260 degrees C, is advanced 10-15 degrees with galena as an impurity.

The cell edges found for diaphorite and freieslebenite beta phases created from synthetic charges were 5.727Å and

and 5.780Å, respectively. These are within ±0.02Å of those suggested by Wernick(1960). A four atom sulfur deficiency forced upon the unit cell of a synthetic freieslebenite was found to be reflected by a larger cell edge of 5.836Å in the beta phase. The beta phases of these minerals are very stable at room temperature but reordering can be initiated at temperatures in the range of 60-70 degrees C.

10. Heated natural and synthetic aikinite specimens were successfully quenched to a high polymorph of increased symmetry(figures#12and #13). Peliminary indexing of the phase indicates a possible, body-centered, orthorhombic cell with $a_o \approx 6.5$Å, $b_o \approx 5.7$Å and $c_o \approx 12.2$Å. The cell is distinctly pseudo-tetragonal.

Differential thermal analysis revealed aikinite to disorder at approximately 270 degrees C and showing two other endothermic reactions at 465 degreesC and 475 degrees C(figure#14). These reactions could possibly represent additional polymorphic transformations of a non-quenchable nature. The quenched, high polymorph of aikinite is very unstable, unlike those of diaphorite and freieslebenite, and re-orders to the low form within a short time.

11. Crystallization of synthetic bournonite and freieslebenite are definitely aided by the addition of Ag-Bi and

Cu-Fe, respectively in their formulas.

12. Lattice parameter ranges for bournonite were found to be as follows by least squares refinement:

A-AXIS	8.145 to 8.174Å
B-AXIS	8.685 to 8.725Å
C-AXIS	7.806 to 7.836Å

13. The discredited mineral berthonite(= bournonite) (Djebal Slata, Tunisia) was found by this writer to contain high Sb and Cu with respect to bournonite. The x-ray diffraction pattern of the mineral shows it to be poorly crystallized as well. It is, therefore, suggested that this mineral, although being structurally similar to bournonite, is not chemically analogous; and is possibly two sulfosalt phases: bournonite plus a secondary, sub-microscopic, exsolved, Cu-Sb-S sulfosalt.

14. Many "new" lines were observed in the diffraction patterns of the five study sulfosalts with the Nonius-Guinier powder camera. It is suggested that these lines be added to Berry and Thompson's(1962) recent publication on the x-ray powder patterns of the ore minerals.

15. The present, non-destructive methods for quantitative x-ray fluorescence analysis of the high Pb, Sb, Cu, Ag and Bi sulfosalts are not suitable, owing to excessive matrix

absorption. Extreme dilution, liquid cell methods were found to be most promising when destruction of the sample is feasible.

16. This writer suggests that x-ray diffraction of oriented sulfosalt crystals in polished section might be utilized in future investigations of exsolved, sulfide and sulfosalt phases. It is also proposed that infra-red light methods used with such sulfosalts might well result in visual evidence of exsolution phases, since many of the complex sulfides have been shown to be transparent to wavelengths of this order(Bailey,1948).

APPENDIX A

DETAILED PROCEDURES

MINERAL SYNTHESIS PROCEDURE

Synthetics were prepared from reagent grade, dry, chemicals that were thoroughly mixed, pelletized and then heated in evacuated, silica glass tubing. The pelletizer was made from a headless drill bushing with 9/16" ID which was fitted with a hardened steel dowell pin of 9/16" plus 0.0002" diameter. An end of the dowell pin was cut off as a plug for the bushing and was fashioned flat with a mill. The dowell surface was then worked with very fine sandpaper to insure a perfect fit. The standard Buehler Press(model AB) was used as the pelletizing instrument and was operated to a maximum of 20,000 psi for the 9/16" bushing mold. More pressure was found to create release fractures in the pellets upon removal of the load.

All pellets were mixed to 2.5000 grams and were stored in a dessicator until sealed in the silica glass tubes. The total 2.5000 grams of the charge was made into a single pellet to insure homogeneity.

The pellets were sealed in Vycor Brand silica glass tubes manufactured by the Corning Glass Co. of New York. The tubes were of 11 mm ID and had 1 mm wall thicknesses. The Vycor tubing is composed of 99 plus percent silica and melts at about 1500 degrees C. The glass has a very low

coefficient of expansion and will not crack when quenched from very high temperatures.

The Vycor tubes containing the charge were evacuated and then sealed with a methane and oxygen torch after first driving out any water with repeated heatings. Evacuation was accomplished with a Duo-Seal Vacuum Pump(Patent No. 2337849, W.M. Welch Manufacturing Co., Chicago) which was operated for a 20-30 minute period on each seal. After a good vacuum was obtained in the tube, an area 3-4 inches above the pellet was heated with the torch and the tube was slowly twisted free with the pump still running.

The sealed pellets were heated in a Tempco furnace (model F-1620-1) with a Barber-Coleman Controller(model 293 C). The thermocouples used were chromel verses alumel and exact temperatures were read to 5 degrees C. on a Leeds-Northrup millivolt potentiometer(Cat. No. 8686).

All synthetic charges were taken to melting for purposes of homogenization and then lowered to temperatures appropriate for experimentation. Samples were heated for time periods ranging from 4 hours to 14 days and all quenching was done in cold water under the protection of a face guard.

APPENDIX B

POLISHED SECTION DATA

The following 12 plates are photomicrographs of textures and mineral associations of 9 specimens in polished section. A total of 27 polished sections were studied. Scale changes are shown on the plates.

The following standard mineral abbreviations will be used:

bournonite	bo
seligmannite	selig
aikinite	ai
diaphorite	diap
freieslebenite	freies
tetrahedrite	td
chalcopyrite	ccp
sphalerite	sp
pyrite	py
galena	gn
bornite	bn
chalcocite	cc
covellite	cv
miagyrite	miag
chryscolla	chrys

PLATE 1

Figure 1 C 768
Bo showing polysynthetic twinning under crossed nicols. Note fracture pattern controlled by twinning.

Figure 2 Same area as figure 1
Plain light. Note differential pitting controlled by twin lamellae.

PLATE 2

Figure 1 C764
Bo, ccp. Anhedral ccp in bo. Ccp is associated with cv and cc elsewhere in the section.

Figure 2 C764
Bo, cv. Bo showing two distinct textures, one heavily pitted (inclusions?), the other less so. Cv disseminated throughout pitted bo phase but generally restricted to a cep-cc association in the less pitted phase of bo.

PLATE 3

Figure 1 R-1052
Sp, gn, py, selig. Sp embaying gn. Large euhedral crystals of py present with very small blebs of py exsolved from sp along crystallographic direction. Gn containing unknown inclusions.

Figure 2 R-1052
Sp, selig, gn, py, x (unknown arsenic? sulfosalt). Selig and gn embayed by sp. Py containing sp and gn inclusions. X phase associated with selig and gn.

PLATE 4

Figure 1 C-768
Bo, td, gn, sp. Bo with inclusions showing rather sharp boundary with slightly greyer td but less sharp relationship with gn.

Figure 2 C-768
Bo, py, sp. Bo with typical texture associated with large, euhedral grains of py and sp.

PLATE 5

Figure 1 94977
Bo, gn. Bo showing very profuse pitting, possibly due to an exsolved phase(?) Note association with gn and also triangular pitting in gn.

Figure 2 94977
Bo, gn. Same as in figure 1. X marks inclusion in gn.

PLATE 6

Figure 1 BM 88839
Gn, diap. Gn with higher relief associated with diap.

Figure 2 BM 88839
Gn, diap(?), sp. Gn with many inclusions(diap?) and sp.

PLATE 7

Figure 1 105571
Ai, td, cv. X-nicols; td with cv filling fractures associated with ai.

Figure 2 105571(same area as figure 1)
Ai, td, cv. Plain light.

PLATE 8

Figure 1 105571
Td, py, cv. Td with abundant veinlets of cv. Euhedral py crystals embayed with cv.

Figure 2 105571
Ai, td, cv. Ai with many cv veinlets. Possibly some chrys associated with cv in veins. Td area surrounded by cv.

PLATE 9

Figure 1 105571
Ai, td, cv. X-nicols; cv veinlets in td associated with ai.

Figure 2 C-768
Bo, gn. Bo with typical texture at boundary with gn.

PLATE 10

Figure 1 S5-A reheat(2)
Ai(high and low phases). Synthetic specimen of high ai reverting to the low form. Lath-like crystals are low ai. The granular, microcrystalline

Figure 2 S5-A reheat(2)
Ai(high and low phases). Close up of same section showing better detail of good cleavage parallel to elongation direction of low ai. Note also the unterminated character of the laths.

PLATE 11

Figure 1 A-864
Bo, py, sp. Typically pitted bo (with inclusions noted) in a course relationship with sp and py. Py is embayed with sp.

Figure 2 BM 88839
Diap, gn, miag. Gn with inclusions, intimately associated with diap. Miag associated with diap.

PLATE 12

Figure 1 R-6846
Bo, bn. Rare association of bo with bn. Bn revealing exsolution lamellae at X while bo exhibits a fine lamellae from top left of picture to bottom right.

Plate 1

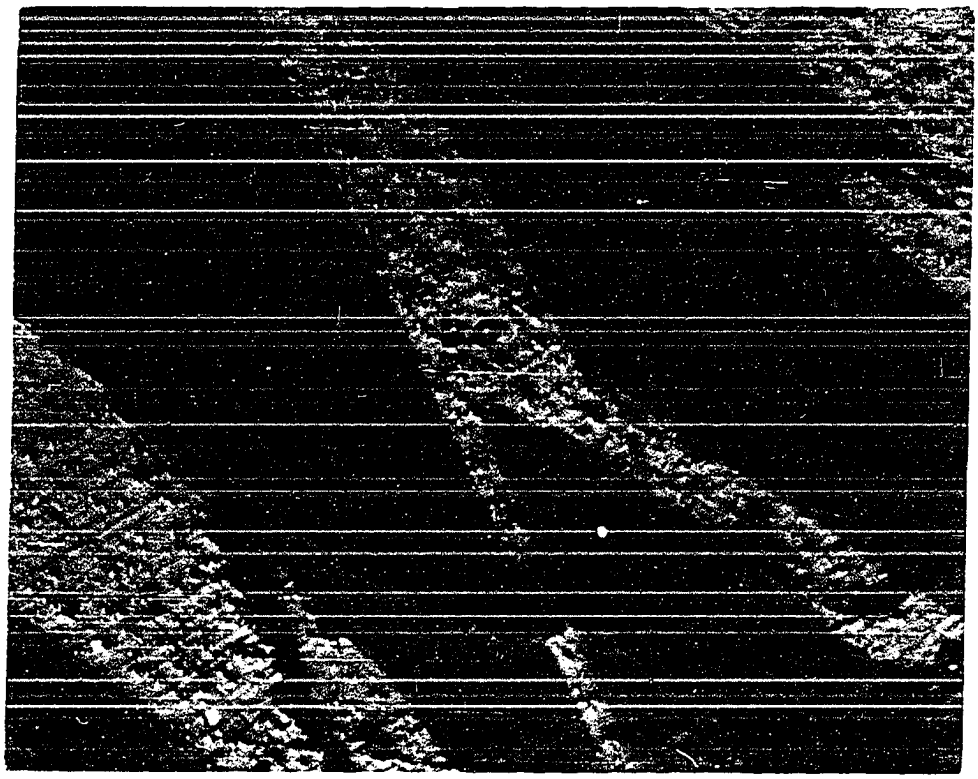
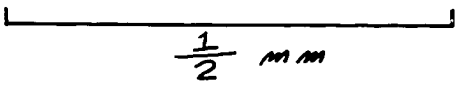


Figure 1



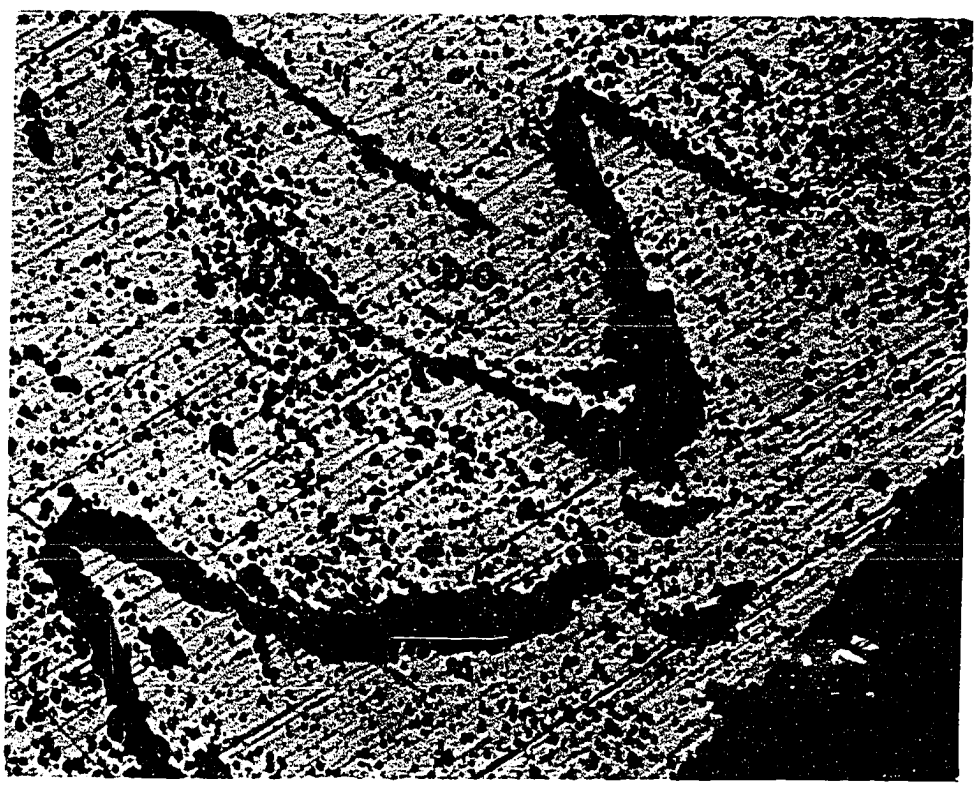
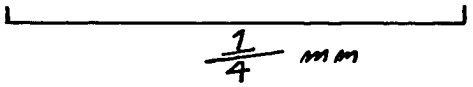


