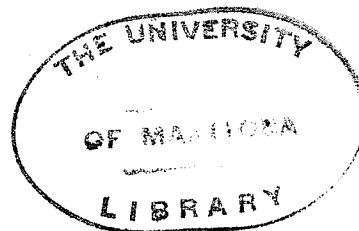


AN INVESTIGATION OF ORE TEXTURES
USING THE VACUUM HEATING STAGE



A Thesis
Presented To
The Faculty of the Department of Geology
of
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In Partial Fulfillment
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Calvert C. Bristol
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ABSTRACT

This study involved the use of the vacuum heating stage and metallographic microscope for the study of microtextures in sulphide ores. Studies of selected specimens have shown alteration of microtextures at relatively low temperatures. These studies were undertaken in the fields of boundary migration (textural change with rise in temperature), solid solution and diffusion, and differences in migration capability of selected minerals.

Alteration of sulphide ore microtextures occurred at temperatures ranging from 105 degrees to 260 degrees centigrade. Microtextures resulting from increase in temperature resembled those typical of replacement in some specimens, exemplified by experiment 'Flin Flon 1' in which a dendritic pattern of sphalerite in pyrite, and veining of chalcopyrite by sphalerite were produced. Two types of microtextural change occur; alteration by vaporization and surface migration, and alteration of the mineral boundaries

by diffusion and solid solution between adjacent mineral grains.

Studies of chalcopyrite specimens undergoing increase in temperature revealed unusual features. At 182 degrees centigrade laths and blades of bornite appeared on the polished specimen face. Junctions between these blades thickened, and the blades lengthened. Because this phenomenon occurred with rising temperature, it is interpreted as being a thermal breakdown product of chalcopyrite, rather than an exsolution product. The shape of the junctions of the blades supports this theory.

Octahedral bornite crystals were formed on upper portions of chalcopyrite specimens used in the diffusion experiments. Its formation was due to thermal breakdown of chalcopyrite and vapor transportation of the constituents. The identity of the sublimation product was proven by X-ray analysis.

It was noted that migration of any particular sulphide mineral is a function of the temperature and concentration of that mineral. In addition, alteration or migration of the boundary between any pair of sulphide minerals is dependent on the degree of solid solution possible between the members of the pair.

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INTRODUCTION

The determination of paragenesis of ore minerals has invoked controversy perhaps since attention was first directed to the study of ore textures. In many specimens, such as with the mixed supergene and hypogene minerals, the relative ages are clearly defined. Elsewhere however, particularly when all the minerals are of apparent hypogene origin, the age relationship may be difficult to ascertain. The crystallization of two or more minerals may be penecontemporaneous, or the early formed minerals may have had time to solidify, be fractured, and other minerals introduced into the fractures. A structural relationship between two ages of crystallization and invading dykes has been defined in several mining areas, notably Butte.

In the present study, microtextures of sulphide ore specimens were observed as the specimens were being heated. This was possible through the use of the Unitron metallographic microscope and vacuum heating stage. With this apparatus it was possible to observe and record photographically any changes in texture which took place with rising specimen temperature.

The equipment had never before been used with sulphide specimens. Therefore, it was necessary to first

discover whether or not the equipment and technique used with metallic specimens could be used, or whether changes must be made. Each experiment brought new discoveries, pointing the way to investigation of new subjects. Because of this, the various experiments are described in order here.

CHAPTER I

Description of the Microscope

The Unitron Model U-11 is an inverted metallographic microscope (see Figure 1a). By use of accessories, the superstructure of the instrument may be adapted for the study of thin sections as well as for the observation of polished sections. Because the observation of thin sections is not concerned in this thesis, the adaptation of the microscope for their use will not be described here.

The illuminating lamp, as arranged for the observation of polished sections, is so positioned that the light passes directly into the right side of the microscope through a small round window. The amount of illumination of the specimen face is controlled by an iris diaphragm located in the lamp, and by the field diaphragm contained in the window unit previously mentioned. Light passing through the window is reflected from a mirror, upward through the objective lens, to the polished face of the specimen. The image is then reflected downward from the face, through the objective lens, to a second mirror which reflects it to the ocular.

A choice of three objective lenses of various

power is available with the instrument. However, if use of the vacuum heating stage is contemplated, it is necessary to employ a forty power long working range objective lens.

If simultaneous observation by more than one person is desired, the stop or slide containing the ocular reflection mirror must be inserted. This allows the mirror to be bypassed; the image then passes downward to the large circular mirror in the base of the instrument. The image is then reflected from this mirror onto a frosted glass screen.

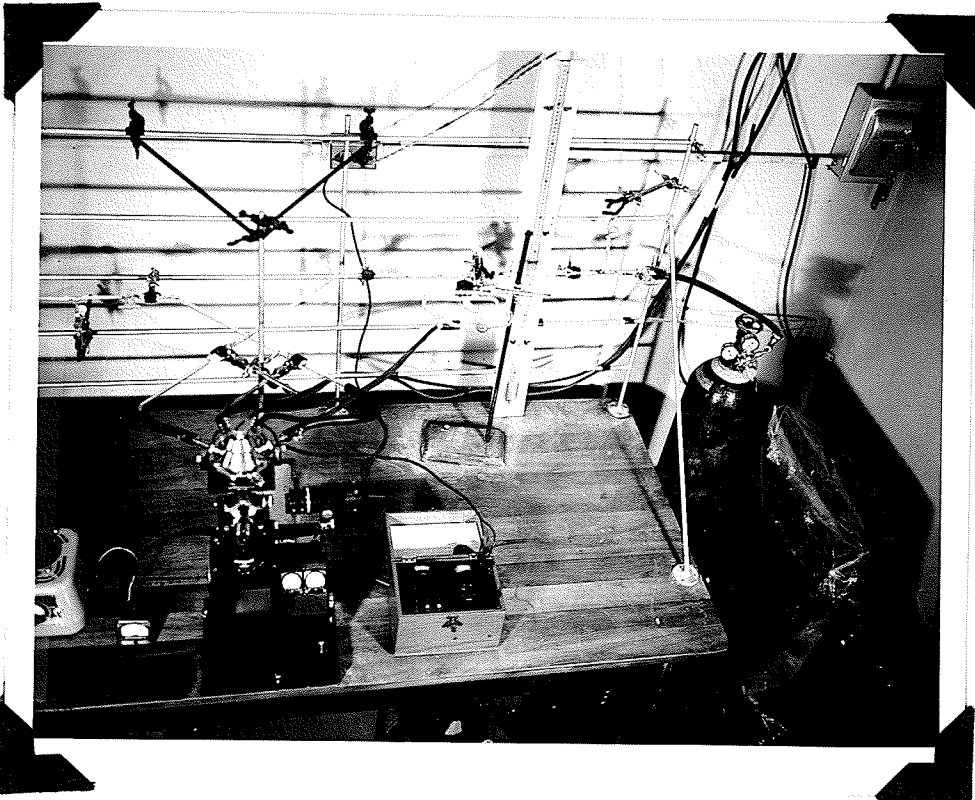
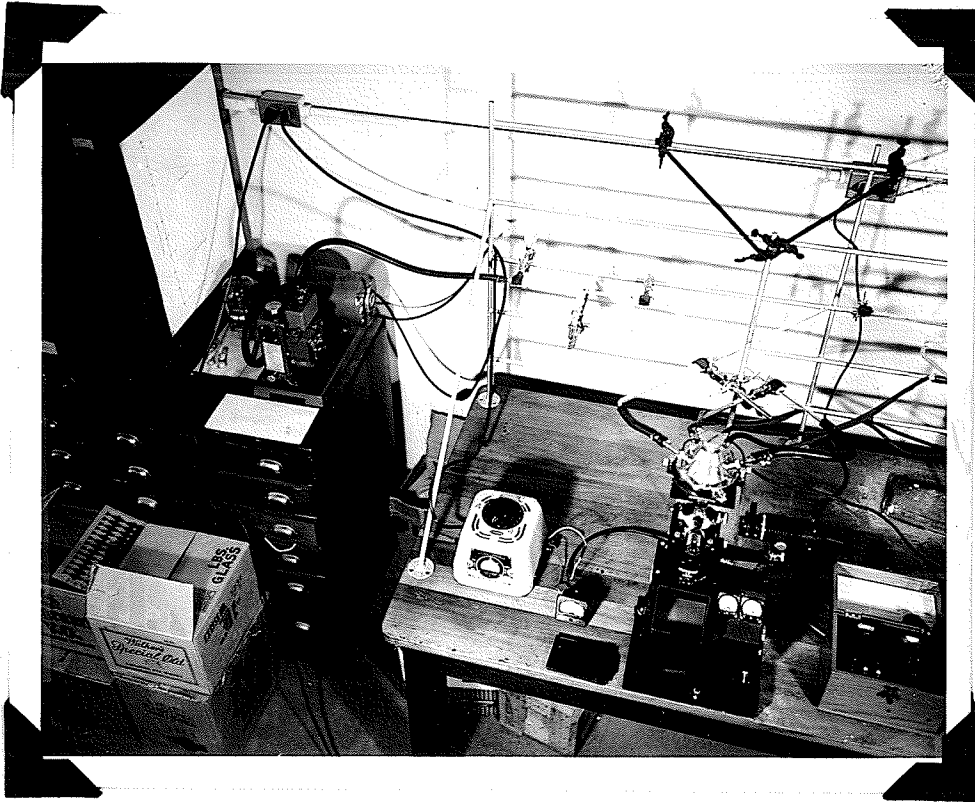
A green filter, yellow filter, converging lens and polarizing lens are built into the lamp unit. The filters are more useful for observing metallic rather than ore specimens, because of the high reflectivity of the former. However, the green filter may be used to ease eye strain encountered with highly reflective specimens containing relatively large amounts of pyrite. The yellow filter was designed for photographic use, but little use was found for it with sulphide specimens because the restriction it places on the amount of light available outbalances any aid in distinction of yellow minerals it may afford. For best results, both polarizing and converging lenses must be used.

Photomicrography

Because of the convenient size of the photographic plates ($3\frac{1}{4}$ " x $4\frac{1}{4}$ ") it was decided to use the camera which is built into the instrument. Exposure times depend on the iris and diaphragm openings used, and the amount of current supplied to the illuminating lamp. In short, photomicrography depends on the amount of light permitted to shine on the specimen, as well as the exposure time, and the type of film used. One more very important factor in photomicrography is the reflectivity of the specific specimen under observation. Specimens containing large amounts of highly reflective minerals obviously require less exposure time than others. Therefore, it is impossible for listed exposure times to have any real meaning. However, it may be helpful to note here that changes of exposure time of less than five seconds have very little effect. Photomicrographs appearing in this thesis were made from Kodak Contrast Process Ortho sheet film.

PLATE I

The Vacuum Heating Stage and Metallographic Microscope



Description of the Model HHS-2 Vacuum Heating Stage

The vacuum heating stage or furnace consists of two stainless steel portions, separated by a rubber gasket, which are bolted together to form an airtight seal. Both portions of the stage are constructed with an integral water cooled jacket for the protection of the stage and adjacent microscope parts while operating at elevated temperatures (see Fig. 1).

Six tapered connection pipes project from the exterior of the heating stage. Two of these are vacuum connections; two are cooling water intake connections, and two are cooling water exhaust connections. Heavy rubber vacuum hose connects the vacuum connections to the rest of the vacuum system. Light, flexible rubber hose connects the cooling water exhaust and intake to the drain and reservoir respectively.

The flat bottom of the stage contains a round quartz window through which the specimen may be observed during the heating process.

Internally, the stage has a moveable quartz shutter which protects the window from condensation and possible obstruction of the view of the specimen in the event of vaporization. Should vapor condense on the shutter,

the shutter may be turned to a clean section, and the polished face of the specimen is again visible. The quartz table upon which the specimen rests lies above the shutter. This table is circular with a round hole 6 mm. in diameter in the centre. Part of the edge of the table has been ground off to provide space for the shutter operating lever. The thermocouple lies across the specimen table, in direct contact with the specimen face. The thermocouple passes through two pinholes in the rubber gasket separating the two halves of the stage, and connects with two terminals on opposite sides of the stage.

The furnace element consists of 0.3 mm. coiled tungsten wire arranged in a spiral groove inside a two-part ceramic sleeve. This sleeve is supported by a hollow ceramic cylinder which in turn is suspended from a stainless steel collar. This collar screws upward into the top half of the heating stage. The two element terminals are built into the top half of the heating stage; the element power wires are connected to the terminals within the heating stage, thus eliminating a possible vacuum leak. The element power lead wires are connected to the external projections of the element terminals (see Fig. 2).

Specimens may be placed in the heating stage in two ways. The usual and easiest method is to lower the

specimen through the opening in the top of the heating stage, until it rests on the specimen table. The second method is to place the specimen on the table previous to bolting the two halves of the stage together. This second method was found useful in dealing with the "two piece" type specimen explained later in this thesis.

The vacuum heating stage is bolted directly on top of the mobile microscope stage with finger bolts. When the rack and pinion indices are aligned, the centre of the specimen face is directly above the centre of the objective lens. Only the 40 power long working range objective lens may be used with the heating stage because the specimen face cannot be brought into focus with other objective lenses.

FIGURE 1

Model HHS-2 Vacuum Heating Stage

1. Upper portion
2. Lower portion
3. Cooling jackets
4. Pressure cap
5. Pressure cap frame and screw
6. Main furnace gasket
7. Pressure cap gasket
8. Vacuum connections
9. Cooling water connections
10. Quartz window
11. Quartz shutter
12. Quartz specimen table
13. Shutter control lever
14. Furnace element
15. Furnace element terminals
16. Thermocouple
17. Interior ceramic cap

VACUUM HEATING STAGE

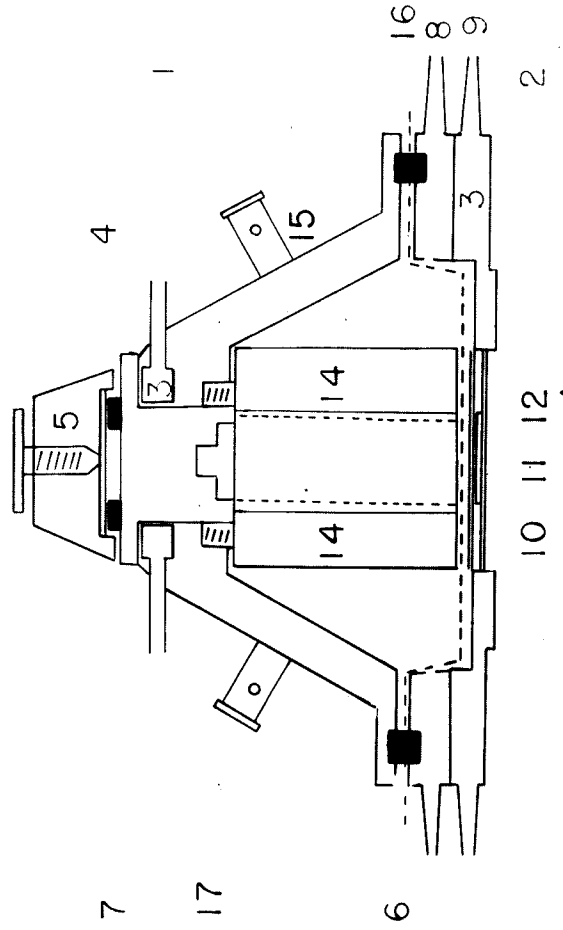


FIGURE 1

FIGURE 2

Furnace Element Designs

1. Ceramic cap
2. Threaded stainless steel suspension socket
3. Mica insulating washer
4. Element suspension adapter for "B" type unit (as modified for use with sulphide specimens)
5. Element holder (type "A")
6. Tungsten wire heating coils
7. Ceramic heating coil container