Figure 2

Figure 1



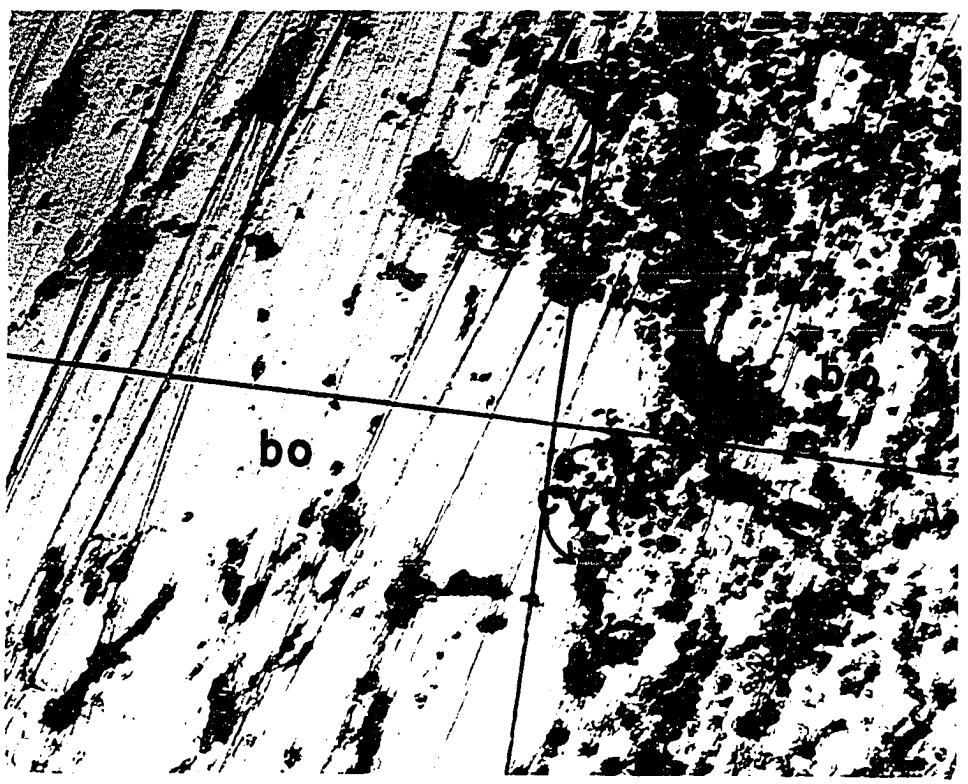


Figure 2

Figure 1

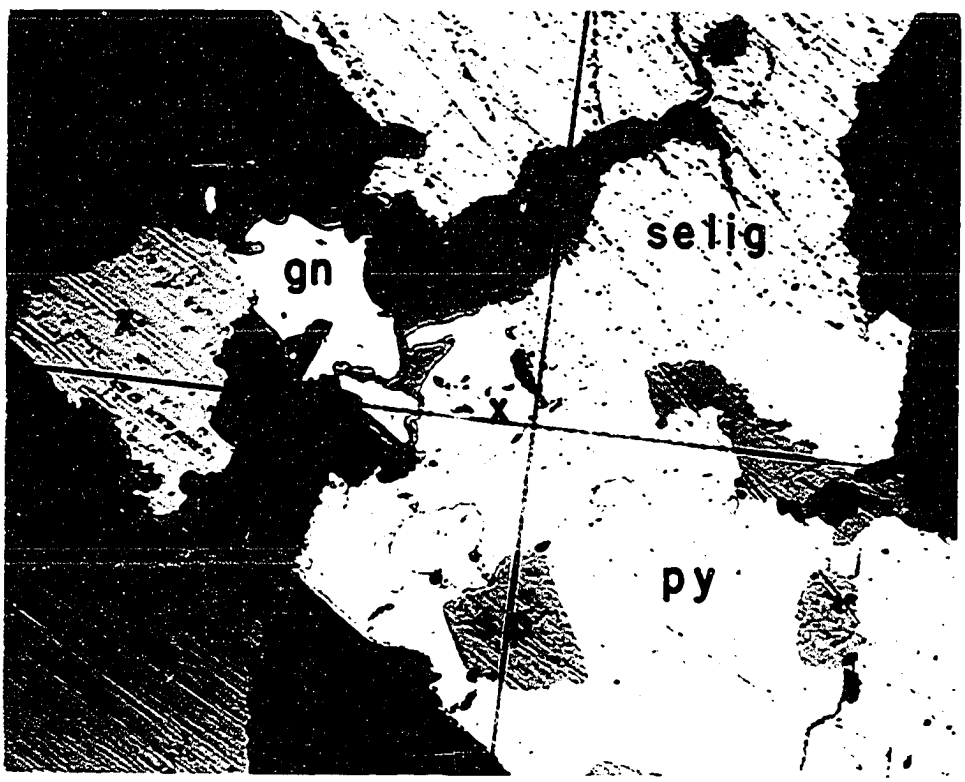


Figure 2

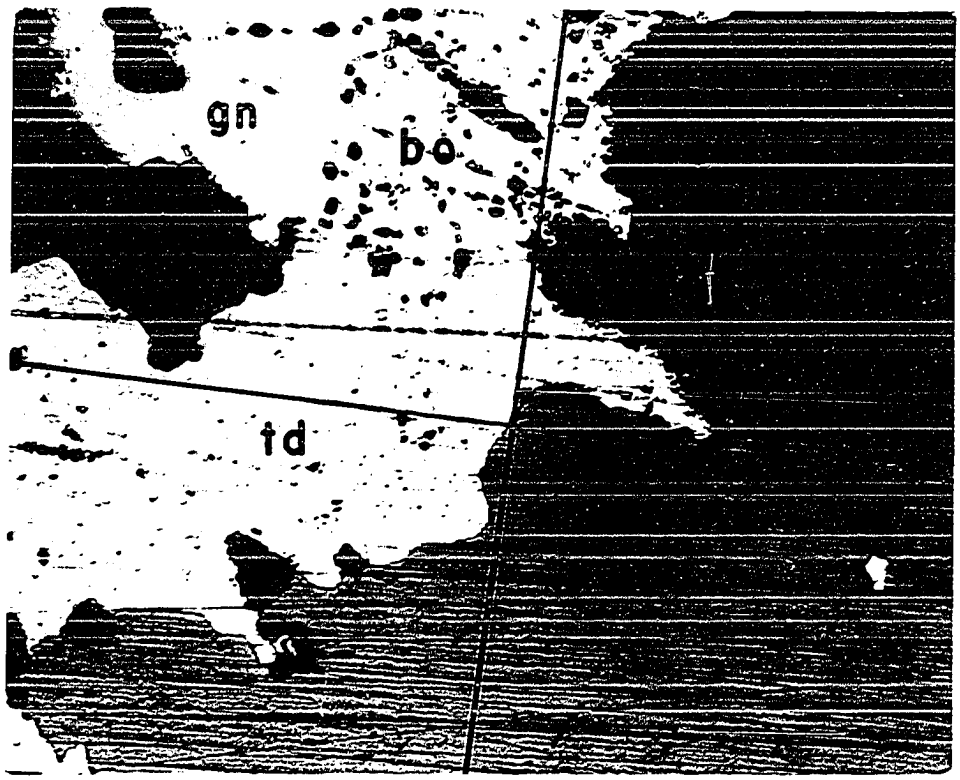


Figure 1

Figure 2

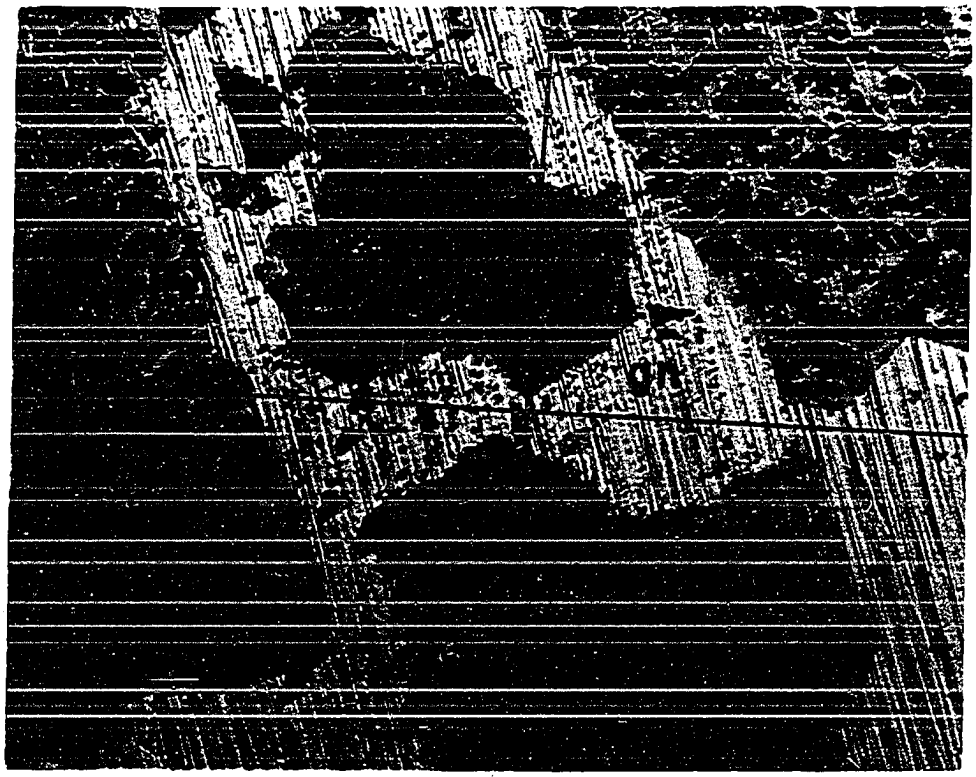


Figure 1

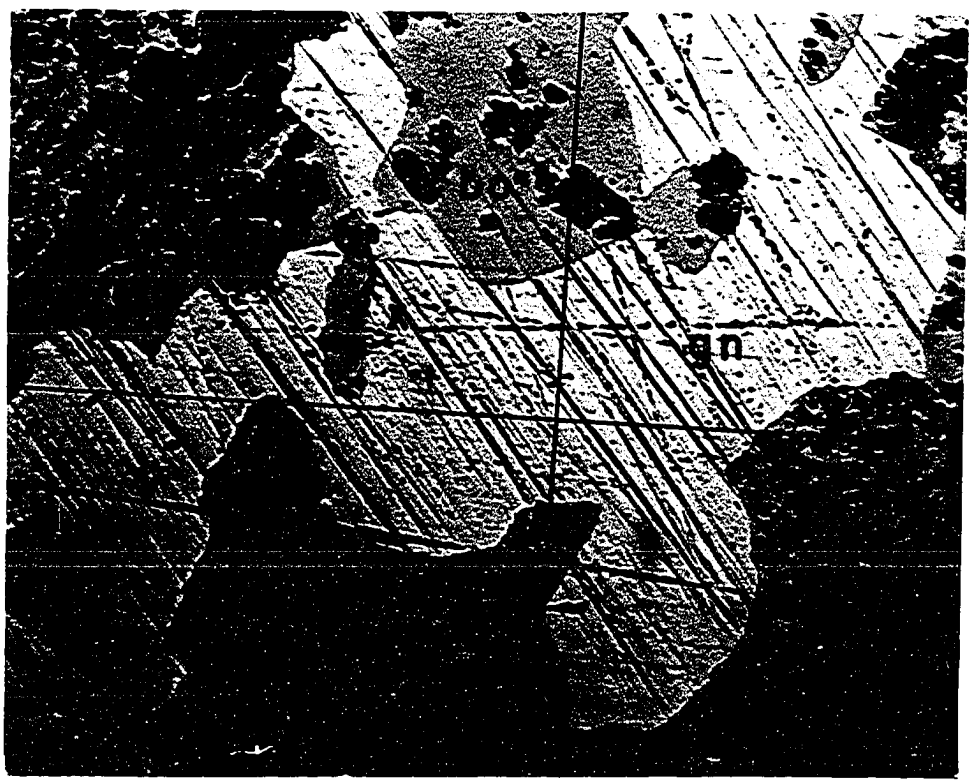


Figure 2

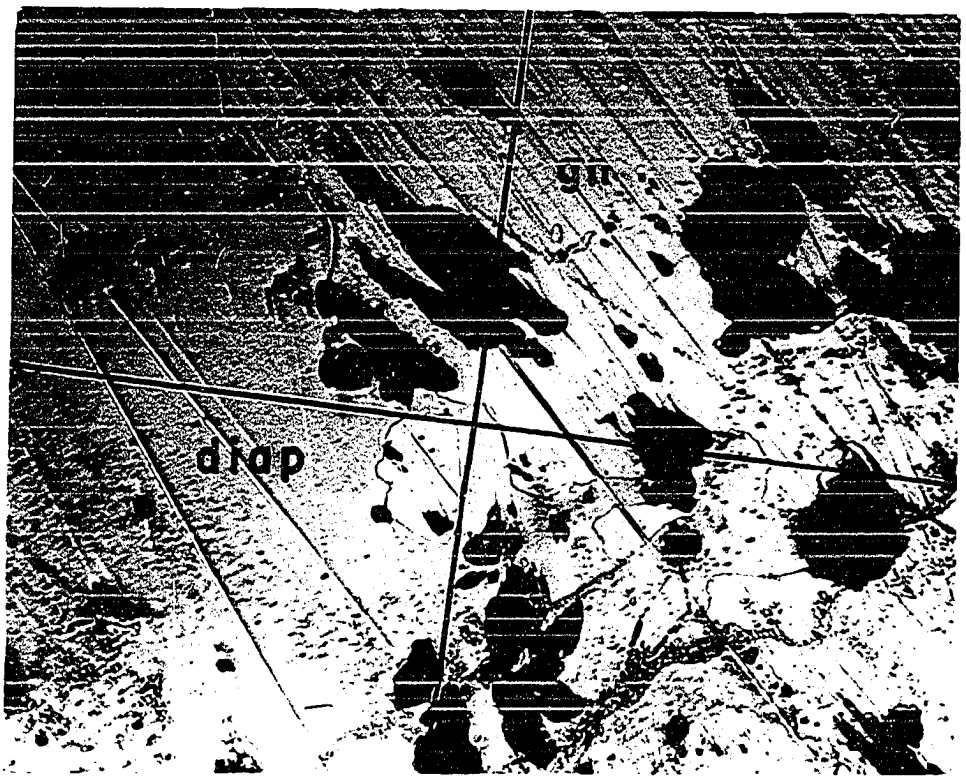


Figure 1

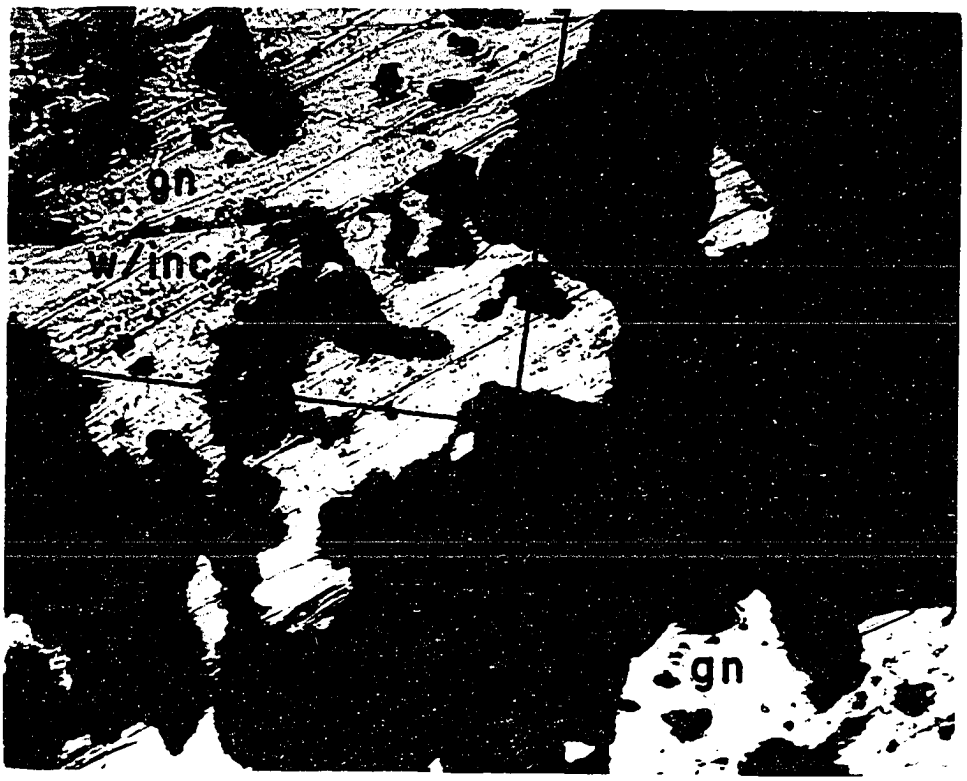


Figure 2

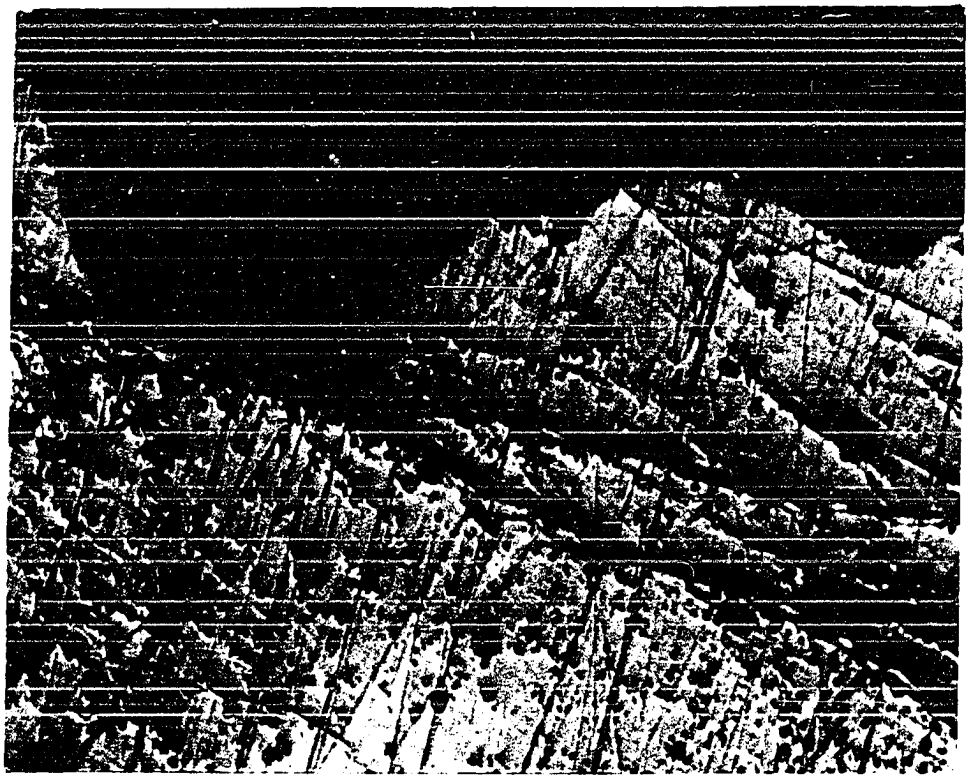
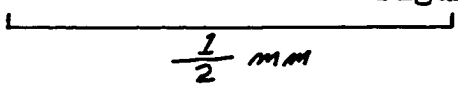