FURNACE ELEMENT DESIGNS

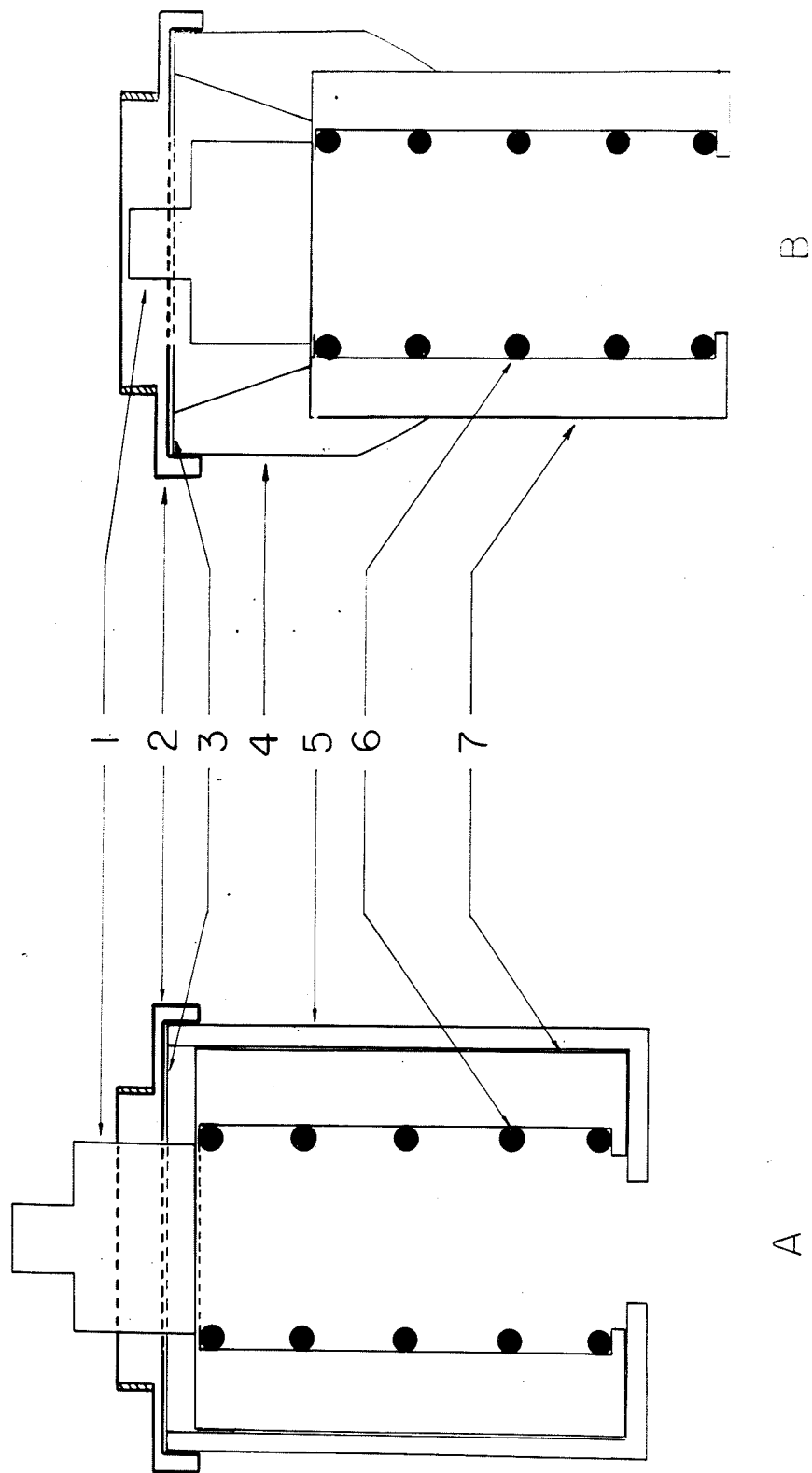


FIGURE 2

Description of the Vacuum - Argon System

The heating stage must be operated with either a high vacuum or an inert gas in its interior because most specimens would oxidize if heated in air (see Fig. 3). The vacuum-argon system constructed for this study was as follows.

One quarter inch glass tubing was employed as extensively as possible to minimize the number of possible vacuum leaks. This tubing was firmly clamped to a steel supporting rack screwed to the table. The Welch Duo-Seal vacuum pump was connected to one end of a single glass tube, the other end of which connected to the vacuum exhaust of the heating stage. The intake vacuum connection projects from the opposite side of the vacuum heating stage from the vacuum exhaust. This was connected to glass tubing which extended to a McLeod vacuum gauge, and from there to a manometer. A short section of glass tubing extended beyond the manometer. To this was connected the argon tank and its accompanying flow regulator and needle valve. Vacuum stopcocks were incorporated into the system as follows:

Two stopcocks were located between the pump and the heating stage, one to release the vacuum and admit air when the system is not in use, and the

other one to seal the evacuated portion of the system from that in which the presence of argon under pressure was desired. One stopcock was placed in the evacuated side of the manometer to seal this from the rest of the system when a measurement of argon pressure was made. One stopcock was located between the manometer and the argon tank to close off that end of the system.

Although not employed in the system used for this study, an additional stopcock, located between the heating stage and the McLeod vacuum gauge, is recommended. Its presence completes the compartmentation of the system and facilitates the search for vacuum leaks.

All stopcocks used are those of the vacuum type, with oblique bore and vacuum bulb. Elastic bands must be employed to hold the stopcock barrels and the McLeod gauge in place when argon is used under pressure in the system. The pressure would otherwise blow these out with possible resulting breakage.

All connections between glass tubing and the heating stage, the argon tank, and the pump were made with medium walled heavy rubber vacuum hose.

Maintenance of the Vacuum-Argon System

Suggestions for the maintenance of vacuum systems are available in many physics and chemistry publications. However, most geologists are not familiar with these. Therefore, a few of the remedies for problems particular to this system will be noted here.

Leaks in the vacuum system occur most often in the main rubber gasket which separates the upper and lower portions of the heating stage. Light to medium applications of heavy silicone vacuum grease on this and the pressure cap gasket usually rectify this situation. After continual use, or long periods of disuse, small leaks develop in the main gasket. These are probably in the pinholes through which the thermocouple passes. Regreasing of the gasket almost invariably fails to correct this condition and it is necessary to replace the gasket. This involves threading the thermocouple through the pinholes in the new gasket. Care must be taken not to kink the thermocouple during this process.

All connections between the metal parts of the heating stage and the rubber vacuum hose, and between the vacuum hose and the glass tubing of the system must be

greased and clamped with music wire to guard against pressure leaks.

FIGURE 3

Combination Vacuum-Pressure System Employed with
the Vacuum Heating Stage

1. Vacuum pump
2. Exhaust stopcock
3. Pressure stopcock
4. Heating stage and microscope
5. McLeod vacuum guage
6. Manometer
7. Manometer stopcock
8. Vacuum stopcock
9. Needle valve
10. Argon tank