Figure 1



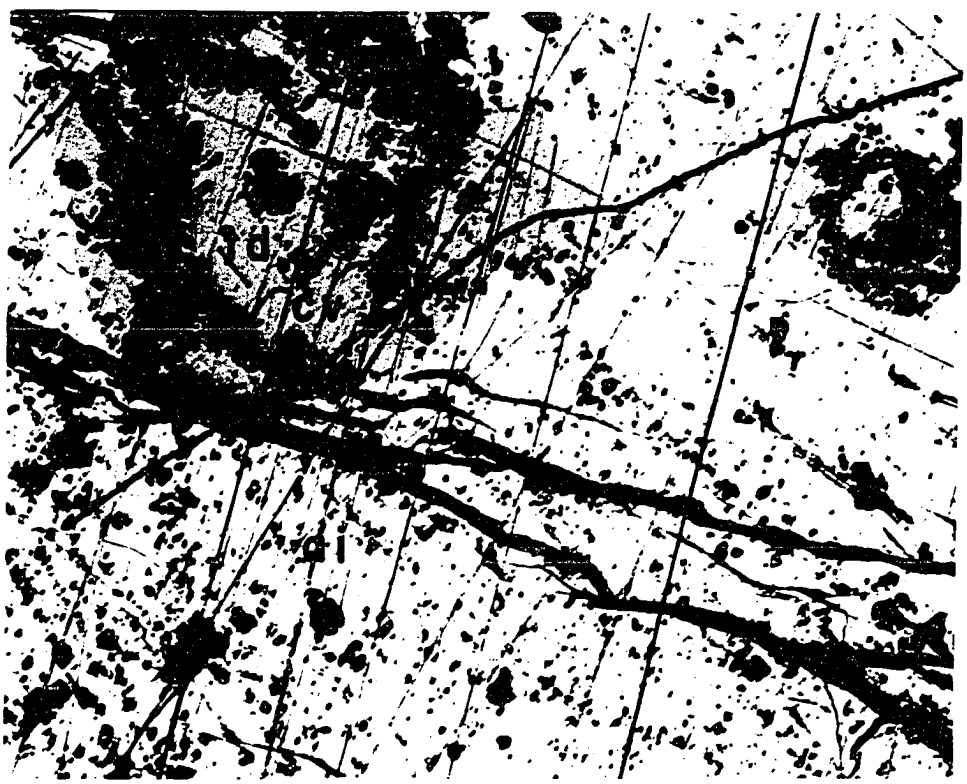


Figure 2

Figure 1

Figure 2

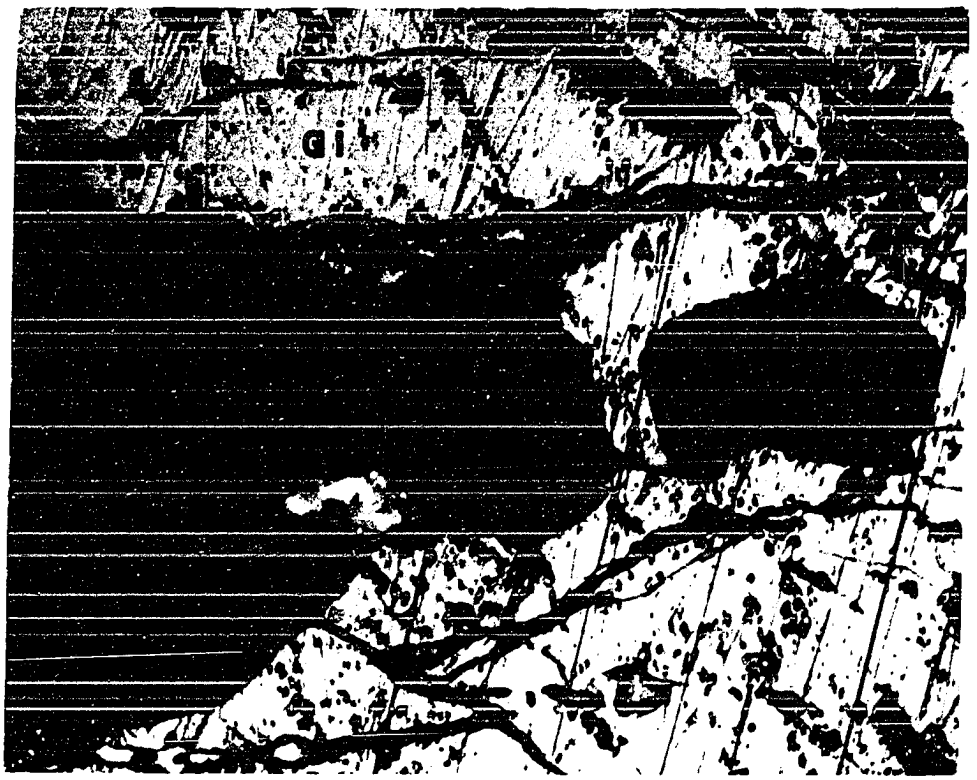


Figure 1

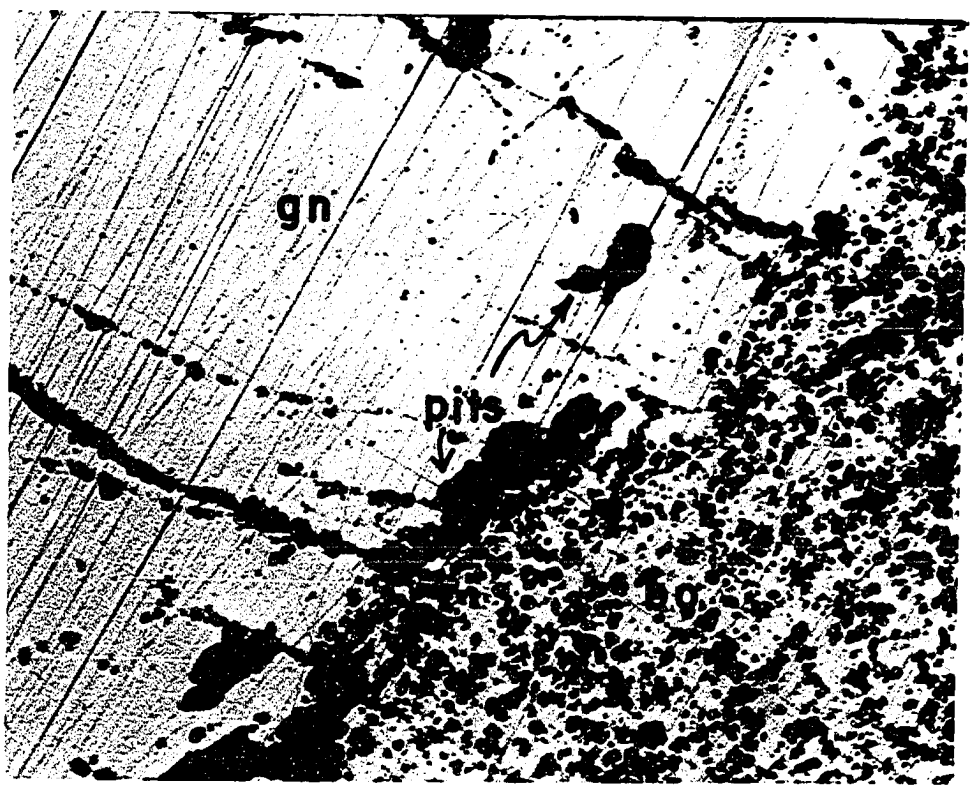


Figure 2

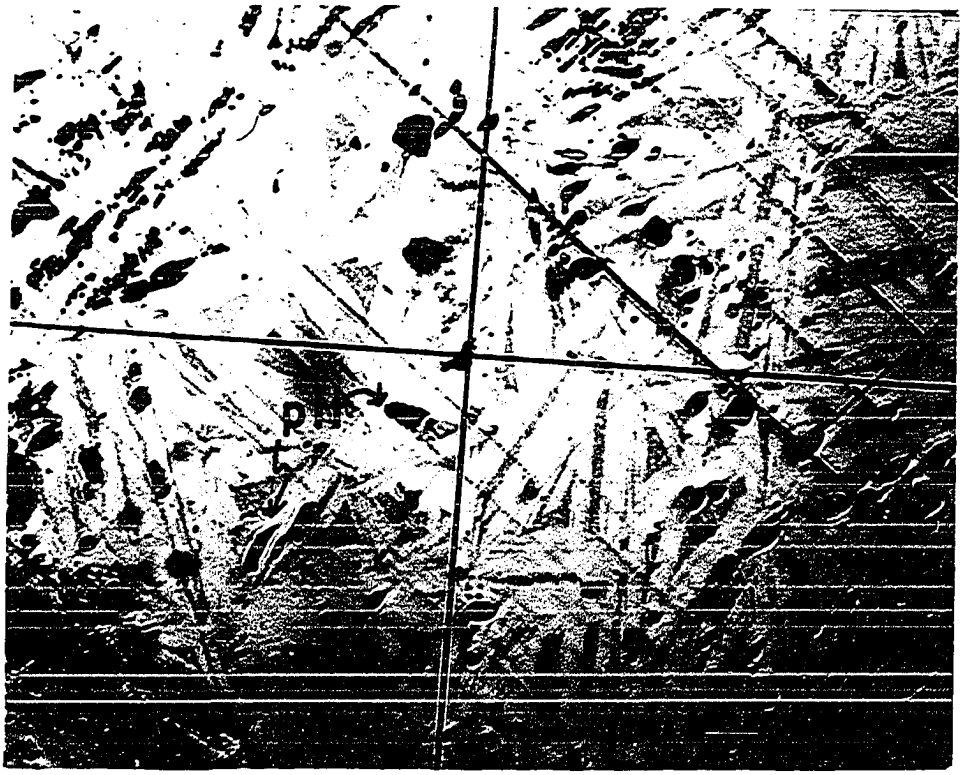


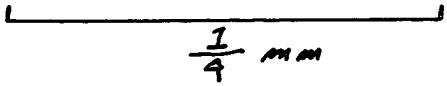
Figure 1

$\frac{1}{4}$ mm

Figure 2

$\frac{1}{8}$ mm

Figure 1



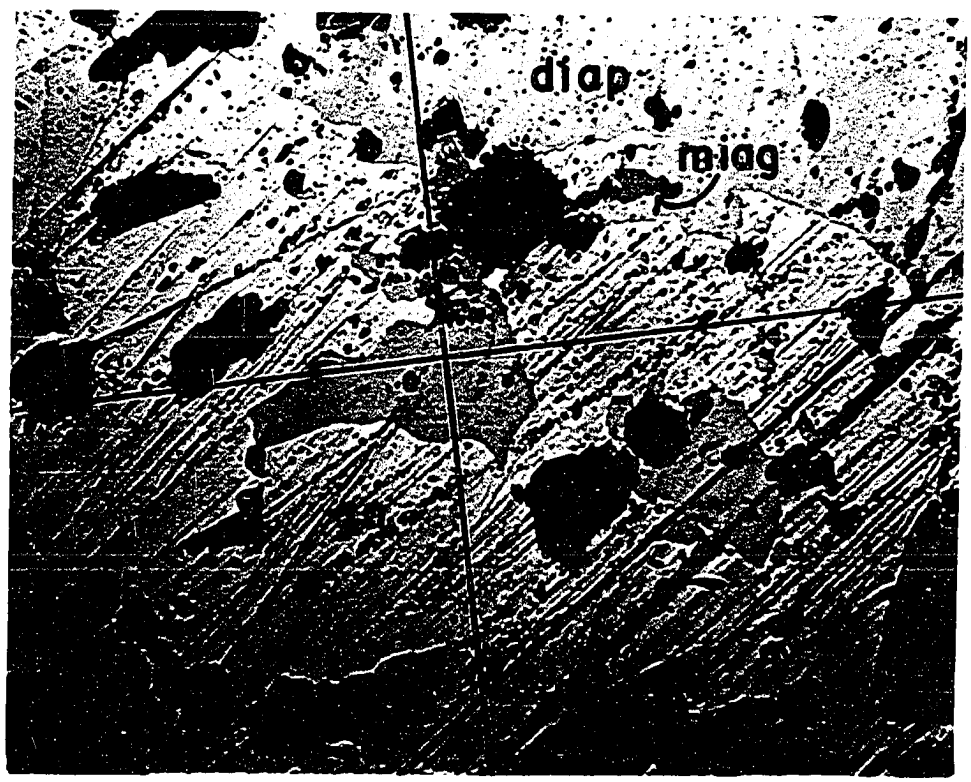


Figure 2

Plate 12

Figure 1

APPENDIX C

DATA FOR CONSTRUCTION OF SULFOSALT MODELS

BOURNONITE $4PbCuSbS_3$ C_{2v}^7 -Pn2$_1$m

2a) xyo
$-x,\frac{1}{2}+y,\frac{1}{2}$

4b) xyz
$x\bar{y}-z$
$-x,\frac{1}{2}+y,\frac{1}{2}-z$
$-x,\frac{1}{2}+\bar{y},\frac{1}{2}+z$

	X	Y	Z	X	Y	Z
Pb (2a)	0.079	0	0	0.079	0.500	0.500
Pb (2a)	-0.560	0.670	0	0.560	0.170	0.500
Sb (2a)	-0.073	0.550	0	0.073	0.050	0.500
Sb (2a)	0.515	0.125	0	-0.515	0.625	0.500
S (2a)	0.225	0.310	0	-0.225	0.710	0.500
S (2a)	-0.225	0.710	0	0.225	0.310	0.500

	X	Y	Z
Cu (4b)	0.269	0.440	0.249
	0.269	0.440	-0.249
	-0.269	0.940	(0.500-0.249)
	-0.269	0.940	0.749
S (4b)	0.084	0.706	0.248
	0.084	0.706	-0.248
	-0.084	0.206	(0.500-0.248)
	-0.084	0.206	(0.500+0.248)

APPENDIX C
CONT.

	X	Y	Z
S (4b)	0.564	0.425	0.267
	0.564	0.425	-0.267
	-0.564	0.925	(0.500/0.267)
	-0.564	0.925	(0.500-0.267)

FREIESLEBENITE $4PbAgSbS_3$ $C_{2h}^5-P2_1/a$

4e) xyz
$\frac{1}{2}-x,\frac{1}{2}/y,\frac{1}{2}/z$
$x-\frac{1}{2},\frac{1}{2}-y,z$
$-x,-y,\frac{1}{2}-/z$

	X	Y	Z
Pb (4e)	0.113	0.085	0.240
	(.500-0.113)	(.500/0.085)	(.500/0.240)
	(.113-0.500)	(.500-0.085)	0.240
	-0.113	-0.085	(.500/z)
Ag (4e)	0.095	0.415	0.240
	(.500-0.095)	(.500/0.415)	(.500/0.240)
	(.095-0.500)	(.500-0.415)	0.240
	-0.095	-0.415	(.500/0.240)
Sb (4e)	0.385	0.256	0.720
	(.500-0.385)	(.500/0.256)	(.500/0.720)
	(.385-0.500)	(.500-0.256)	0.720
	-0.385	-0.256	(.500/0.720)

APPENDIX C
CONT.