ARGON VACUUM
SYSTEM

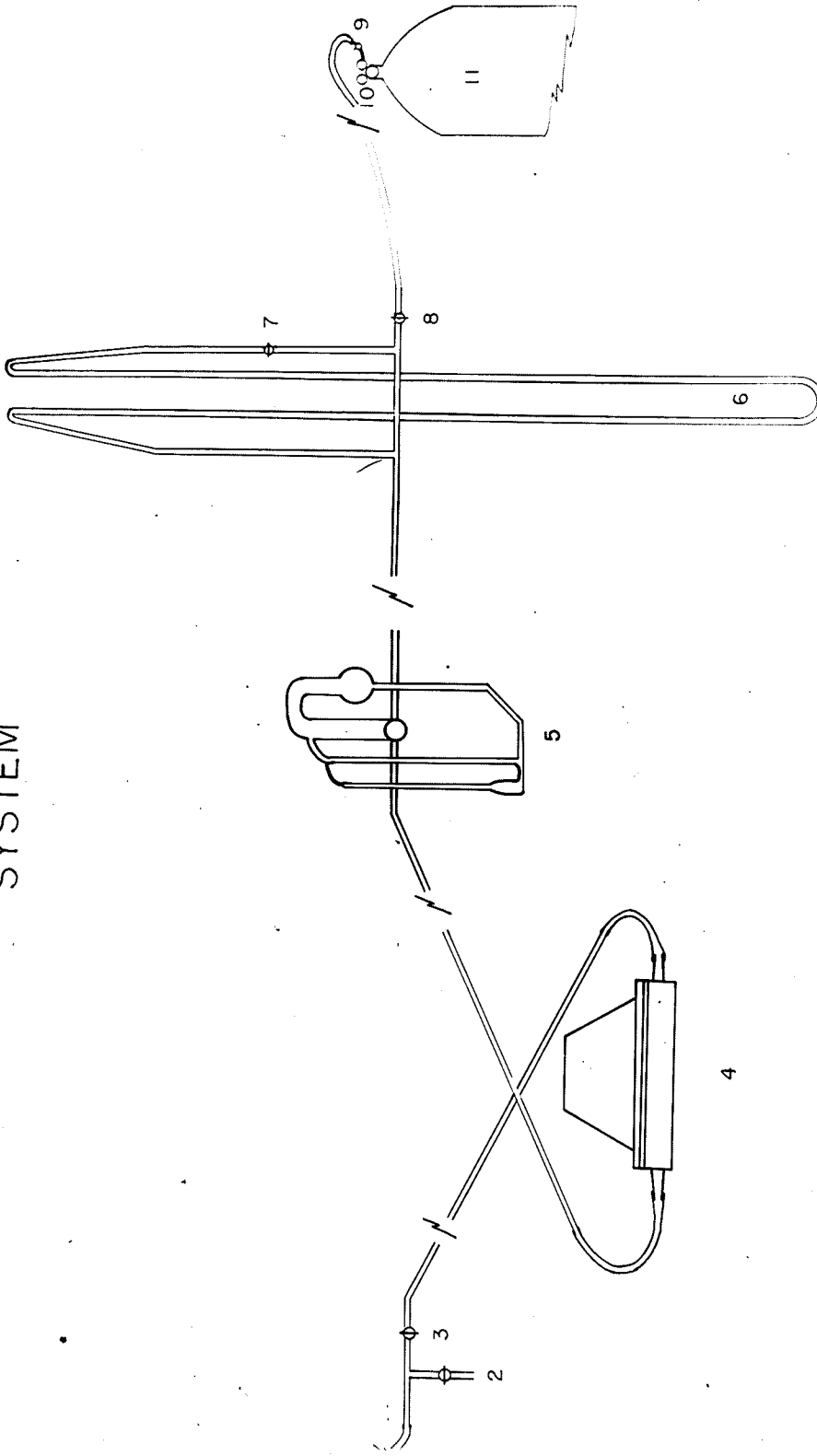


FIGURE 3

Description of the Electrical Heating Circuit

The voltbox with rheostat was plugged into the ordinary 115 volt A.C. outlet. The voltbox, ammeter, and heating stage element were connected in a series circuit. Control of the amount of current supplied to the heating stage was provided by the built-in rheostat in the voltbox.

Description of the Heating Stage Cooling Stage

A circulating cooling water system was incorporated in the heating stage to protect the stage and neighboring parts during periods of high operating temperature (see Fig. 4). Therefore, both the upper and lower halves of the stage are manufactured with integral water cooling jackets. Intake and exhaust connections project from the two halves of the stage. These are connected by ordinary thin walled rubber hoses to glass tubing which lead to the water reservoir and the drain respectively.

To avoid fluctuations of the interior heating stage temperature during an experiment, it is necessary to maintain a constant rate of flow of water through the cooling jackets. The rate of water flow was controlled by the height of water in the reservoir.

FIGURE 4

Electrical and Cooling Systems

1. Vacuum heating stage
2. Voltbox
3. AC ammeter
4. Heavy insulated copper wire
5. Cooling system - water reservoir
6. Cooling system - intake hoses and glass tubes
7. Cooling system - exhaust hoses and glass tubes
8. Drain
9. Water supply to reservoir
10. Leeds and Northrup multirange pyrometer
11. Thermocouple connecting wires

ELECTRICAL and COOLING SYSTEMS

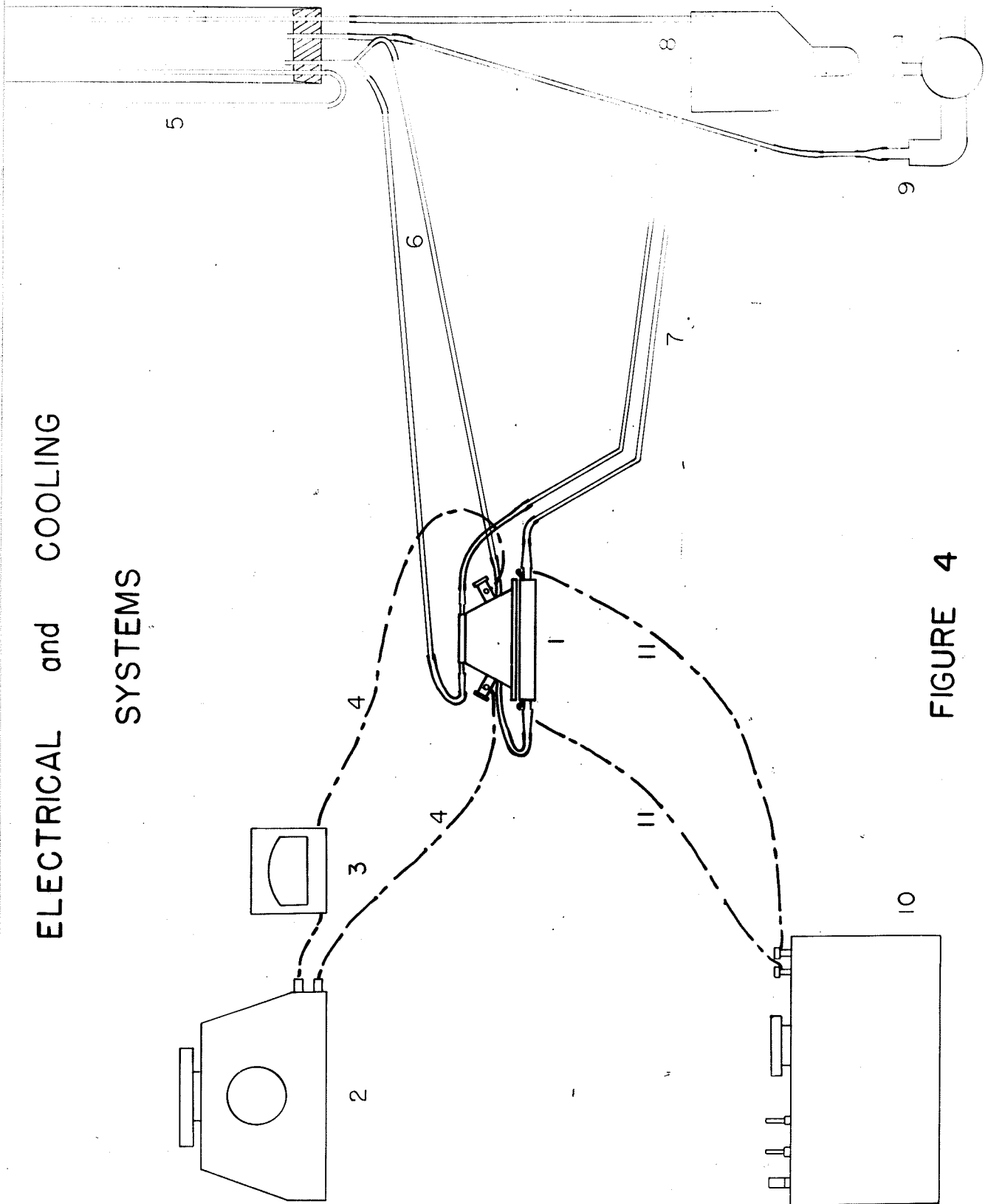


FIGURE 4

CHAPTER II

PROCEDURESSelection and Preparation of the Specimen

Specimens are chosen primarily for a given mineral assemblage. Secondly, the specimens should be fine grained, contain little if any gangue, and be capable of easy shaping or milling. Large crystals, such as are common to Tri-State ore, must be avoided because they expand, and shatter along cleavages during heating. Specimens containing large amounts of gangue heat unevenly, and may crack or even shatter. At best, variable phenomena occur on the polished faces of these specimens due to the uneven heating. Friable ore, such as that from Sullivan mine, British Columbia, and banded ore, typical of the New Brunswick copper-lead-zinc camp, is very difficult to shape. Careful cutting and grinding of specimens of these latter types produce only short cylinders which must be placed in the heating stage by method number two, previously described.

Specimens were first cut from the hand specimens to approximately the correct size, using the diamond saw. They were then rounded on the electric grindstone. The sides of the upper one-fourth of the cylindrical specimens were ground flat to form a small handle with which to grasp

them with the forceps, prior to placing or removing the specimens in or from the heating stage.

The specimen should have the following dimensions:

Diameter	8.0 - 8.5 mm.
Length	20.0 - 25.0 mm.

Minerals with good cleavage which will not withstand the vibration of shaping on the edge of the grinding wheel, such as sphalerite, may sometimes be shaped by holding them with their sides against the side of the grinding wheel. In milling or shaping, care should be taken to ensure that the face of the specimen to be polished is perpendicular to the long axis of the specimen, as any deviation from this will cause the side of the specimen to rest against the coils of the heating element. In the latter case two things may happen, either the polished face will not be perpendicular to the optic "train" of the microscope and the image is not visible, or uneven heating may cause vaporization.

Diamond abrasives were employed in the polishing process to eliminate optical relief between minerals of different hardness. The use of diamond abrasives yields much faster and better results than those obtained with other abrasives.

Solid specimens were polished on one face only.

Specimens of the 'two part' type, described later, had the two interfaces as well as the primary face polished so that the interfaces could be studied optically after the experiment had been completed.

Operation of the Vacuum Heating Stage

The specimen is placed in the interior of the heating stage using the forceps provided and the inner ceramic lid is lowered in place. The pressure cap is fitted to the top of the stage and is held by the clamp. The exhaust stopcock is now closed, and the system checked to see that all other stopcocks are open. The vacuum pump is then started and argon is flushed through the system. The system must next be evacuated until a reading of at least 10^{-4} is obtained on the McLeod vacuum gauge. This may take as much as two hours. During this time, the face of the specimen may be observed so that an interesting area may be chosen as an initial viewing point during heating. Prior to heating, one or several photomicrographs of the original texture of the area to be observed during heating must be taken. This is necessary because changes occurring in the texture during heating are not always easily noticed, and former textures are almost impossible to remember.

When the required vacuum is attained, the electricity may be turned on, and a current of 2 - 3 volts and about 1 - $1\frac{1}{2}$ amperes is supplied to the element. This voltage is held constant for at least ten minutes to allow the element to warm up slowly. Further current increases should be very small when heating ore specimens. Heating rates supplied by the manufacturer are for highly conductive metals and alloys. Attempts to heat sulphide specimens at these rates invariably end in partial vaporization of the specimen, obscuring observation by condensation on the quartz window. This condensation is due to the low sublimation temperature of the sulphur in the sulphides and it has been found that vaporization (or sublimation) results primarily from increasing the temperature of the specimen too rapidly rather than from too high a temperature. However, there is an upper limit to the temperature to which a specimen may be raised at the chosen operating pressure. This limit to the temperature to which any specimen may be raised is dependent on the maximum pressure under which the heating stage may operate. There is one further reason for a low heating rate. The furnace element is made of coiled tungsten wire and with increasing temperature, the electrical resistance of the tungsten increases, thus with too high a heating rate, there is risk of melting the furnace element.

At 125 degrees centigrade, the pressure and manometer stopcocks are closed, the argon regulator is already open so that only argon is present between it and the needle valve. Argon is now introduced slowly into the system until a pressure of approximately 91 cm. Hg. is shown on the manometer. Care must be taken that a higher pressure is not reached because the argon expands during heating. The pressure may increase to the point where the mercury column moves above or below the ends of the meter stick used as reference. With the closing of the pressure stopcock, and the introduction of the argon, the pump may be shut off and the exhaust stopcock opened until such time as the heating stage has cooled to a temperature where a pressure inside the heating stage is not needed to inhibit vaporization. However, it is wise to leave the exhaust stopcock closed and the pump running, maintaining a vacuum in that short section of the system directly connected to the pump. Should the specimen inadvertently be allowed to vaporize, the condition may often be rectified thusly:

1. Stop the heating by shutting off the voltbox rheostat. This is important, particularly at elevated temperatures.
2. Open the pressure stopcock allowing the pump

to evacuate the hot contaminated argon. It will be noticed that the field of the microscope clears.

3. Open the needle valve, flush clean argon through the system. This further clears the field.
4. Close the pressure stopcock, fill the system with fresh argon, restoring to the original operating pressure.
5. The voltbox rheostat may now be turned up to the previous high reading and the heating continued.

The above steps must be carried out as rapidly as possible, having due regard for such possible accidents as knocking the microscope or introducing too high an argon pressure. The speed with which this operation can be done is important, particularly at high temperatures, because further vaporization can be prevented by quickly replacing the gas pressure on the specimen.

During the heating process, changes in the polished face of the specimen may take place. As these are observed, they may be recorded photographically.

It will be noted that argon is introduced into the heating stage when it has attained a temperature of between 100 and 150 degrees centigrade, the lower of these temperatures is not critical, and argon may be introduced anytime after the stage has been evacuated, and before the temperature has risen to 150 degrees centigrade.

When the experiment has been completed, the electric current is shut off, using the voltbox rheostat. The heating stage will immediately start to cool. When the temperature has fallen to approximately 125 degrees centigrade, the pressure stopcock may be opened, and the hot gas evacuated. The vacuum must be maintained however, until the inside heating stage temperature has fallen to about room temperature. Then, the vacuum pump may be shut off and the heating stage opened to extract the specimen for further study with the regular reflecting microscope and X-ray methods.

CHAPTER III

DESCRIPTION AND RESULTS OF SULPHIDE HEATINGEXPERIMENTS

Early experiments in the heating of sulphide ore specimens in the vacuum heating stage were directed primarily towards determining the feasibility of using the equipment for this purpose. The first specimens were cut from drill core from the Bathurst, New Brunswick district.

In the hope of inhibiting any sublimation or vaporization of the specimen during heating, a pressure of 0.5 atmosphere of argon was chosen as the first operating pressure. With limited knowledge of the sublimation or vaporization temperatures and pressures of the sulphide minerals, it was understandable that these first experiments should end in partial vaporization of the specimen. It was observed that as the vaporization progressed, the polished face of the specimen remained intact so it was concluded that vaporization was taking place on the remote upper portions of the specimens. Development of better technique facilitated continuous observation from room temperature to 437 degrees centigrade.

Surface Migration

In early work, alteration of the mineral boundaries was observed, particularly that of sphalerite and chalcopyrite. This alteration appeared to be a superficial type caused by migration of material over the polished surface. The migrating material appeared dark brown to dark gray with feather-like edges and pebbly looking interior.

Development of surface migration progresses in the following manner. The migrating material spreads over the other minerals in the section as a thin, feather-like film which develops into a continuous film with a pebbly appearance through which the underlying minerals may be poorly seen. The development of these films was due to local sublimation on the polished surface.

The following series of photomicrographs taken during the heating of specimen number 'Anaconda Caribou B.H. 28 368' shows the progressive surface migration of sphalerite over pyrite and chalcopyrite.

Photomicrograph 1 (Plate 2). Shows the original texture of the area under observation. Pyrite, chalcopyrite, and sphalerite present. Exposed at room temperature.

Photomicrograph 2 (Plate 2). Same area; surface migration of sphalerite has begun in top centre and right centre of photo. Photo exposed at 156 degrees centigrade.

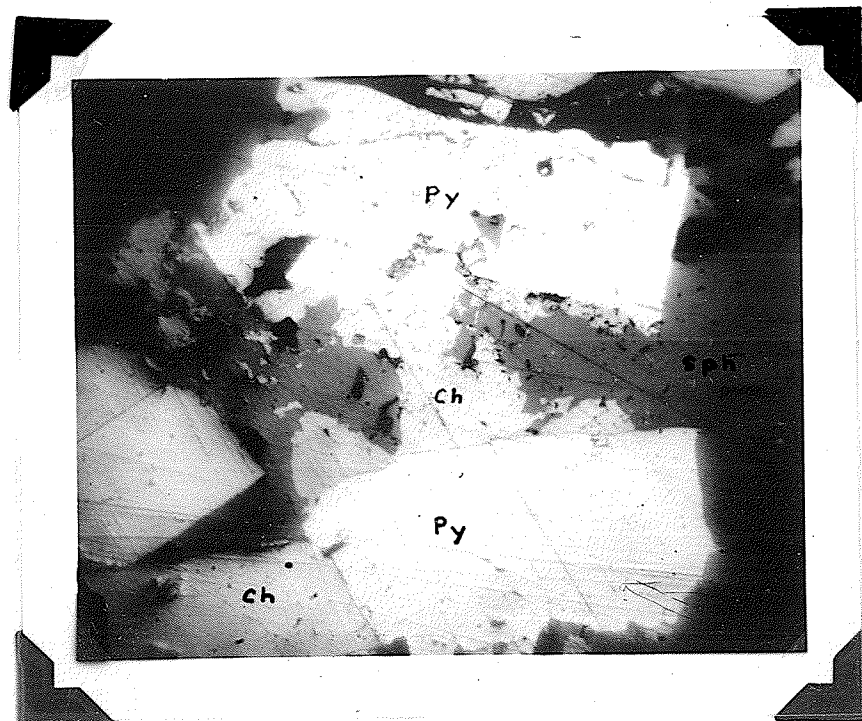
Photomicrograph 3 (Plate 3). Illustrates the extent of migration at 171 degrees centigrade, 0.5 atm. of argon pressure.