	X	Y	Z
S_I (4e)	0.100	0.100	0.740
	(.500-0.100)	(.500/0.100)	(.500/0.720)
	(.100-0.500)	(.500-0.100)	0.740
	-0.100	-0.100	(.500/0.720)
S_{II} (4e)	0.100	0.413	0.680
	(.500-0.100)	(.500/0.413)	(.500/0.680)
	(.100-0.500)	(.500-0.413)	0.680
	-.100	-.100	(.500/0.680)
S_{III} (4e)	0.340	0.260	0.140
	(.500-0.340)	(.500/0.260)	(.500/0.140)
	(.340-0.500)	(.500-0.260)	0.140
	-0.340	-0.260	(.500/0.140)

NOTE: Point positions (2a),(4b) and (4e) were recalculated from those given in International Tables for X-ray Crystallography

APPENDIX D

LEAST SQUARES REFINEMENT DATA FOR STUDY SPECIMENS

(1) The least squares parameter is $1/d^2_{hkl}$.

(2) All axis parameters are given in $\mathring{A}$.

(3) Axes parameters given just under specimen name and number are approximate parameters given to computer as starting point for refinement.

(4) R equals degree of total refinement. Perfect refinement is rated as 0.9999999

(5) Parameters given on last line of the following pages is the computer refined set of values.

(6) Delta corresponds to the deviation(+ or -) of the observed d-spacings with the computer calculated values.

(7) The fourth decimal place given in the calculated lattice parameter values is not significant.

82782 BOURNONITE LEAST SQUARES
8.1620 8.7100 7.8100

H	K	L	OBSD	CALCD	DELTA
0	1	1	5.8820	5.8264	.0555
1	0	1	5.7120	5.6500	.0619
1	1	1	4.7920	4.7406	.0513
0	2	0	4.3820	4.3566	.0253
2	0	0	4.1010	4.0771	.0238
0	0	2	3.9140	3.9179	-.0039
1	2	0	3.8640	3.8425	.0214
2	1	0	3.7050	3.6928	.0121
1	1	2	3.2760	3.2729	.0030
2	2	0	2.9860	2.9769	.0090
0	2	2	2.9230	2.9132	.0097
2	0	2	2.8330	2.8250	.0079
1	3	0	2.7440	2.7360	.0079
3	0	0	2.6880	2.7181	-.0301
2	1	2	2.6760	2.6873	-.0113
0	1	3	2.5090	2.5019	.0070
2	2	2	2.3720	2.3703	.0016
3	2	0	2.3100	2.3061	.0038
1	3	2	2.2470	2.2432	.0037
0	4	0	2.1740	2.1783	-.0043
1	4	0	2.1110	2.1045	.0064
1	4	1	2.0340	2.0324	.0015
4	1	0	1.9920	1.9849	.0070
2	2	3	1.9590	1.9633	-.0043
1	1	4	1.8570	1.8608	-.0038
4	0	2	1.8020	1.8084	-.0064
4	1	2	1.7730	1.7707	.0022
0	5	0	1.7420	1.7426	-.0006
1	5	0	1.7050	1.7041	.0008
4	3	0	1.6680	1.6685	-.0005
1	4	3	1.6360	1.6387	-.0027
2	5	0	1.6020	1.6024	-.0004
0	5	2	1.5910	1.5922	-.0012
1	1	5	1.5180	1.5155	.0024
4	2	3	1.5070	1.5077	-.0007
5	1	2	1.4850	1.4836	.0013

Sum DELTA = .2567 R = .9999916
Sum of Squares = .37194203E-04
8.1543 8.7132 7.8359

53234 BOURNONITE
8.1620 8.7100 7.8100

H	K	L	OBSD	CALCD	DELTA
0	1	1	5.8050	5.8169	-.0119
1	0	1	5.6400	5.6411	-.0011
1	1	1	4.7410	4.7350	.0059
0	2	0	4.3500	4.3556	-.0056
2	0	0	4.0730	4.0759	-.0029
0	0	2	3.8970	3.9071	-.0101
1	2	0	3.8470	3.8416	.0053
2	1	0	3.6970	3.6918	.0051
1	1	2	3.2640	3.2663	-.0023
2	2	0	2.9760	2.9761	-.0001
0	2	2	2.9100	2.9084	.0015
2	0	2	2.8290	2.8205	.0084
1	3	0	2.7360	2.7354	.0005
2	1	2	2.6880	2.6834	.0045
3	1	0	2.5970	2.5940	.0029
0	1	3	2.4930	2.4955	-.0025
2	3	0	2.3660	2.3649	.0010
3	2	0	2.3080	2.3054	.0025
0	2	3	2.2360	2.2355	.0004
3	1	2	2.1690	2.1611	.0078
1	4	0	2.1020	2.1040	-.0020
2	3	2	2.0300	2.0232	.0067
4	1	0	1.9840	1.9844	-.0004
0	0	4	1.9510	1.9535	-.0025
2	4	0	1.9220	1.9208	.0011
1	4	2	1.8500	1.8525	-.0025
4	2	1	1.7940	1.7964	-.0024
4	1	2	1.7700	1.7692	.0007
0	5	0	1.7420	1.7422	-.0002
2	4	2	1.7230	1.7237	-.0007
3	4	0	1.6970	1.6993	-.0023
3	4	1	1.6640	1.6605	.0034
4	3	1	1.6270	1.6313	-.0043
3	0	4	1.5860	1.5861	-.0001
3	4	2	1.5600	1.5583	.0016

Sum DELTA = .0053 R = .9999954
Sum of Squares = .16928745E-04
8.1519 8.7113 7.8142

94977 BOURNONITE
8.1620 8.7100 7.8100

H	K	L	OBSD	CALCD	DELTA
0	1	1	5.7860	5.8156	-.0296
1	1	1	4.7280	4.7339	-.0059
0	2	0	4.3290	4.3430	-.0140
2	0	0	4.0830	4.0750	.0079
2	1	0	3.7050	3.6891	.0158
2	2	0	2.9660	2.9717	-.0057
1	3	0	2.7200	2.7283	-.0083
3	1	0	2.5900	2.5928	-.0028
2	3	0	2.3600	2.3602	-.0002
0	4	1	2.0970	2.0925	.0044
4	0	1	1.9750	1.9718	.0031
4	2	1	1.7890	1.7954	-.0064
3	1	3	1.8400	1.8393	.0006
2	0	4	1.7600	1.7643	-.0043
3	4	1	1.6570	1.6577	-.0007
0	3	4	1.6220	1.6215	.0004
3	4	2	1.5500	1.5564	-.0064
2	5	2	1.4780	1.4795	-.0015
4	0	4	1.4160	1.4115	.0044
5	0	3	1.3810	1.3825	-.0015
6	0	0	1.3580	1.3583	-.0003
4	5	0	1.3260	1.3219	.0040

Sum DELTA = -.0472 R = .9999897
Sum of Squares = .47154740E-04
8.1500 8.6861 7.8295

81295 BOURNONITE
8.1620 8.7100 7.8100

H	K	L	OBSD	CALCD	DELTA
0	1	1	5.8420	5.8114	.0305
1	0	1	5.6400	5.6362	.0037
0	2	0	4.3290	4.3547	-.0257
2	0	0	4.0640	4.0753	-.0113
2	2	0	2.9710	2.9755	-.0045
0	2	2	2.8960	2.9057	-.0097
2	0	2	2.8160	2.8181	-.0021
1	3	0	2.7240	2.7348	-.0108
2	1	2	2.6730	2.6812	-.0082
1	3	1	2.5900	2.5808	.0091
0	1	3	2.4930	2.4920	.0009
2	3	0	2.3660	2.3645	.0014
3	2	0	2.3040	2.3050	-.0010
0	2	3	2.2360	2.2328	.0031
3	1	2	2.1640	2.1598	.0041
1	4	0	2.1020	2.1035	-.0015
2	3	2	2.0260	2.0221	.0038
3	3	0	1.9820	1.9837	-.0017
0	0	4	1.9510	1.9506	.0003
1	3	3	1.8830	1.8846	-.0016
4	2	0	1.8500	1.8456	.0043
4	2	1	1.7920	1.7960	-.0040
3	3	2	1.7700	1.7682	.0017
1	2	4	1.7380	1.7391	-.0011
2	4	2	1.7230	1.7229	0.0000
3	4	1	1.6610	1.6601	.0008
4	3	1	1.6300	1.6310	-.0010
3	4	2	1.5580	1.5577	.0002
2	3	4	1.5050	1.5046	.0003

Sum DELTA = -.0431 R = .9999966
Sum of Squares = .12166226E-04
8.1507 8.7094 7.8024

78894 BOURNONITE
8.1620 8.7100 7.8100

H	K	L	OBSD	CALCD	DELTA
0	1	1	5.8050	5.8138	-.0088
1	0	1	5.6760	5.6383	.0376
1	1	1	4.7290	4.7322	-.0032
0	2	0	4.3500	4.3520	-.0020
2	0	0	4.0640	4.0730	-.0090
1	2	0	3.8390	3.8385	.0004
2	1	0	3.6900	3.6891	.0008
1	1	2	3.2640	3.2648	-.0008
2	2	0	2.9660	2.9738	-.0078
2	0	2	2.8160	2.8191	-.0031
1	3	0	2.7280	2.7331	-.0051
2	1	2	2.6760	2.6820	-.0060
3	1	0	2.5940	2.5921	.0018
2	3	0	2.3660	2.3631	.0028
3	2	0	2.3050	2.3037	.0012
0	2	3	2.2380	2.2345	.0034
1	2	3	2.1540	2.1549	-.0009
1	4	0	2.1020	2.1023	-.0003
3	3	0	1.9790	1.9825	-.0035
0	0	4	1.9510	1.9530	-.0020
1	4	2	1.8520	1.8512	.0007
4	2	1	1.7890	1.7952	-.0062
3	3	2	1.7680	1.7678	.0001
1	2	4	1.7420	1.7406	.0013
2	4	2	1.7250	1.7225	.0024
1	5	1	1.6650	1.6633	.0016
4	3	1	1.6300	1.6301	-.0001
0	5	2	1.5890	1.5900	-.0010
3	4	2	1.5600	1.5572	.0027
2	4	3	1.5410	1.5449	-.0039
4	2	3	1.5070	1.5051	.0018
5	1	2	1.4830	1.4817	.0012

Sum DELTA = -.0039 R = .9999957
Sum of Squares = .18358673E-04
8.1461 8.7040 7.8120

113077 BERTHONITE
8.1620 8.7100 7.8100

H	K	L	OBSD	CALCD	DELTA
0	1	1	5.8620	5.8183	.0436
0	2	0	4.3710	4.3541	.0168
2	0	0	4.1300	4.0871	.0428
0	0	2	3.8970	3.9099	-.0129
2	1	0	3.7050	3.6998	.0051
1	1	2	3.2760	3.2692	.0067
2	0	2	2.8290	2.8253	.0036
1	3	0	2.7360	2.7354	.0005
2	1	2	2.6960	2.6874	.0085
0	0	3	2.6050	2.6066	-.0016
3	2	0	2.3160	2.3097	.0062
0	4	0	2.1740	2.1770	-.0030
1	4	0	2.1090	2.1037	.0052
4	3	0	1.6680	1.6709	-.0029
5	1	1	1.5740	1.5738	.0001
0	0	4	1.9550	1.9549	0.0000
1	4	2	1.8500	1.8526	-.0026
0	5	0	1.7410	1.7416	-.0006
0	6	0	1.4520	1.4513	.0006
4	1	2	1.7730	1.7731	-.0001

Sum DELTA = .1163R = .9999962
Sum of Squares = .83917402E-05
8.1742 8.7083 7.8199

M-17539 BERTHONITE
8.1620 8.7100 7.8100

H	K	L	OBSD	CALCD	DELTA
0	1	1	5.8820	5.8051	.0768
1	0	1	5.7120	5.6392	.0727
0	2	0	4.3290	4.3391	-.0101
2	0	0	4.0730	4.0758	-.0028
1	2	0	3.8550	3.8303	.0246
2	1	0	3.6970	3.6892	.0077
1	1	2	3.3000	3.2631	.0368
2	2	0	2.9860	2.9707	.0152
2	2	1	2.7940	2.7766	.0173
1	3	0	2.7120	2.7262	-.0142
1	3	1	2.5900	2.5738	.0161
2	3	0	2.3540	2.3590	-.0050
3	2	0	2.3080	2.3029	.0050
3	1	2	2.1540	2.1601	-.0061
4	0	1	1.9710	1.9718	-.0008
0	0	4	1.9470	1.9524	-.0054
4	2	0	1.8430	1.8446	-.0016
2	0	4	1.7600	1.7608	-.0008
3	2	3	1.7320	1.7248	.0071
2	4	2	1.7170	1.7194	-.0024
3	4	1	1.6570	1.6568	.0001
4	3	1	1.6270	1.6293	-.0023

Sum DELTA = .2278 R = .9999851
Sum of Squares = .30979995E-04
8.1516 8.6783 7.8096

112640 BOURNONITE
8.1620 8.7100 7.8100

H	K	L	OBSD	CALCD	DELTA
0	1	1	5.8240	5.8157	.0082
1	0	1	5.6760	5.6481	.0278
1	1	1	4.7920	4.7363	.0556
0	2	0	4.3500	4.3468	.0031
2	0	0	4.0730	4.0810	-.0080
0	0	2	3.8970	3.9121	-.0151
1	2	0	3.8470	3.8366	.0103
2	1	0	3.6900	3.6942	-.0042
2	0	1	3.6160	3.6183	-.0023
1	2	1	3.4770	3.4447	.0322
2	1	1	3.3480	3.3405	.0074
0	2	2	2.9100	2.9078	.0021
2	0	2	2.8200	2.8240	-.0040
1	3	0	2.7360	2.7308	.0051
2	1	2	2.6880	2.6859	.0020
3	1	0	2.5970	2.5964	.0005
2	2	2	2.3660	2.3681	-.0021
3	1	2	2.1670	2.1633	.0036
1	4	0	2.0740	2.1002	-.0262
1	4	1	2.0340	2.0284	.0055
4	0	1	1.9790	1.9744	.0045
2	2	3	1.9590	1.9612	-.0022
0	4	2	1.9010	1.8998	.0011
4	2	0	1.8480	1.8471	.0008
4	2	1	1.7920	1.7976	-.0056
3	3	2	1.7670	1.7691	-.0021
1	2	4	1.7370	1.7426	-.0056
3	4	1	1.6600	1.6594	.0005
0	3	4	1.6220	1.6212	.0007
2	5	1	1.5690	1.5671	.0018
3	4	2	1.5580	1.5576	.0003
3	2	4	1.4930	1.4917	.0012
1	5	3	1.4260	1.4245	.0014
1	5	4	1.2840	1.2833	.0006

Sum DELTA = .0993 R = .9999884
Sum of Squares = .54418967E-04
8.1620 8.6936 7.8242

A-862 D-136 BOURNONITE
8.1620 8.7100 7.8100

H	K	L	OBSD	CALCD	DELTA
0	1	1	5.9010	5.8208	.0801
1	0	1	5.7120	5.6484	.0635
0	2	0	4.4140	4.3587	.0552
2	0	0	4.1110	4.0840	.0269
0	0	2	3.9310	3.9097	.0212
1	2	0	3.8720	3.8454	.0265
2	1	0	3.7050	3.6983	.0066
2	2	0	2.9960	2.9802	.0157
0	2	2	2.9280	2.9104	.0175
2	0	2	2.8380	2.8242	.0137
1	3	0	2.7530	2.7377	.0152
2	1	2	2.7000	2.6867	.0132
3	1	0	2.6050	2.5989	.0060
0	1	3	2.5030	2.4972	.0057
2	2	2	2.3720	2.3701	.0018
1	3	2	2.2490	2.2425	.0064
3	1	2	2.1640	2.1643	-.0003
1	4	0	2.1040	2.1056	-.0016
4	1	0	1.9920	1.9882	.0037
2	2	3	1.9610	1.9619	-.0009
1	4	2	1.8570	1.8539	.0030
4	2	1	1.7990	1.7995	-.0005
4	1	2	1.7710	1.7722	-.0012
0	5	0	1.7430	1.7434	-.0004
2	1	4	1.7260	1.7282	-.0022
4	3	0	1.6680	1.6707	-.0027
1	4	3	1.6350	1.6379	-.0029
0	5	2	1.5910	1.5923	-.0013
1	5	2	1.5630	1.5629	0.0000

SumDELTA = .3179 R = .9999901
Sum of Squares = .30470929E-04
8.1681 8.7174 7.8195

A-861 BOURNONITE

H	K	L	OBSD	CALCD	DELTA
1	0	0	8.2290	8.1639	.0650
1	1	0	5.9880	5.9611	.0268
0	1	1	5.8600	5.8233	.0366
1	0	1	5.6800	5.6473	.0326
1	1	1	4.7560	4.7408	.0151
0	2	0	4.3810	4.3623	.0186
2	0	0	4.1000	4.0819	.0180
0	0	2	3.9290	3.9101	.0188
1	2	0	3.8600	3.8475	.0124
2	1	0	3.7100	3.6973	.0126
2	1	1	3.3510	3.3425	.0084
1	1	2	3.2770	3.2695	.0074
2	2	0	2.9880	2.9805	.0074
0	2	2	2.9160	2.9116	.0043
2	0	2	2.8310	2.8236	.0073
2	2	1	2.7900	2.7851	.0048
1	3	0	2.7460	2.7395	.0064
2	1	2	2.6920	2.6864	.0055
0	0	3	2.6030	2.6067	-.0037
1	3	1	2.5890	2.5855	.0034
3	0	1	2.5760	2.5701	.0058
0	1	3	2.5030	2.4976	.0053
1	1	3	2.3890	2.3883	.0006
3	2	0	2.3120	2.3088	.0031
2	3	1	2.2690	2.2668	.0021
1	3	2	2.2480	2.2436	.0043
0	2	3	2.2390	2.2376	.0013
0	4	0	2.1840	2.1811	.0028
3	1	2	2.1640	2.1638	.0001
1	4	0	2.1090	2.1072	.0017
1	4	1	2.0360	2.0346	.0013
2	2	3	1.9600	1.9621	-.0021
4	1	1	1.9250	1.9261	-.0011
0	1	4	1.9060	1.9077	-.0017
1	3	3	1.8870	1.8884	-.0014
1	1	4	1.8570	1.8576	-.0006
4	0	2	1.8030	1.8093	-.0063
0	2	4	1.7860	1.7840	.0019
4	1	2	1.7750	1.7716	.0033
0	5	0	1.7460	1.7449	.0010
3	2	3	1.7290	1.7283	.0006
1	5	0	1.7050	1.7063	-.0013
0	4	3	1.6740	1.6728	.0011
1	5	1	1.6660	1.6671	-.0011
1	4	3	1.6360	1.6387	-.0027

A-861 BOURNONITE (Cont'd.)