Photomicrograph 4 (Plate 3). Shows clearly the type of migration and its extent at 240 degrees centigrade, 0.5 atm. argon pressure.

Photomicrograph 5 (Plate 4). Note pitting caused by vaporization of the polished surface, and the streaks and blades of light coloured material in the gray sphalerite. This latter is possibly an exsolution of incipient chalcopyrite from solid solution in the sphalerite.

PLATE 2

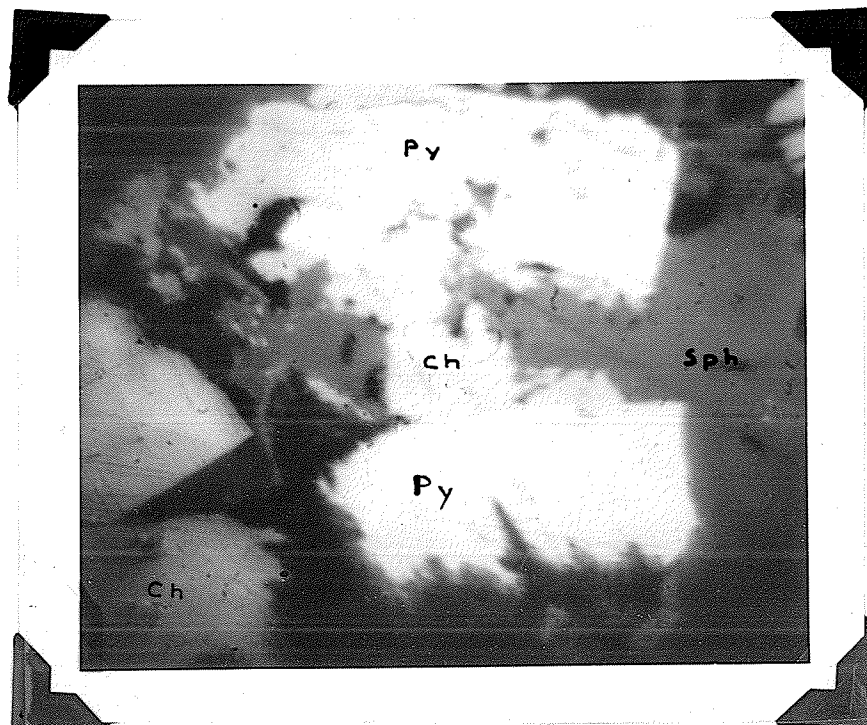
Photomicrographs of Anaconda Caribou B.H. 28 368' (2)



1

X 400

Room Temperature



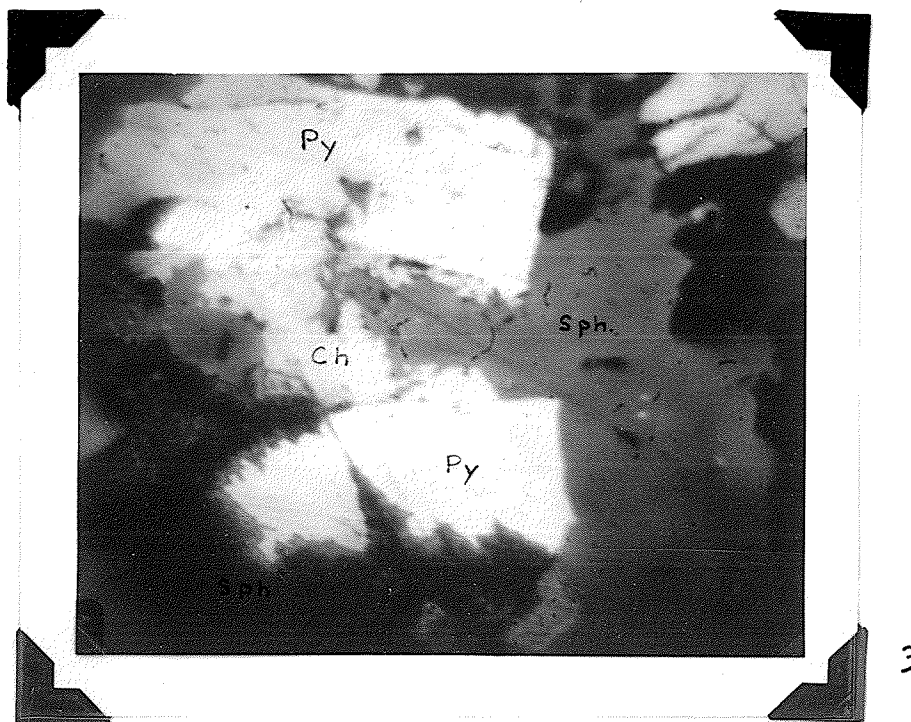
2

X 400

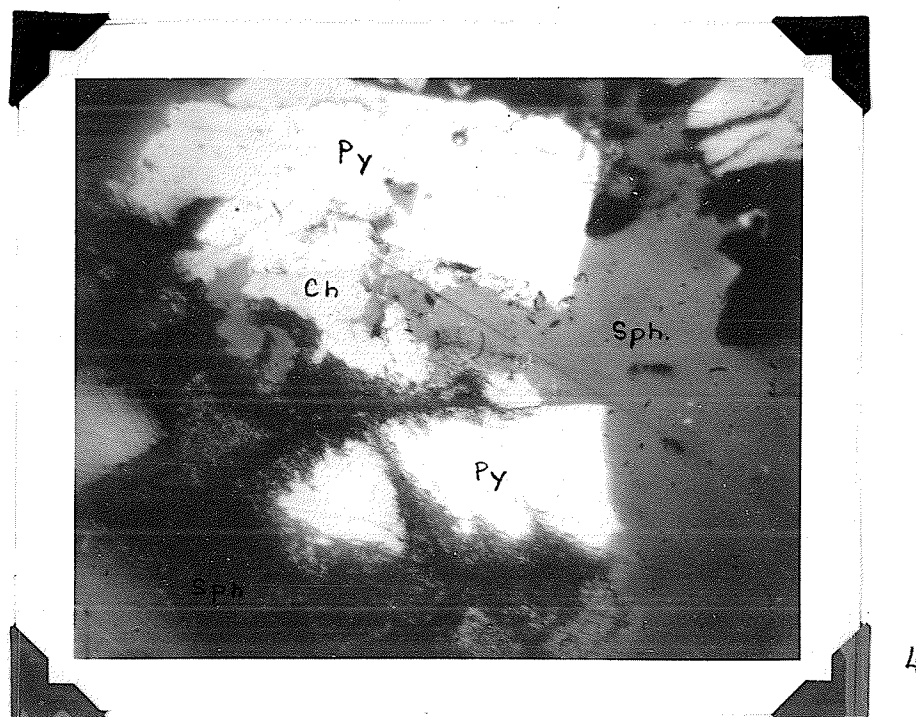
156 Degrees Centigrade

PLATE 3

Anaconda Caribou B.H. 28 368' (2)