H	K	L	OBSD	CALCD	DELTA
0	5	2	1.5920	1.5934	-.0014
1	5	2	1.5630	1.5639	-.0009
5	2	0	1.5300	1.5291	.0008
4	2	3	1.5070	1.5079	-.0009
3	2	4	1.4920	1.4920	0.0000
5	1	2	1.4840	1.4847	-.0007
1	4	4	1.4340	1.4332	.0007

Sum DELTA = .3243 R = .9999972
Sum of Squares = .18615933E-04
8.1639 8.7246 7.8202

A-2891 D-3411 BOURNONITE
8.1620 8.7100 7.8100

H	K	L	OBSD	CALCD	DELTA
0	1	1	5.8440	5.8118	.0321
1	0	1	5.6760	5.6394	.0365
0	2	0	4.3500	4.3500	0.0000
2	0	0	4.0820	4.0757	.0062
1	2	0	3.8310	3.8377	-.0067
2	1	0	3.6900	3.6908	-.0008
1	1	2	3.2640	3.2644	-.0004
2	2	0	2.9660	2.9742	-.0082
0	3	0	2.9010	2.9000	.0009
2	0	2	2.8160	2.8197	-.0037
1	3	0	2.7280	2.7322	-.0042
2	1	2	2.6760	2.6823	-.0063
1	3	1	2.5900	2.5790	.0109
2	3	0	2.3600	2.3629	-.0029
3	2	0	2.3080	2.3045	.0034
0	2	3	2.2360	2.2338	.0021
3	1	2	2.1690	2.1605	.0084
1	4	0	2.1020	2.1015	.0004
3	3	0	1.9840	1.9828	.0011
0	0	4	1.9510	1.9525	-.0015
1	4	2	1.8520	1.8505	.0014
4	2	1	1.7920	1.7959	-.0039
3	3	2	1.7700	1.7679	.0020
1	2	4	1.7380	1.7402	-.0022
2	4	2	1.7230	1.7222	.0007
1	5	0	1.6970	1.7016	-.0046
1	5	1	1.6640	1.6626	.0013
0	5	2	1.5890	1.5893	-.0003
3	4	2	1.5590	1.5571	.0018
4	2	3	1.5070	1.5055	.0014
5	1	2	1.4810	1.4824	-.0014

Sum DELTA = .0635 R = .9999957
Sum of Squares = .16774941E-04
8.1515 8.7000 7.8101

A3920 BOURNONITE
8.1620 8.7100 7.8100

H	K	L	OBSD	CALCD	DELTA
0	2	0	4.3710	4.3572	.0137
2	0	0	4.1110	4.0869	.0240
0	0	2	3.8970	3.9034	-.0064
2	1	0	3.7050	3.7002	.0047
1	1	2	3.3000	3.2657	.0342
2	2	0	2.9960	2.9808	.0151
0	2	2	2.9100	2.9074	.0025
2	0	2	2.8290	2.8228	.0061
1	3	0	2.7360	2.7371	-.0011
2	1	2	2.6880	2.6854	.0025
3	1	0	2.5970	2.6004	-.0034
1	1	3	2.3780	2.3850	-.0070
3	2	0	2.3130	2.3101	.0028
1	4	0	2.1060	2.1051	.0008
4	1	0	1.9880	1.9895	-.0015
2	2	3	1.9590	1.9603	-.0013
1	1	4	1.8540	1.8548	-.0008
4	1	2	1.7730	1.7725	.0004
1	5	1	1.6650	1.6653	-.0003
2	2	4	1.6330	1.6328	.0001
1	3	4	1.5890	1.5891	-.0001
3	4	2	1.5590	1.5598	-.0008
5	1	2	1.4850	1.4858	-.0008
1	5	3	1.4260	1.4259	0.0000
4	1	4	1.3940	1.3932	.0007
2	5	3	1.3650	1.3649	0.0000
2	6	1	1.3480	1.3480	0.0000

Sum DELTA = .0842 R = .9999982
Sum of Squares = .87637876E-05
8.1739 8.7145 7.8069

BM 1912-151 BOURNONITE
8.1620 8.7100 7.8100

H	K	L	OBSD	CALCD	DELTA
0	1	1	5.8820	5.8185	.0634
1	0	1	5.7120	5.6467	.0652
1	1	1	4.7790	4.7383	.0406
0	2	0	4.3820	4.3557	.0262
2	0	0	4.0920	4.0822	.0097
0	0	2	3.9060	3.9091	-.0031
1	2	0	3.8560	3.8430	.0129
2	1	0	3.7050	3.6964	.0084
1	1	2	3.2760	3.2682	.0077
2	2	0	2.9810	2.9785	.0024
0	2	2	2.9190	2.9092	.0097
2	0	2	2.8290	2.8233	.0056
1	3	0	2.7400	2.7359	.0040
2	1	2	2.6880	2.6858	.0021
3	1	0	2.5970	2.5976	-.0006
0	1	3	2.4930	2.4967	-.0037
2	2	2	2.3720	2.3691	.0028
3	2	0	2.3080	2.3080	0.0000
1	3	2	2.2470	2.2414	.0055
0	4	0	2.1740	2.1778	-.0038
1	4	0	2.1090	2.1042	.0047
1	4	1	2.0340	2.0319	.0020
4	1	0	1.9880	1.9872	.0007
2	2	3	1.9590	1.9613	-.0023
1	3	3	1.8840	1.8870	-.0030
1	1	4	1.8560	1.8571	-.0011
4	2	1	1.7970	1.7986	-.0016
4	1	2	1.7730	1.7715	.0014
0	5	0	1.7420	1.7423	-.0003
3	4	0	1.6980	1.7004	-.0024
4	3	0	1.6680	1.6698	-.0018
5	1	2	1.4850	1.4846	.0003
0	6	0	1.4520	1.4519	0.0000
4	1	4	1.3940	1.3935	.0004

8.1644 8.7115 7.8182

3411 4073 BOURNONITE
8.1620 8.7100 7.8100

H	K	L	OBSD	CALCD	DELTA
1	1	0	5.9010	5.9561	-.0551
1	0	1	5.6400	5.6460	-.0060
1	1	1	4.7660	4.7376	.0283
0	2	0	4.3500	4.3546	-.0046
2	0	0	4.0920	4.0817	.0102
0	0	2	3.9310	3.9085	.0224
2	1	0	3.7050	3.6960	.0089
1	1	2	3.2760	3.2677	.0082
2	2	0	2.9760	2.9780	-.0020
0	2	2	2.9100	2.9087	.0012
2	0	2	2.8290	2.8230	.0059
1	3	0	2.7440	2.7352	.0087
2	1	2	2.6880	2.6854	.0025
3	1	0	2.5970	2.5973	-.0003
0	1	3	2.4930	2.4963	-.0033
2	3	0	2.3660	2.3657	.0002
3	2	0	2.3080	2.3076	.0003
0	2	3	2.2410	2.2359	.0050
3	1	2	2.1590	2.1632	-.0042
1	4	0	2.1020	2.1037	-.0017
4	1	0	1.9840	1.9870	-.0030
0	0	4	1.9550	1.9542	.0007
2	4	0	1.9200	1.9210	-.0010
1	3	3	1.8830	1.8866	-.0036
1	4	2	1.8500	1.8524	-.0024
4	1	2	1.7700	1.7713	-.0013
0	5	0	1.7420	1.7418	.0001
2	4	2	1.7260	1.7240	.0019
3	4	0	1.7000	1.7000	0.0000
3	4	1	1.6650	1.6612	.0037
4	3	1	1.6330	1.6327	.0002
2	5	0	1.6010	1.6020	-.0010
5	1	1	1.5720	1.5719	0.0000
3	4	2	1.5570	1.5589	-.0019
4	2	3	1.5070	1.5073	-.0003
5	1	2	1.4850	1.4845	.0004
4	4	1	1.4640	1.4627	.0012
1	4	4	1.4320	1.4318	.0001

Sum DELTA = .0180 R = .9999977
Sum of Squares = .12726479E-04
8.1635 8.7092 7.8171

BM 32909 BOURNONITE
8.1620 8.7100 7.8100

H	K	L	OBSD	CALCD	DELTA
0	1	1	5.7860	5.8147	-.0287
1	0	1	5.5860	5.6404	-.0544
1	1	1	4.7290	4.7334	-.0044
0	2	0	4.3390	4.3518	-.0128
2	0	0	4.0730	4.0747	-.0017
1	2	0	3.8640	3.8388	.0251
2	1	0	3.6970	3.6903	.0066
1	1	2	3.2700	3.2658	.0041
2	2	0	2.9710	2.9744	-.0034
0	3	0	2.8960	2.9012	-.0052
2	0	2	2.8120	2.8202	-.0082
1	3	0	2.7200	2.7331	-.0131
2	1	2	2.6730	2.6829	-.0099
1	3	1	2.5830	2.5799	.0030
0	1	3	2.4930	2.4955	-.0025
2	3	0	2.3660	2.3633	.0026
3	2	0	2.2990	2.3044	-.0054
3	0	2	2.2310	2.2304	.0005
1	2	3	2.1440	2.1554	-.0114
0	4	1	2.0990	2.0961	.0028
4	0	1	1.9790	1.9714	.0075
0	0	4	1.9490	1.9536	-.0046
2	4	0	1.9200	1.9194	.0005
3	0	3	1.8790	1.8801	-.0011
1	4	2	1.8500	1.8513	-.0013
4	2	1	1.7940	1.7958	-.0018
2	0	4	1.7650	1.7616	.0033
3	2	3	1.7320	1.7259	.0060
2	4	2	1.7210	1.7227	-.0017
3	4	0	1.6970	1.6982	-.0012
1	5	1	1.6640	1.6633	.0006
4	3	1	1.6270	1.6306	-.0036
5	0	1	1.5990	1.5955	.0034
3	0	4	1.5870	1.5860	.0009
3	4	2	1.5580	1.5575	.0004
2	3	4	1.5040	1.5057	-.0017
2	5	2	1.4790	1.4812	-.0022
3	4	3	1.4240	1.4226	.0013
4	4	2	1.3900	1.3899	0.0000
0	6	2	1.3620	1.3599	.0020
5	3	2	1.3350	1.3354	-.0004
6	1	1	1.3220	1.3226	-.0006
0	1	6	1.2870	1.2880	-.0010
5	0	4	1.2510	1.2515	-.0005
1	2	6	1.2350	1.2333	.0016

BM 32909 BOURNONITE (Cont'd.)

Sum DELTA = -.1109 R = .9999957
Sum of Squares = .43235318E-04
8.1495 8.7036 7.8146

BM 43625 BOURNONITE
8.1620 8.7100 7.8100

H	K	L	OBSD	CALCD	DELTA
1	1	0	5.9010	5.9468	-.0458
1	0	1	5.7120	5.6393	.0726
1	1	1	4.7790	4.7326	.0463
0	2	0	4.3710	4.3514	.0195
2	0	0	4.0820	4.0725	.0094
1	2	0	3.8640	3.8380	.0259
2	1	0	3.6970	3.6886	.0083
1	1	2	3.2640	3.2658	-.0018
2	2	0	2.9760	2.9734	.0025
0	3	0	2.9000	2.9009	-.0009
2	0	2	2.8120	2.8196	-.0076
1	3	0	2.7200	2.7328	-.0128
2	1	2	2.6800	2.6824	-.0024
3	1	0	2.5900	2.5918	-.0018
0	1	3	2.4930	2.4958	-.0028
3	2	0	2.3050	2.3034	.0015
1	3	2	2.2390	2.2395	-.0005
1	2	3	2.1590	2.1555	.0034
1	4	0	2.1020	2.1020	0.0000
1	4	1	2.0300	2.0298	.0001
4	0	1	1.9780	1.9704	.0075
0	0	4	1.9510	1.9539	-.0029
1	3	3	1.8830	1.8856	-.0026
0	2	4	1.7890	1.7824	.0065
2	0	4	1.7650	1.7616	.0033
0	5	0	1.7420	1.7405	.0014
2	1	4	1.7250	1.7266	-.0016
1	5	1	1.6650	1.6631	.0018
3	0	4	1.5850	1.5859	-.0009
3	4	2	1.5570	1.5572	-.0002
2	3	4	1.5040	1.5057	-.0017
5	3	0	1.4200	1.4203	-.0003
4	4	2	1.3880	1.3895	-.0015

Sum DELTA = .1219 R = .9999950
Sum of Squares = .21569483E-04
8.1450 8.7028 7.8156

BM 54797 BOURNONITE
8.1620 8.7100 7.8100

H	K	L	OBSD	CALCD	DELTA
0	1	1	5.8240	5.8143	.0096
1	0	1	5.7120	5.6426	.0693
1	1	1	4.7920	4.7349	.0570
0	2	0	4.3710	4.3525	.0184
2	0	0	4.0640	4.0792	-.0152
1	2	0	3.8640	3.8402	.0237
2	1	0	3.6900	3.6937	-.0037
1	2	1	3.4240	3.4463	-.0223
1	1	2	3.2640	3.2659	-.0019
2	2	0	2.9760	2.9763	-.0003
0	2	2	2.9190	2.9071	.0118
2	0	2	2.8200	2.8213	-.0013
1	3	0	2.7320	2.7339	-.0019
2	1	2	2.6760	2.6838	-.0078
3	1	0	2.5970	2.5957	.0012
0	1	3	2.4930	2.4949	-.0019
3	2	0	2.3080	2.3063	.0016
1	3	2	2.2390	2.2398	-.0008
3	1	2	2.1690	2.1619	.0070
1	4	0	2.1020	2.1027	-.0007
1	4	1	2.0340	2.0304	.0035
3	3	0	1.9820	1.9842	-.0022
0	0	4	1.9530	1.9531	-.0001
1	4	2	1.8520	1.8515	.0004
4	2	1	1.7940	1.7973	-.0033
3	3	2	1.7680	1.7691	-.0011
0	5	0	1.7420	1.7410	.0009
2	1	4	1.7260	1.7266	-.0006
4	3	0	1.6670	1.6686	-.0016
5	0	1	1.5990	1.5972	.0017
3	0	4	1.5860	1.5864	-.0004
3	4	2	1.5580	1.5581	-.0001
5	1	2	1.4850	1.4835	.0014
0	4	4	1.4540	1.4535	.0004
5	3	0	1.4220	1.4222	-.0002
4	4	2	1.3900	1.3906	-.0006