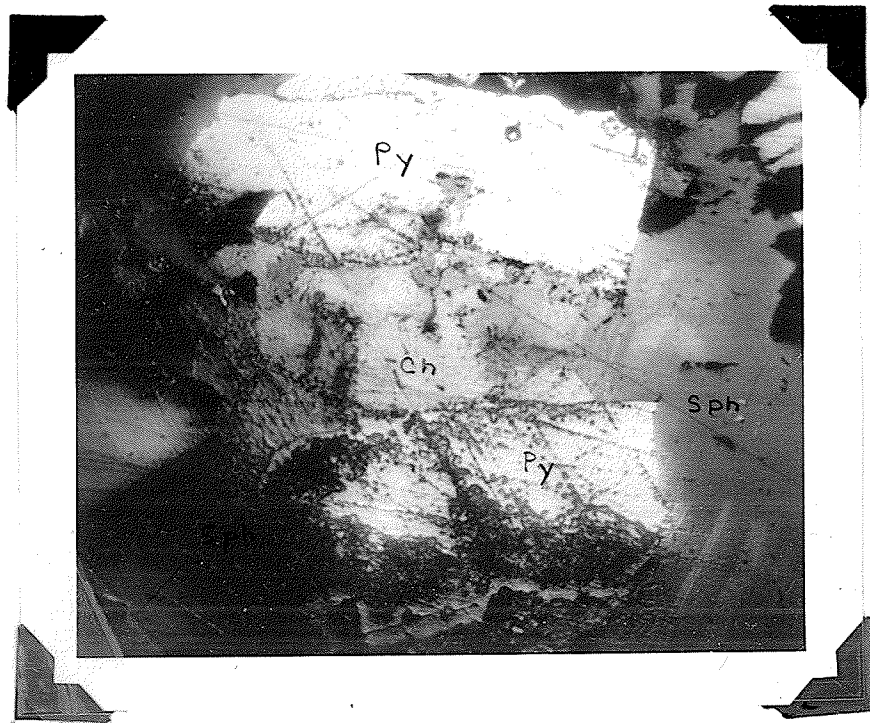
X 400 171 degrees centigrade.
0.5 Atm. Argon pressure



X 400 240 degrees centigrade
0.5 Atm. Argon pressure

PLATE 4

Anaconda Caribou B.H. 28 368' (2)



X 400

254 Degrees Centigrade

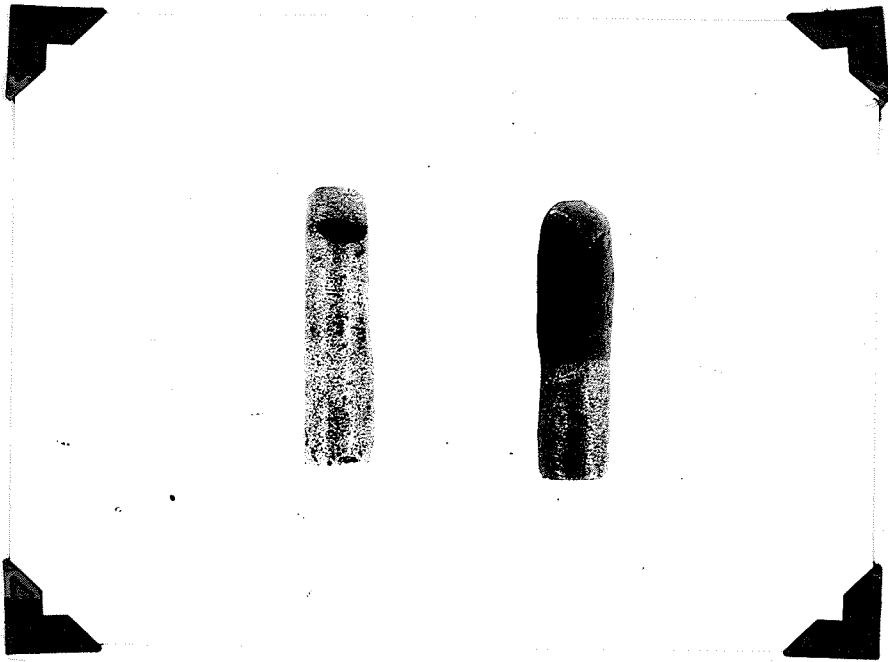
0.5 Atm. Argon Pressure

When the specimens used in these early experiments were removed from the heating stage, it was noticed that their upper portions were swollen and in some extreme cases split open, while their lower portions had not experienced the same phenomena (see Plate 5, page 38). Minor fracturing was noted in the polished face of some specimens after modifications of the heating stage interior had been made. It was apparent therefore, that an appreciable temperature gradient was present within the heating stage. This condition was partially corrected by unscrewing the steel suspension collar several turns, thus lowering the furnace element to cover more of the specimen.

Observation of ore minerals during heating was attempted by P. E. Auger and O. Maurice at Laval University in 1945, (1945, pp. 345 - 352). The purpose of their work was to find a new method for identification of ore minerals. As the temperature of the minerals rose, Auger and Maurice noted a thin scum or film forming on the polished face of the specimen. This film, and its tenacity, were used as criteria for mineral identification. The specimens treated by Auger and Maurice were heated in air, and probably oxidized, so that the observed films were not true migrational products. Auger and Maurice obtained varying results in re-heating some specimens. They believed this was due to the

loss of volatiles during the first runs on the specimens, and explained the variation thusly, "According to Schwartz this may be due to the fact that certain minerals have an inversion point which is below the temperature of affectation". The "affectation" temperature mentioned by Auger and Maurice is apparently the temperature at which the thin films are noticeable. They therefore preheated all specimens at 200 degrees centigrade for specified lengths of time prior to placing them in the furnace. Preheating drove off all volatiles and forced the inversion to a higher form of all minerals whose inversion temperature lay below the affectation temperature. Current work with the vacuum heating stage has shown that some solid solutions take place at lower temperatures and also at higher pressures than those present when a specimen is preheated at 200 degrees centigrade in air. The result being, depending on the mineral assemblage, that the minerals identified by the heating method may be solid solutions of the original minerals.

Comparison of swollen and split specimen with
unheated specimen



X 2

Development of Replacement Textures

Results of early experiments showed that two changes, one in technique, the other in equipment, were required prior to further experimentation. In subsequent tests the pressure of the argon gas was raised to 91 cm. Hg. and the heating stage element was lowered relative to the specimen as previously described. As a result of these changes, vaporization was reduced to a point where it could be controlled. Surface migration was held to a minimum. The work of this section was concerned with textural changes in sulphide mineral assemblages induced by heating in inert atmosphere. Some of these changes are exemplified in experiment 'Flin Flon 1', performed just after the above outlined changes were made.

Flin Flon 1

Photomicrograph 1 (Plate 6) shows the original microtexture of the area under study, containing pyrite, sphalerite, chalcopyrite. This was exposed at room temperature.

At 82 degrees centigrade, in a vacuum, the chalcopyrite-pyrite boundaries began to tarnish. This is illustrated in photomicrograph 2 (Plate 6).

At 85 degrees centigrade argon was introduced into the system until a pressure of 45 Cm. Hg. was reached.

At 99 degrees centigrade, reaction rims surrounding grains of chalcopyrite originally embedded in large grains of pyrite were observed. These reaction rims took the form of yellow halos, fading outward into the brass yellow of the pyrite grains. These reaction rims are not illustrated here.

At 129 degrees centigrade a minor vaporization occurred, partially fogging the shutter. The temperature was raised to 170 degrees centigrade, the microscope field clearing with rising temperature. Simultaneous with this temperature rise, small areas of sphalerite located between large grains of pyrite (observed in the original texture) appeared to grow dendritically into the pyrite and to react with chalcopyrite blebs in the same area. The pattern resembled a typical replacement texture. Photomicrograph 3 (Plate 7) shows the migration of sphalerite and minor vaporization phenomena developed in this temperature range.

Photomicrograph 4 (Plate 7) shows the replacement texture after the section had been chilled, removed from the heating stage, and repolished to remove any surface phenomena. See centre area photo 4 (Plate 7). This indicates that this migration was not of the surface type.