Sum DELTA = .1393 R = .9999974
Sum of Squares = .12972262E-04
8.1584 8.7051 7.8126

C762 BOURNONITE NONIUS
8.1620 8.7100 7.8100

H	K	L	OBSD	CALCD	DELTA
0	2	2	2.9130	2.9092	.0037
2	0	2	2.8260	2.8221	.0038
2	2	1	2.7840	2.7826	.0013
1	3	0	2.7420	2.7361	.0058
2	1	2	2.6880	2.6848	.0031
3	1	0	2.5980	2.5960	.0019
3	2	0	2.3080	2.3069	.0010
1	3	2	2.2390	2.2414	-.0024
0	4	0	2.1790	2.1782	.0007
1	2	3	2.1600	2.1566	.0033
1	4	0	2.1050	2.1045	.0004
3	3	0	1.9850	1.9851	-.0001
0	0	4	1.9550	1.9542	.0007
2	4	0	1.9220	1.9214	.0005
0	1	4	1.9050	1.9068	-.0018
1	3	3	1.8870	1.8869	0.0000
1	1	4	1.8540	1.8568	-.0028
4	2	1	1.7970	1.7977	-.0007
4	1	2	1.7710	1.7705	.0004
0	5	0	1.7430	1.7426	.0003
2	4	2	1.7240	1.7243	-.0003
1	5	0	1.7020	1.7041	-.0021
3	4	1	1.6620	1.6613	.0006
2	5	0	1.6020	1.6025	-.0005
1	3	4	1.5890	1.5902	-.0012
3	2	4	1.4910	1.4911	-.0001
5	1	2	1.4840	1.4837	.0002
1	4	4	1.4340	1.4320	.0019
5	3	0	1.4220	1.4225	-.0005
2	2	0	2.9780	2.9777	.0002
1	1	2	3.2690	3.2676	.0013
2	1	1	3.3410	3.3402	.0007
2	1	0	3.6970	3.6944	.0025
1	2	0	3.8430	3.8429	0.0000
0	0	2	3.9080	3.9084	-.0004
2	0	0	4.0810	4.0793	.0016
0	2	0	4.3590	4.3565	.0024
1	1	1	4.7430	4.7372	.0057
1	0	1	5.6490	5.6443	.0046
0	1	1	5.8200	5.8185	.0014
1	1	0	5.9610	5.9554	.0055

Sum DELTA = .0434 R = .9999988
Sum of Squares = .59946033E-05
8.1586 8.7131 7.8168

C764 BOURNONITE
8.1620 8.7100 7.8100

H	K	L	OBSD	CALCD	DELTA
0	1	1	5.7860	5.8175	-.0315
0	2	0	4.3920	4.3578	.0341
2	0	0	4.0730	4.0821	-.0091
1	2	0	3.8640	3.8444	.0195
2	1	0	3.7200	3.6967	.0232
2	0	2	2.8290	2.8222	.0067
0	3	1	2.7280	2.7230	.0049
3	1	0	2.5970	2.5977	-.0007
3	1	1	2.4600	2.4650	-.0050
2	3	0	2.3660	2.3669	-.0009
4	0	0	2.0470	2.0410	.0059
4	0	1	1.9790	1.9747	.0042
0	0	4	1.9510	1.9531	-.0021
0	1	4	1.9090	1.9058	.0031
1	4	2	1.8500	1.8532	-.0032
4	1	2	1.7700	1.7712	-.0012
3	4	1	1.6620	1.6619	0.0000
4	3	1	1.6300	1.6332	-.0032
4	1	3	1.5790	1.5798	-.0008
1	5	2	1.5640	1.5624	.0015

Sum DELTA = .0452 R = .9999950
Sum of Squares = .1177002IE-04
8.1642 8.7157 7.8126

C767 BOURNONITE NONIUS
8.1620 8.7100 7.8100

H	K	L	OBSD	CALCD	DELTA
0	2	2	2.9150	2.9081	.0068
2	0	2	2.8260	2.8221	.0038
2	2	1	2.7840	2.7824	.0015
1	3	0	2.7430	2.7352	.0077
2	1	2	2.6900	2.6846	.0053
3	1	0	2.5990	2.5966	.0023
3	2	0	2.3070	2.3071	-.0001
1	3	2	2.2390	2.2407	-.0017
0	4	0	2.1780	2.1773	.0006
1	2	3	2.1620	2.1559	.0060
1	4	0	2.1050	2.1037	.0012
0	0	4	1.9560	1.9535	.0024
0	4	2	1.9020	1.9019	0,0000
3	0	3	1.8820	1.8814	.0005
4	2	1	1.7970	1.7979	-.0009
4	1	2	1.7710	1.7707	.0002
2	1	4	1.7250	1.7270	-.0020
0	5	1	1.7010	1.7001	.0008
0	4	3	1.6700	1.6705	-.0005
3	4	1	1.6610	1.6610	0.0000
2	5	0	1.6020	1.6020	0.0000
4	2	3	1.5070	1.5069	0.0000
3	2	4	1.4900	1.4909	-.0009
2	5	2	1.4810	1.4822	-.0012
1	4	4	1.4310	1.4315	-.0005
2	2	0	2.9830	2.9775	.0054
1	1	2	3.2750	3.2668	.0081
2	1	1	3.3450	3.3404	.0045
2	1	0	3.7020	3.6951	.0068
1	2	0	3.8510	3.8419	.0090
0	0	2	3.9200	3.9071	.0128
2	0	0	4.0880	4.0806	.0073
0	2	0	4.3700	4.3546	.0153
1	1	1	4.7560	4.7365	.0194
1	0	1	5.6680	5.6442	.0237
0	1	1	5.8340	5.8163	.0176
1	1	0	5.9610	5.9551	.0058

Sum DELTA = .1679 R = .9999985
Sum of Squares = .66672861E-05
8.1612 8.7093 7.8142

D-864 BOURNONITE
8.1620 8.7100 7.8100

H	K	L	OBSD	CALCD	DELTA
0	1	1	5.8420	5.8160	.0259
1	0	1	5.7120	5.6444	.0675
1	1	1	4.7410	4.7369	.0040
0	2	0	4.3710	4.3554	.0155
2	0	0	4.1110	4.0819	.0290
0	0	2	3.9140	3.9062	.0077
1	2	0	3.8470	3.8427	.0042
2	1	0	3.7050	3.6962	.0087
1	1	2	3.2640	3.2665	-.0025
2	2	0	2.9760	2.9783	-.0023
0	2	2	2.9100	2.9080	.0019
2	0	2	2.8240	2.8222	.0017
1	3	0	2.7320	2.7357	-.0037
2	1	2	2.6680	2.6848	-.0168
3	1	0	2.5970	2.5975	-.0005
2	3	0	2.3720	2.3660	.0059
3	2	0	2.3080	2.3078	.0001
0	2	3	2.2410	2.2350	.0059
3	1	2	2.1640	2.1629	.0010
1	4	0	2.1040	2.1041	-.0001
4	1	0	1.9880	1.9871	.0008
0	0	4	1.9510	1.9531	-.0021
1	4	2	1.8520	1.8524	-.0004
4	1	2	1.7700	1.7711	-.0011
0	5	0	1.7380	1.7421	-.0041
2	4	2	1.7260	1.7241	.0018
3	4	1	1.6650	1.6614	.0035
4	3	1	1.6300	1.6328	-.0028
3	4	2	1.5600	1.5590	.0009

Sum DELTA = .1500 R = .9999943
Sum of Squares = .15017550E-04
8.1639 8.7109 7.8124

J-1 BOURNONITE LEAST SQUARES
8.1620 8.7100 7.8100

H	K	L	OBSD	CALCD	DELTA
1	1	0	5.9010	5.9507	-.0497
1	1	1	4.7920	4.7362	.0557
0	2	0	4.3820	4.3561	.0258
2	0	0	4.1200	4.0736	.0463
0	0	2	3.9220	3.9116	.0103
1	2	0	3.8640	3.8415	.0224
2	1	0	3.7050	3.6902	.0147
1	1	2	3.2810	3.2686	.0123
2	2	0	2.9810	2.9753	.0056
0	2	2	2.9190	2.9104	.0085
2	0	2	2.8290	2.8214	.0075
1	3	0	2.7400	2.7355	.0044
2	1	2	2.6920	2.6842	.0077
0	0	3	2.6050	2.6077	-.0027
0	1	3	2.4930	2.4982	-.0052
3	2	0	2.3080	2.3046	.0033
1	3	2	2.2440	2.2417	.0022
3	1	2	2.1690	2.1611	.0078
1	4	0	2.1040	2.1041	-.0001
4	0	0	2.0300	2.0368	-.0068
1	3	3	1.8830	1.8875	-.0045
0	5	0	1.7420	1.7424	-.0004
1	5	1	1.6650	1.6648	.0001
4	4	0	1.4870	1.4876	-.0006

Sum DELTA = .1515 R = .9999914
Sum of Squares = .15638673E-04
8.1473 8.7122 7.8232

J-2 BOURNONITE LEAST SQUARES
8.1620 8.7100 7.8100

H	K	L	OBSD	CALCD	DELTA
0	1	1	5.8240	5.8126	.0113
1	0	1	5.6760	5.6388	.0371
1	1	1	4.7410	4.7333	.0076
0	2	0	4.3390	4.3545	-.0155
2	0	0	4.0830	4.0774	.0055
0	0	2	3.8880	3.9027	-.0147
1	2	0	3.8390	3.8412	-.0022
2	1	0	3.6900	3.6927	-.0027
1	1	2	3.2640	3.2638	.0001
2	2	0	2.9710	2.9763	-.0053
0	3	0	2.8960	2.9030	-.0070
0	3	1	2.7280	2.7209	.0070
2	1	2	2.6730	2.6823	-.0093
1	3	1	2.5830	2.5810	.0019
0	1	3	2.4930	2.4929	0.0000
3	2	0	2.3050	2.3058	-.0008
0	2	3	2.2360	2.2335	.0024
2	0	3	2.1940	2.1933	.0006
3	1	2	2.1690	2.1608	.0081
1	4	0	2.1070	2.1035	.0034
0	0	4	1.9510	1.9513	-.0003
1	4	2	1.8520	1.8517	.0002
4	2	1	1.7940	1.7967	-.0027
4	1	2	1.7700	1.7693	.0006
1	2	4	1.7400	1.7397	.0002
2	4	2	1.7230	1.7232	-.0002
3	4	0	1.6980	1.6993	-.0013
3	4	1	1.6620	1.6604	.0015
1	3	4	1.5890	1.5884	.0005
3	4	2	1.5580	1.5580	0.0000
2	3	4	1.5040	1.5051	-.0011
2	5	2	1.4810	1.4818	-.0008
4	4	2	1.3910	1.3905	.0004

Sum DELTA = .0244 R = .9999980
Sum of Squares = .86806397E-05
8.1548 8.7091 7.8055

M-BOURNONITE NONIUS
8.1620 8.7100 7.8100

H	K	L	OBSD	CALCD	DELTA
1	0	0	8.2030	8.1752	.0277
1	1	0	5.9750	5.9613	.0136
0	1	1	5.8400	5.8174	.0225
1	0	1	5.6800	5.6492	.0307
1	1	1	4.7560	4.7398	.0161
0	2	0	4.3650	4.3557	.0092
2	0	0	4.1000	4.0876	.0123
0	0	2	3.9200	3.9076	.0123
1	2	0	3.8530	3.8441	.0088
2	1	0	3.7080	3.7005	.0074
2	0	1	3.6310	3.6221	.0088
1	0	2	3.5370	3.5256	.0113
2	1	1	3.3490	3.3445	.0044
1	1	2	3.2770	3.2681	.0088
2	2	0	2.9840	2.9806	.0033
0	2	2	2.9130	2.9087	.0042
2	0	2	2.8300	2.8246	.0053
2	2	1	2.7880	2.7850	.0029
1	3	0	2.7420	2.7363	.0056
2	1	2	2.6910	2.6869	.0040
3	1	0	2.6030	2.6008	.0021
1	3	1	2.5780	2.5826	-.0046
0	1	3	2.4980	2.4959	.0020
1	1	3	2.3940	2.3871	.0068
2	2	2	2.3710	2.3699	.0010
3	2	0	2.3130	2.3102	.0027
2	3	1	2.2700	2.2656	.0043
1	3	2	2.2430	2.2414	.0015
0	4	0	2.1710	2.1778	-.0068
1	4	0	2.1050	2.1044	.0005
1	4	1	2.0300	2.0321	-.0021
4	1	0	1.9890	1.9897	-.0007
2	2	3	1.9580	1.9615	-.0035
4	1	1	1.9270	1.9282	-.0012
0	1	4	1.9030	1.9064	-.0034
1	3	3	1.8870	1.8867	.0002
1	1	4	1.8540	1.8566	-.0026
4	2	1	1.8020	1.8004	.0015
4	1	2	1.7740	1.7731	.0008
0	5	0	1.7450	1.7423	.0026
3	2	3	1.7280	1.7284	-.0004
1	5	0	1.7020	1.7040	-.0020
0	4	3	1.6730	1.6709	.0020
1	5	1	1.6640	1.6649	-.0009
3	0	4	1.5830	1.5878	-.0048
1	1	5	1.5150	1.5119	.0030

M-BOURNONITE NONIUS (Cont'd.)

Sum DELTA = .2183 R = .9999949
Sum of Squares = .21742700E-04
8.1752 8.7115 7.8153

M704 BOURNONITE NONIUS
8.1620 8.7100 7.8100

H	K	L	OBSD	CALCD	DELTA
1	0	0	8.1510	8.1556	-.0046
1	1	0	5.9640	5.9519	.0120
0	1	1	5.8300	5.8136	.0163
1	0	1	5.6550	5.6407	.0142
1	1	1	4.7460	4.7339	.0120
0	2	0	4.3650	4.3530	.0119
2	0	0	4.0840	4.0778	.0061
0	0	2	3.9100	3.9050	.0049
1	2	0	3.8420	3.8402	.0017
2	1	0	3.6970	3.6927	.0042
2	1	1	3.3370	3.3384	-.0014
1	1	2	3.2670	3.2650	.0019
2	2	0	2.9760	2.9759	0.0000
0	2	2	2.9080	2.9068	.0011
2	0	2	2.8200	2.8203	-.0003
2	2	1	2.7810	2.7809	0.0000
1	3	0	2.7370	2.7340	.0029
0	3	1	2.7210	2.7203	.0006
2	1	2	2.6830	2.6830	0.0000
3	1	0	2.5970	2.5949	.0020
1	3	1	2.5810	2.5805	.0004
3	0	1	2.5660	2.5674	-.0014
0	1	3	2.4960	2.4942	.0017
1	1	3	2.3840	2.3851	-.0011
2	3	0	2.3660	2.3644	.0015
0	3	2	2.3250	2.3292	-.0042
3	2	0	2.3050	2.3058	-.0008
2	3	1	2.2650	2.2629	.0020
1	3	2	2.2390	2.2397	-.0007
0	4	0	2.1750	2.1765	-.0015
1	2	3	2.1580	2.1548	.0031
1	4	0	2.1040	2.1029	.0010
3	3	0	1.9840	1.9839	0.0000
0	0	4	1.9540	1.9525	.0014
2	4	0	1.9220	1.9201	.0018
0	4	2	1.9000	1.9011	-.0011
1	3	3	1.8830	1.8853	-.0023
1	4	2	1.8510	1.8515	-.0005
4	2	1	1.7950	1.7968	-.0018
0	2	4	1.7810	1.7815	-.0005
3	3	2	1.7690	1.7687	.0002
2	0	4	1.7600	1.7610	-.0010
1	2	4	1.7400	1.7404	-.0004
2	4	2	1.7230	1.7230	0.0000
4	3	0	1.6680	1.6683	-.0003

M704 BOURNONITE NONIUS (Cont'd.)

H	K	L	OBSD	CALCD	DELTA
3	4	1	1.6610	1.6602	.0007
3	0	4	1.5870	1.5858	.0011
3	4	2	1.5580	1.5579	0.0000

Sum DELTA = .0834 R = .9999991
Sum of Squares = .39472330E-05
8.1556 8.7060 7.8100

M-8367 BOURNONITE
8.1620 8.7100 7.8100

H	K	L	OBSD	CALCD	DELTA
0	1	1	5.8620	5.8125	.0494
1	0	1	5.6760	5.6409	.0350
1	1	1	4.7670	4.7335	.0334
0	2	0	4.3710	4.3514	.0195
2	0	0	4.1110	4.0783	.0326
0	0	2	3.8800	3.9048	-.0248
2	1	0	3.7050	3.6929	.0120
1	1	2	3.2640	3.2648	-.0008
2	2	0	2.9769	2.9756	.0003
0	2	2	2.9100	2.9062	.0037
2	0	2	2.8200	2.8204	-.0004
1	3	0	2.7320	2.7332	-.0012
2	1	2	2.6800	2.6831	-.0031
3	1	0	2.5970	2.5951	.0018
0	1	3	2.4930	2.4940	-.0010
3	2	0	2.3080	2.3057	.0022
0	2	3	2.2360	2.2339	.0020
3	1	2	2.1690	2.1613	.0076
1	4	0	2.1040	2.1022	.0017
2	3	2	2.0240	2.0222	.0017
0	0	4	1.9510	1.9524	-.0014
4	2	1	1.7960	1.7969	-.0009
2	4	2	1.7220	1.7227	-.0007
3	4	1	1.6620	1.6599	.0020
4	3	1	1.6270	1.6314	-.0044
3	0	4	1.5860	1.5858	.0001
3	4	2	1.5570	1.5577	-.0007
4	2	3	1.5070	1.5060	.0009
5	1	2	1.4850	1.4832	.0017
5	3	0	1.4220	1.4219	0.0000
4	4	2	1.3900	1.3903	-.0003
3	1	5	1.3380	1.3382	-.0002
6	1	1	1.3230	1.3237	-.0007

Sum DELTA = .1670-R = .9999976
Sum of Squares = .13440532E-04
8.1566 8.7029 7.8097

R-8055 BOURNONITE
8.1620 8.7100 7.8100

H	K	L	OBSD	CALCD	DELTA
1	1	0	5.9010	5.9546	-.0536
0	2	0	4.3920	4.3537	.0382
2	0	0	4.1300	4.0806	.0493
0	0	2	3.8970	3.9058	-.0088
2	1	0	3.7120	3.6950	.0169
1	1	2	3.2760	3.2659	.0100
2	2	0	2.9860	2.9773	.0086
0	2	2	2.9140	2.9073	.0066
2	0	2	2.8200	2.8216	-.0016
1	3	0	2.7360	2.7347	.0012
2	1	2	2.6920	2.6842	.0077
3	1	0	2.5970	2.5966	.0003
2	2	2	2.3720	2.3678	.0041
3	2	0	2.3100	2.3070	.0029
0	4	0	2.1740	2.1768	-.0028
1	4	0	2.1060	2.1033	.0026
3	3	0	1.9840	1.9848	-.0008
0	0	4	1.9550	1.9529	.0020
4	2	0	1.8500	1.8475	.0024
4	1	2	1.7700	1.7706	-.0006
1	2	4	1.7380	1.7408	-.0028
2	4	2	1.7230	1.7235	-.0005
3	4	1	1.6620	1.6608	.0011
4	3	1	1.6300	1.6323	-.0023
5	3	0	1.4210	1.4227	-.0017
3	3	4	1.3920	1.3920	0.0000

Sum DELTA = .0799 R = .9999969
Sum of Squares = .12209408E-04
8.1613 8.7075 7.8116

R6845 BOURNONITE
8.1620 8.7100 7.8100

H	K	L	OBSD	CALCD	DELTA
0	1	1	5.8620	5.8151	.0468
1	1	1	4.7660	4.7338	.0321
0	2	0	4.3920	4.3528	.0391
2	0	0	4.0550	4.0755	-.0205
1	2	0	3.8640	3.8396	.0243
2	1	0	3.7050	3.6910	.0139
1	1	2	3.2880	3.2658	.0221
2	2	0	2.9760	2.9750	.0009
0	2	2	2.9010	2.9075	-.0065
1	3	0	2.7280	2.7338	-.0058
2	1	2	2.6800	2.6830	-.0030
1	3	1	2.5830	2.5804	.0025
2	2	2	2.3720	2.3669	.0050
3	2	0	2.3080	2.3048	.0031
0	2	3	2.2360	2.2350	.0009
3	1	2	2.1640	2.1608	.0031
0	4	1	2.0970	2.0966	.0003
4	0	1	1.9790	1.9718	.0071
0	0	4	1.9510	1.9534	-.0024
1	3	3	1.8830	1.8857	-.0027
4	2	0	1.8470	1.8455	.0014
4	2	1	1.7920	1.7961	-.0041
3	3	2	1.7670	1.7685	-.0015
1	2	4	1.7350	1.7411	-.0061
2	4	2	1.7230	1.7230	0.0000
3	4	1	1.6620	1.6598	.0021
0	3	4	1.6270	1.6205	.0064
3	4	2	1.5570	1.5577	-.0007
1	6	0	1.4280	1.4284	-.0004
5	3	0	1.4200	1.4212	-.0012
4	4	2	1.3900	1.3901	-.0001

Sum DELTA = .1561 R = .9999932
Sum of Squares = .30246907E-04
8.1510 8.7057 7.8139

R 10829 FH BOURNONITE NONIUS
8.1620 8.7100 7.8100

H	K	L	OBSD	CALCD	DELTA
1	0	0	8.1830	8.1692	.0137
1	1	0	5.9740	5.9593	.0146
0	1	1	5.8470	5.8155	.0314
1	0	1	5.6710	5.6452	.0257
1	1	1	4.7560	4.7376	.0183
0	2	0	4.3700	4.3562	.0137
2	0	0	4.0920	4.0846	.0073
0	0	2	3.9200	3.9050	.0149
1	2	0	3.8570	3.8438	.0131
2	1	0	3.7030	3.6983	.0046
2	1	1	3.3490	3.3425	.0064
1	1	2	3.2730	3.2662	.0067
2	2	0	2.9830	2.9796	.0033
0	2	2	2.9130	2.9077	.0052
2	0	2	2.8260	2.8226	.0033
2	2	1	2.7880	2.7839	.0040
1	3	0	2.7440	2.7363	.0076
2	1	2	2.6900	2.6852	.0047
3	1	0	2.6000	2.5990	.0009
1	3	1	2.5840	2.5824	.0015
3	0	1	2.5710	2.5712	-.0002
1	1	3	2.3900	2.3856	.0043
2	3	0	2.3720	2.3668	.0051
3	2	0	2.3120	2.3090	.0029
1	3	2	2.2440	2.2409	.0030
0	4	0	2.1810	2.1781	.0028
3	1	2	2.1650	2.1636	.0013
1	4	0	2.1070	2.1046	.0023
2	2	3	1.9570	1.9604	-.0034
4	1	1	1.9250	1.9269	-.0019
0	1	4	1.9050	1.9052	-.0002
1	3	3	1.8850	1.8861	-.0011
1	1	4	1.8540	1.8554	-.0014
4	2	1	1.7990	1.7994	-.0004
0	2	4	1.7840	1.7817	.0022
4	1	2	1.7710	1.7719	-.0009
0	5	0	1.7430	1.7425	.0004
1	5	0	1.7030	1.7041	-.0011
0	4	3	1.6710	1.6705	.0004
1	5	1	1.6630	1.6649	-.0019
1	4	3	1.6340	1.6366	-.0026
1	5	2	1.5620	1.5619	0.0000

Sum DELTA = .2115 R = .9999975
Sum of Squares = .94967483E-05
8.1692 8.7125 7.8100

R 10829 PB BOURNONITE NONIUS
8.1620 8.7100 7.8100

H	K	L	OBSD	CALCD	DELTA
1	0	0	8.2490	8.1653	.0836
1	1	0	5.9880	5.9594	.0285
0	1	1	5.8530	5.8216	.0313
1	0	1	5.6800	5.6481	.0318
1	1	1	4.7620	4.7401	.0218
0	2	0	4.3780	4.3588	.0191
2	0	0	4.1000	4.0826	.0173
0	0	2	3.9280	3.9105	.0174
1	2	0	3.8600	3.8452	.0147
2	1	0	3.7100	3.6972	.0127
2	0	1	3.6310	3.6192	.0117
1	1	2	3.2800	3.2694	.0105
2	2	0	2.9870	2.9797	.0072
0	2	2	2.9180	2.9108	.0071
2	0	2	2.8320	2.8240	.0079
2	2	1	2.7900	2.7844	.0055
1	3	0	2.7460	2.7376	.0083
2	1	2	2.6930	2.6866	.0063
1	3	1	2.5860	2.5839	.0020
3	0	1	2.5730	2.5705	.0024
0	1	3	2.5020	2.4977	.0042
3	1	1	2.4540	2.4656	-.0116
1	1	3	2.3930	2.3884	.0045
2	2	2	2.3730	2.3700	.0029
2	3	1	2.2670	2.2659	.0010
1	3	2	2.2440	2.2427	.0012
0	4	0	2.1830	2.1794	.0035
3	1	2	2.1660	2.1640	.0019
1	4	0	2.1090	2.1057	.0032
2	3	2	2.0200	2.0252	-.0052
4	1	0	1.9900	1.9875	.0024
2	2	3	1.9580	1.9620	-.0040
0	3	3	1.9430	1.9405	.0024
4	1	1	1.9250	1.9263	-.0013
0	1	4	1.9050	1.9078	-.0028
1	3	3	1.8870	1.8879	-.0009
1	1	4	1.8560	1.8578	-.0018
3	1	3	1.8410	1.8402	.0007
4	2	1	1.8010	1.7990	.0019
0	2	4	1.7860	1.7840	.0019
4	1	2	1.7730	1.7718	.0011
0	5	0	1.7440	1.7435	.0004
3	2	3	1.7290	1.7283	.0006
1	5	0	1.7040	1.7050	-.0010
0	4	3	1.6730	1.6721	.0008

R 10829 PB BOURNONITE NONIUS (Cont'd.)

H	K	L	OBSD	CALCD	DELTA
1	5	1	1.6650	1.6659	-.0009
1	4	3	1.6360	1.6381	-.0021
5	1	0	1.6040	1.6051	-.0011
0	5	2	1.5920	1.5924	-.0004
5	1	1	1.5710	1.5723	-.0013
1	5	2	1.5620	1.5629	-.0009
5	2	0	1.5290	1.5292	-.0002

Sum DELTA = .3599 R = .9999970
Sum of Squares = .19155821E-04
8.1653 8.7176 7.8210

R12108 BOURNONITE
8.1620 8.7100 7.8100

H	K	L	OBSD	CALCD	DELTA
1	1	0	5.9010	5.9525	-.0515
0	2	0	4.3710	4.3527	.0182
2	0	0	4.0920	4.0788	.0131
0	0	2	3.9140	3.9049	.0090
2	1	0	3.7050	3.6934	.0115
1	1	2	3.2760	3.2651	.0108
2	2	0	2.9860	2.9762	.0097
0	2	2	2.9190	2.9067	.0122
2	0	2	2.8290	2.8206	.0083
1	3	0	2.7360	2.7340	.0019
2	1	2	2.6880	2.6833	.0046
3	1	0	2.5970	2.5955	.0014
2	2	2	2.3720	2.3671	.0048
3	2	0	2.3080	2.3061	.0018
0	2	3	2.2360	2.2342	.0017
3	1	2	2.1640	2.1616	.0023
1	4	0	2.1040	2.1028	.0011
3	2	2	1.9860	1.9857	.0002
0	0	4	1.9510	1.9524	-.0014
1	4	2	1.8500	1.8514	-.0014
4	1	2	1.7700	1.7699	0.0000
1	2	4	1.7380	1.7404	-.0024
2	4	2	1.7230	1.7230	0.0000
3	4	1	1.6620	1.6603	.0016
4	3	1	1.6300	1.6317	-.0017
3	4	2	1.5570	1.5580	-.0010
4	4	0	1.4870	1.4881	-.0011
3	4	3	1.4240	1.4228	.0011
4	4	2	1.3900	1.3905	-.0005

Sum DELTA = .0548 R = .9999978
Sum of Squares = .86493635E-05
8.1576 8.7054 7.8099

R 13491 BOURNONITE
8.1620 8.7100 7.8100

H	K	L	OBSD	CALCD	DELTA
2	2	0	2.9760	2.9767	-.0007
0	2	2	2.9100	2.9080	.0019
2	0	2	2.8200	2.8229	-.0029
1	3	0	2.7400	2.7335	.0064
2	1	2	2.6840	2.6852	-.0012
3	1	0	2.5970	2.5967	.0002
2	3	0	2.3660	2.3645	.0014
3	2	0	2.3050	2.3069	-.0019
0	2	3	2.2410	2.2358	.0051
0	4	0	2.1740	2.1758	-.0018
1	4	0	2.1020	2.1024	-.0004
1	4	1	2.0340	2.0302	.0037
3	3	0	1.9850	1.9845	.0004
0	0	4	1.9550	1.9545	.0004
1	3	3	1.8830	1.8862	-.0032
1	4	2	1.8520	1.8516	.0003
3	3	2	1.7680	1.7695	-.0015
1	2	4	1.7420	1.7419	0.0000
2	4	2	1.7240	1.7233	.0006
3	4	0	1.7000	1.6992	.0007
1	5	1	1.6620	1.6634	-.0014
3	4	2	1.5580	1.5583	-.0003
4	3	1	1.6330	1.6322	.0007

Sum DELTA = .0066 R = .9999985
Sum of Squares = .44281924E-05
8.1619 8.7033 7.8182

S14-B3 BOURNONITE
8.1620 8.7100 7.8100

H	K	L	OBSD	CALCD	DELTA
0	1	1	5.8620	5.8059	.0560
0	2	0	4.1680	4.3499	-.1819
2	0	0	4.0920	4.0787	.0132
0	0	2	3.8720	3.8980	-.0260
2	1	0	3.7120	3.6929	.0190
1	0	2	3.4900	3.5171	-.0271
1	1	2	3.2700	3.2607	.0092
2	2	0	2.9860	2.9753	.0106
0	2	2	2.9140	2.9029	.0110
2	0	2	2.8160	2.8180	-.0020
1	3	0	2.7320	2.7324	-.0004
2	1	2	2.6840	2.6808	.0031
3	1	0	2.5900	2.5953	-.0053
2	2	2	2.3690	2.3650	.0039
3	2	0	2.3080	2.3057	.0022
0	2	3	2.2360	2.2309	.0050
3	1	2	2.1640	2.1602	.0037
1	4	0	2.1020	2.1015	.0004
4	0	0	2.0430	2.0393	.0036
3	3	0	1.9840	1.9835	.0004
0	0	4	1.9510	1.9490	.0019
1	0	4	1.8950	1.8956	-.0006
4	2	0	1.8480	1.8464	.0015
3	1	3	1.8290	1.8363	-.0073
4	2	1	1.7920	1.7967	-.0047
3	3	2	1.7670	1.7678	-.0008
1	2	4	1.7380	1.7378	.0001
2	4	2	1.7230	1.7217	.0012
3	4	1	1.6620	1.6595	.0024
4	3	1	1.6270	1.6312	-.0042
3	4	2	1.5570	1.5570	0.0000
5	1	2	1.4850	1.4829	.0020
5	3	0	1.4220	1.4219	0.0000
4	4	2	1.3900	1.3898	.0001

Sum DELTA = -.1092 R = .9999901
Sum of Squares = .46405495E-04
8.1574 8.6998 7.7960

W-2 BOURNONITE LEAST SQUARES NONIUS
8.1620 8.7100 7.8100

H	K	L	OBSD	CALCD	DELTA
1	0	0	8.1770	8.1524	.0245
1	1	0	5.9750	5.9516	.0233
0	1	1	5.8400	5.8178	.0221
1	0	1	5.6620	5.6428	.0191
1	1	1	4.7520	4.7356	.0163
0	2	0	4.3700	4.3543	.0156
2	0	0	4.0940	4.0762	.0177
0	0	2	3.9140	3.9091	.0048
1	2	0	3.8540	3.8408	.0131
2	1	0	3.7000	3.6918	.0081
1	1	2	3.2730	3.2673	.0056
2	2	0	2.9780	2.9758	.0021
0	2	2	2.9100	2.9089	.0010
2	0	2	2.8250	2.8214	.0035
2	2	1	2.7830	2.7811	.0018
1	3	0	2.7420	2.7347	.0072
0	3	1	2.7250	2.7213	.0036
2	1	2	2.6860	2.6840	.0019
3	1	0	2.6000	2.5941	.0058
1	3	1	2.5810	2.5813	-.0003
3	0	1	2.5670	2.5668	.0001
2	2	2	2.3680	2.3678	.0001
3	2	0	2.2840	2.3053	-.0213
2	3	1	2.2650	2.2633	.0016
1	3	2	2.2420	2.2408	.0011
0	2	3	2.2340	2.2362	-.0022
0	4	0	2.1780	2.1771	.0008
3	1	2	2.1610	2.1614	-.0004
1	4	0	2.1040	2.1034	.0005
1	4	1	2.0270	2.0312	-.0042
0	0	4	1.9560	1.9545	.0014
0	3	3	1.9380	1.9392	-.0012
2	4	0	1.9230	1.9204	.0025
0	4	2	1.9020	1.9020	0.0000
0	2	4	1.7840	1.7831	.0008
4	1	2	1.7720	1.7695	.0024
0	4	3	1.6710	1.6708	.0001
3	4	1	1.6620	1.6603	.0016
0	3	4	1.6210	1.6213	-.0003
2	5	0	1.6020	1.6016	.0003
3	1	4	1.5600	1.5610	-.0010
5	2	0	1.5270	1.5269	0.0000

W-2 BOURNONITE LEAST SQUARES NONIUS (Cont'd.)

H	K	L	OBSD	CALCD	DELTA
2	5	2	1.4810	1.4820	-.0010
1	4	4	1.4320	1.4318	.0001
3	4	3	1.4230	1.4233	-.0003

Sum DELTA = .1881 R = .9999963
Sum of Squares = .19542148E-04
8.1524 8.7087 7.8183

S2-SX SELIGMANNITE
8.0560 8.6770 7.5750

H	K	L	OBSD	CALCD	DELTA
1	1	0	5.9000	5.9148	-.0148
0	1	1	5.6680	5.7333	-.0653
1	0	1	5.5160	5.5326	-.0166
1	1	1	4.6630	4.6708	-.0078
0	2	0	4.3480	4.3572	-.0092
2	0	0	4.0230	4.0270	-.0040
1	2	0	3.8340	3.8323	.0016
0	0	2	3.8050	3.8065	-.0015
2	1	0	3.6540	3.6556	-.0016
1	2	1	3.4180	3.4231	-.0051
2	1	1	3.2930	3.2954	-.0024
1	1	2	3.2000	3.2009	-.0009
0	2	2	2.8700	2.8666	.0033
2	2	1	2.7620	2.7567	.0052
1	3	0	2.7220	2.7325	-.0105
2	1	2	2.6380	2.6366	.0013
3	1	0	2.5660	2.5657	.0002
3	0	1	2.5310	2.5319	-.0009
3	1	1	2.4330	2.4313	.0016
1	1	3	2.3340	2.3321	.0018
3	2	0	2.2860	2.2856	.0003
2	3	1	2.2530	2.2506	.0023
1	3	2	2.2180	2.2198	-.0018
0	4	1	2.0890	2.0945	-.0055
3	3	0	1.9720	1.9716	.0003
4	1	0	1.9620	1.9618	.0001
2	4	0	1.9260	1.9161	.0098
0	3	3	1.9030	1.9111	-.0081
1	4	2	1.8430	1.8407	.0022
4	2	1	1.7740	1.7773	-.0033
3	3	2	1.7500	1.7507	-.0007
4	1	2	1.7440	1.7438	.0001
2	0	4	1.7240	1.7207	.0032

Sum DELTA = -.1267 R = .9999913
Sum of Squares = .20825467E-04
8.0541 8.7145 7.6130

S-4 SELIGMANNITE REHEAT
8.0560 8.6770 7.5750

H	K	L	OBSD	CALCD	DELTA
1	1	0	5.8620	5.9282	-.0662
1	0	1	5.6040	5.5521	.0518
1	1	1	4.7160	4.6848	.0311
0	2	0	4.3920	4.3646	.0273
2	0	0	4.0550	4.0381	.0168
0	0	2	3.8140	3.8226	-.0086
1	2	1	3.4300	3.4313	-.0013
1	1	2	3.2060	3.2126	-.0066
2	0	2	2.7780	2.7760	.0019
1	3	0	2.7160	2.7375	-.0215
1	3	1	2.5830	2.5772	.0057
1	1	3	2.3360	2.3412	-.0052
1	3	2	2.2310	2.2256	.0053
0	4	1	2.1020	2.0984	.0035
3	3	0	1.9810	1.9760	.0049
0	3	0	2.8870	2.9097	-.0227
3	0	3	1.8500	1.8507	-.0007
4	2	0	1.8270	1.8325	-.0055
4	0	2	1.7890	1.7853	.0036
3	3	2	1.7540	1.7554	-.0014
2	4	2	1.7170	1.7156	.0013

Sum DELTA = .0136 R = .9999874
Sum of Squares = .19823904E-04
8.0763 8.7292 7.6452

S5-A REHEAT LOW AIKINITE
11.3200 11.6600 4.0100

H	K	L	OBSD	CALCD	DELTA
1	2	0	5.1810	5.1754	.0055
2	2	0	4.0730	4.0569	.0160
0	1	1	3.8140	3.8032	.0107
1	3	0	3.6450	3.6700	-.0250
1	1	1	3.6010	3.6051	-.0041
0	2	1	3.3240	3.3099	.0140
1	2	1	3.1730	3.1768	-.0038
2	2	1	2.8640	2.8570	.0069
4	1	0	2.7570	2.7492	.0077
3	1	1	2.6850	2.6783	.0066
2	4	0	2.5760	2.5877	-.0117
4	2	0	2.5440	2.5445	-.0005
2	3	1	2.5060	2.5045	.0014
0	4	1	2.3510	2.3579	-.0069
3	4	0	2.3020	2.3040	-.0020
4	1	1	2.2680	2.2700	-.0020
2	5	0	2.1640	2.1527	.0112
5	2	0	2.0920	2.1095	-.0175
0	5	1	2.0170	2.0149	.0020
1	5	1	1.9840	1.9837	.0002
5	3	0	1.9510	1.9550	-.0040
0	2	2	1.8920	1.9016	-.0096
4	4	1	1.8190	1.8113	.0076
1	3	2	1.7650	1.7643	.0006
3	6	0	1.7230	1.7251	-.0021
4	5	1	1.6410	1.6413	-.0003
2	4	2	1.5890	1.5884	.0005
7	2	0	1.5590	1.5577	.0012
3	4	2	1.5180	1.5155	.0024
5	6	0	1.4740	1.4729	.0010
4	7	0	1.4320	1.4335	-.0015
8	1	0	1.4050	1.4043	.0006

Sum DELTA = .0050 R = .9999898
Sum of Squares = .46965171E-04
11.3174 11.6392 4.0241

106760 AIKINITE
11.3200 11.6600 4.0100

H	K	L	OBSD	CALCD	DELTA
1	1	0	8.1190	8.1204	-.0014
0	2	0	5.7980	5.8330	-.0350
1	2	0	5.1560	5.1841	-.0281
2	2	0	4.0340	4.0602	-.0262
1	0	1	3.7870	3.7856	.0013
1	3	0	3.6490	3.6773	-.0283
1	1	1	3.5970	3.6007	-.0037
0	2	1	3.2970	3.3085	-.0115
2	0	1	3.2830	3.2750	.0079
3	2	0	3.1660	3.1662	-.0002
2	1	1	3.1420	3.1531	-.0111
0	4	0	2.8910	2.9165	-.0255
2	2	1	2.8430	2.8557	-.0127
3	0	1	2.7340	2.7491	-.0151
3	1	1	2.6600	2.6758	-.0158
2	3	1	2.5200	2.5050	.0149
3	2	1	2.4890	2.4867	.0022
3	4	0	2.2940	2.3068	-.0128
5	1	0	2.2260	2.2206	.0053
2	5	0	2.1610	2.1568	.0041
5	2	0	2.0850	2.1090	-.0240
0	0	2	2.0040	2.0086	-.0046
5	0	1	1.9700	1.9710	-.0010
5	3	0	1.9530	1.9552	-.0022
6	0	0	1.8820	1.8850	-.0030
2	1	2	1.8640	1.8683	-.0043
2	6	0	1.8390	1.8386	.0003
4	4	1	1.8190	1.8118	.0071
6	2	0	1.7930	1.7937	-.0007
1	3	2	1.7620	1.7628	-.0008
0	6	1	1.7440	1.7501	-.0061
6	0	1	1.7130	1.7065	.0064
2	6	1	1.6730	1.6719	.0010
0	4	2	1.6580	1.6542	.0037
4	2	2	1.5790	1.5765	.0024
6	3	1	1.5650	1.5626	.0023
0	7	1	1.5380	1.5393	-.0013
4	3	2	1.5090	1.5091	-.0001
0	8	0	1.4590	1.4582	.0007
4	7	0	1.4380	1.4357	.0022

Sum DELTA = -.2141 R = .9999849
Sum of Squares = .82021897E-04
11.3102 11.6660 4.0173

A-6 AIKINITE SYNTHETIC
11.3200 11.6600 4.0100

H	K	L	OBSD	CALCD	DELTA
1	2	0	5.2730	5.1837	.0892
2	2	0	4.1110	4.0641	.0468
0	3	0	3.8550	3.8854	-.0304
1	3	0	3.6970	3.6757	.0212
0	2	1	3.3300	3.2984	.0315
2	3	0	3.2010	3.2051	-.0041
0	4	0	2.8820	2.9141	-.0321
4	1	0	2.7730	2.7548	.0181
3	3	0	2.7040	2.7094	-.0054
2	4	0	2.6010	2.5918	.0091
0	5	0	2.3250	2.3312	-.0062
1	5	0	2.2910	2.2835	.0074
3	3	1	2.2550	2.2434	.0115
2	4	1	2.1690	2.1752	-.0062
5	2	0	2.1090	2.1136	-.0046
4	4	0	2.0340	2.0320	.0019
4	3	1	1.9960	1.9876	.0083
5	3	0	1.9630	1.9587	.0042
3	5	1	1.7730	1.7776	-.0046
1	6	1	1.7310	1.7272	.0037
1	7	0	1.6460	1.6475	-.0015
2	7	0	1.5990	1.5977	.0012
6	3	1	1.5620	1.5643	-.0023
3	7	0	1.5250	1.5238	.0011
0	8	0	1.4590	1.4570	.0019
3	5	2	1.4080	1.4087	-.0007
5	6	1	1.3830	1.3843	-.0013
3	8	0	1.3580	1.3595	-.0015

Sum DELTA = .1562 R = .9999902
Sum of Squares = .46896149E-04
11.3405 11.6564 4.0008

DIAPHORITE HIGH PHASE
5.7330

H	K	L	OBSD	CALCD	DELTA
1	1	1	3.3100	3.3065	.0034
2	0	0	2.8700	2.8635	.0064
2	0	2	2.0200	2.0248	-.0048
3	1	1	1.7300	1.7267	.0032
2	2	2	1.6500	1.6532	-.0032
4	0	0	1.4300	1.4317	-.0017
3	1	3	1.3200	1.3138	.0061
4	2	0	1.2800	1.2806	-.0006
4	2	2	1.1700	1.1690	.0009
3	3	3	1.1000	1.1021	-.0021

Sum DELTA = .0074 R = .9999903
Sum of Squares = .47951481E-04
5.7271

BM 88839 DIAPHORITE
15.8490 5.9010 17.9140 116.4200

H	K	L	OBSD	CALCD	DELTA
2	0	-3	5.6760	5.6440	.0319
2	1	-2	4.5480	4.5409	.0070
3	1	0	3.6740	3.6851	-.0111
3	0	2	3.4370	3.4470	-.0100
0	1	4	3.3120	3.3142	-.0022
3	0	3	2.9380	2.9429	-.0049
1	2	0	2.8820	2.8890	-.0070
0	1	5	2.8200	2.8159	.0040
1	2	4	2.2470	2.2478	-.0008
2	2	-6	2.0970	2.0953	.0016
4	2	2	2.0340	2.0336	.0003
3	0	-9	1.9840	1.9836	.0003
5	0	-9	1.9510	1.9496	.0013
0	3	2	1.9120	1.9106	.0013
6	0	3	1.8720	1.8708	.0011
3	3	-1	1.8400	1.8400	0.0000
7	0	-9	1.7890	1.7903	-.0013
6	2	1	1.7630	1.7620	.0009
1	3	4	1.7110	1.7114	-.0004
3	1	7	1.6970	1.6968	.0001
0	2	8	1.6570	1.6571	-.0001
3	2	6	1.6410	1.6419	-.0009

Sum DELTA = .0110 R = .9999991
Sum of Squares = .23549004E-05
15.8191 5.9024 17.9068 116.5336

R1034 FREIESLEBENITE NONIUS
7.5325 12.7869 5.9534 9.2268

H	K	L	OBSD	CALCD	DELTA
1	1	0	6.4863	6.4870	-.0006
0	1	1	5.3936	5.4050	-.0113
1	2	0	4.8727	4.8890	-.0162
1	1	-1	4.4606	4.4630	-.0023
1	2	-1	3.8178	3.8200	-.0021
2	0	0	3.7633	3.7630	.0003
1	2	1	3.7230	3.7230	0.0000
2	1	0	3.6102	3.6110	-.0007
0	3	1	3.4647	3.4760	-.0112
2	2	0	3.2431	3.2410	.0021
2	0	1	3.1249	3.1290	-.0040
2	1	1	3.0356	3.0420	-.0063
0	0	2	2.9744	2.9740	.0004
0	1	2	2.8970	2.8940	.0030
2	3	0	2.8210	2.8260	-.0049
1	1	-2	2.7393	2.7390	.0003
0	2	2	2.6968	2.6960	.0008
2	3	-1	2.5787	2.5760	.0027
1	2	2	2.5103	2.5100	.0003
3	1	0	2.4619	2.4630	-.0010
2	0	-2	2.3798	2.3820	-.0021
3	2	0	2.3354	2.3350	.0004
2	4	-1	2.2751	2.2750	.0001
1	5	-1	2.2527	2.2540	-.0012
1	5	1	2.2328	2.2320	.0008
3	2	-1	2.2017	2.2010	.0007
0	6	0	2.1311	2.1370	-.0058
2	3	-2	2.0778	2.0780	-.0001
2	3	2	2.0171	2.0180	-.0008
1	6	1	1.9321	1.9270	.0051
4	0	0	1.8816	1.8810	.0006

Sum DELTA = -.0529
Sum Delta 1/D Square = 0.0000

S-F-3 FREIESLEBENITE HIGH PHASE
5.7760

H	K	L	OBSD	CALCD	DELTA
1	1	1	3.3300	3.3373	-.0073
2	0	0	2.8820	2.8902	-.0082
2	0	2	2.0410	2.0436	-.0026
3	1	1	1.7420	1.7428	-.0008
2	2	2	1.6680	1.6686	-.0006
4	0	0	1.4460	1.4451	.0008
3	1	3	1.3260	1.3261	-.0001
4	2	0	1.2930	1.2925	.0004

Sum DELTA = -.0185 R = .9999993
Sum of Squares = .17508918E-05
5.7804

S4-F ISOMETRIC HIGH PHASE PB3AG5SB5S12
5.7330

H	K	L	OBSD	CALCD	DELTA
1	1	1	3.3120	3.3088	.0031
2	0	0	2.8640	2.8655	-.0015
2	0	2	2.0300	2.0262	.0037
3	1	1	1.7290	1.7279	.0010
2	2	2	1.6570	1.6544	.0025
4	0	0	1.4340	1.4327	.0012
3	1	3	1.3180	1.3147	.0032
4	2	0	1.2800	1.2815	-.0015
4	2	2	1.1690	1.1698	-.0008
3	3	3	1.1020	1.1029	-.0009

Sum DELTA = .0101 R = .9999967
Sum of Squares = .16067946E-04
5.7310

S15-BR-2 ISOMETRIC HIGH PHASE PBAG2SB2S5
5.7330

H	K	L	OBSD	CALCD	DELTA
1	1	1	3.3000	3.3040	-.0040
2	0	0	2.8640	2.8614	.0025
2	0	2	2.0300	2.0233	.0066
3	1	1	1.7260	1.7254	.0005
4	0	0	1.4330	1.4307	.0022
3	1	3	1.3130	1.3129	0.0000
4	2	0	1.2780	1.2796	-.0016
4	2	2	1.1670	1.1681	-.0011
3	3	3	1.1020	1.1013	.0006

Sum DELTA = .0058 R = .9999977
Sum of Squares = .10758948E-04
5.7228

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