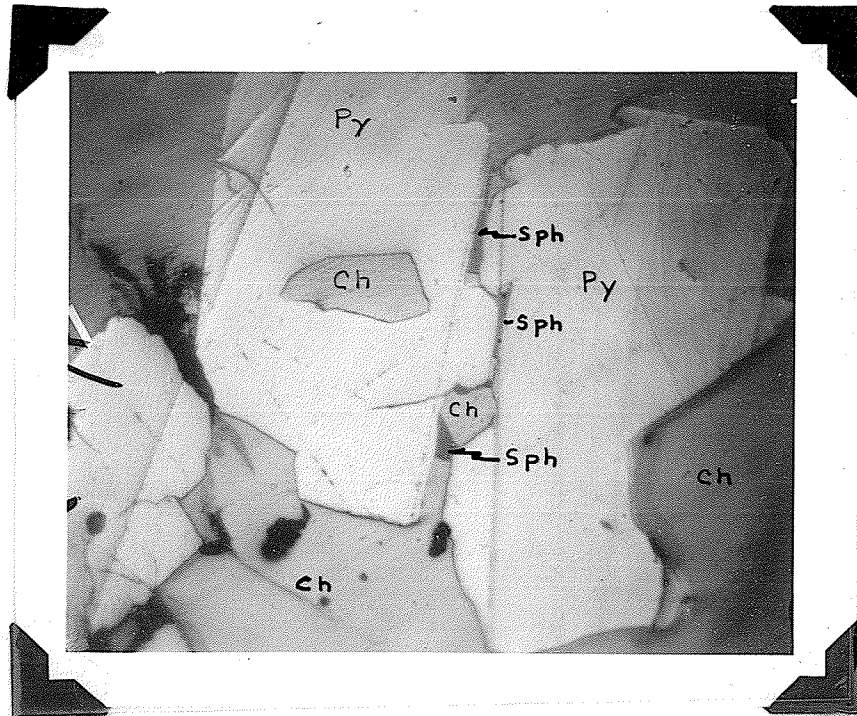
A comparison of photomicrographs 1 (Plate 6) and 4 (Plate 7) shows the type and extent of non-surface migration developed in this experiment. Development of replacement textures is clear. Comparison of photomicrographs 1, 5, and 6 (Plates 6 and 8 respectively) also reveals considerable amounts of sphalerite in chalcopyrite. This is shown in the right centre and upper right portions of the aforementioned photomicrographs. Photomicrograph 1 (Plate 6) (original microtexture) shows relatively small amounts of sphalerite present in the original polished surface. Photomicrographs 5 and 6 (Plate 8) show large areas of sphalerite relative to the original texture Photomicrograph 1 (Plate 6). Photomicrographs 4 to 7 (Plates 7 to 9) record the development of sphalerite veining in chalcopyrite over the temperature range 165 degrees to 273 degrees centigrade.

Positive identification of the migrating material was accomplished by ordinary methods using the reflecting microscope and X-ray diffraction method. X-ray analysis information can be found in appendix A.



PLATE 6

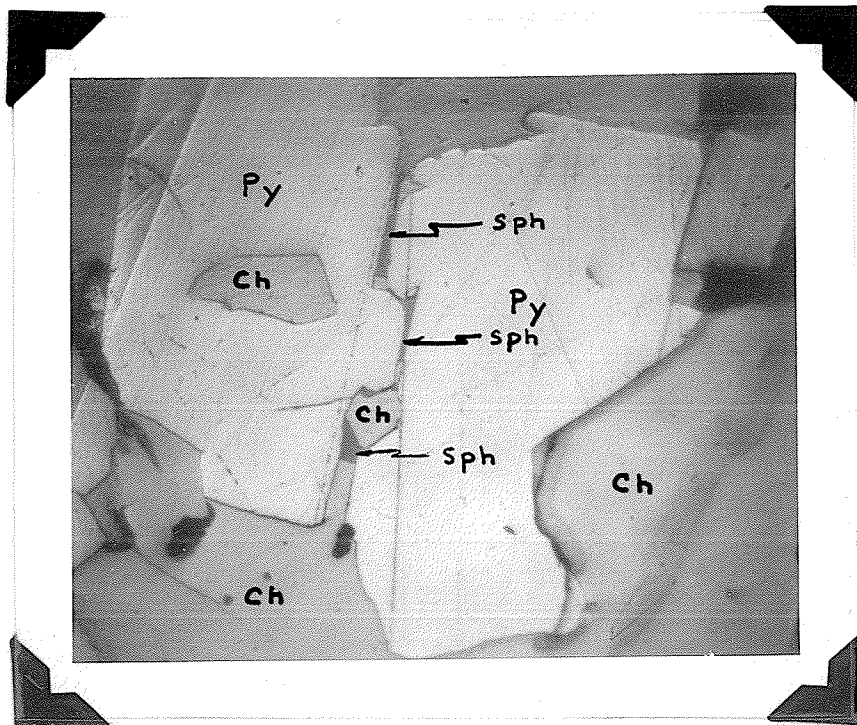
Development of Replacement Microtextures in
Specimen 'Flin Flon 1'



1

X 400

Room Temperature



2

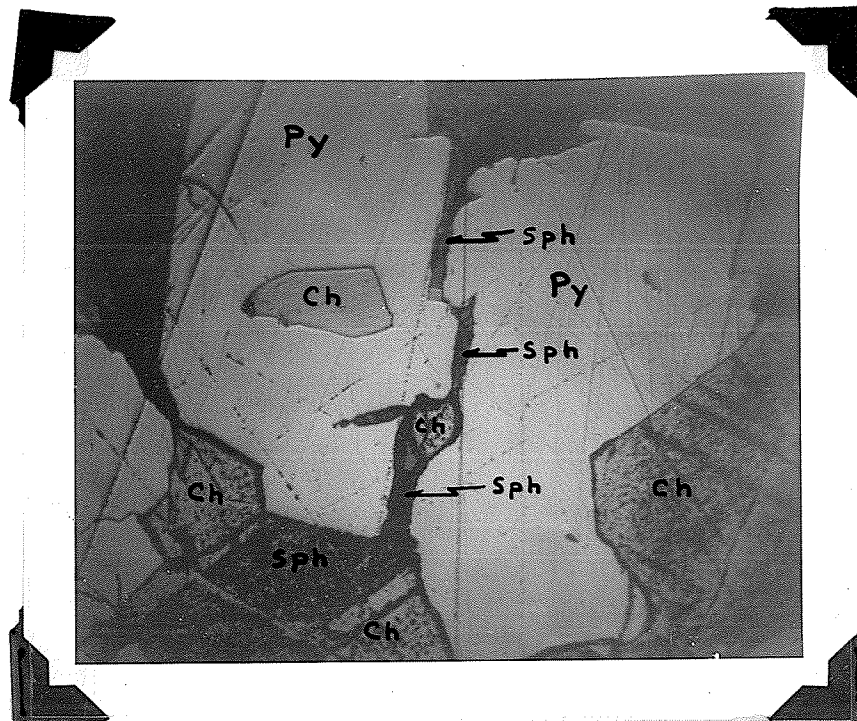
X 400

82 Degrees Centigrade

Vacuum

PLATE 7

Flin Flon 1

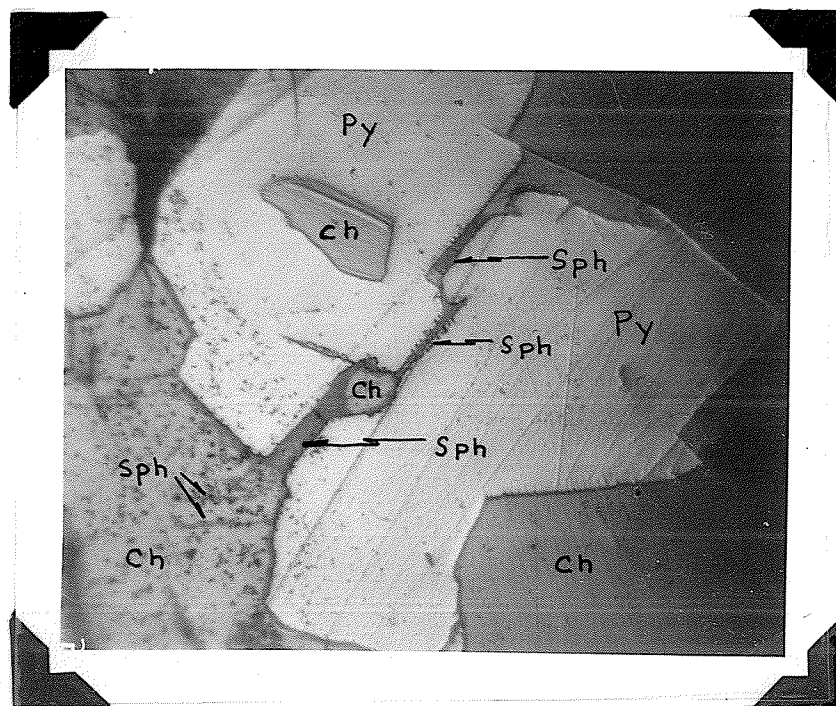


3

X 400

170 Degrees Centigrade

45 Cm. Hg. Argon Pressure



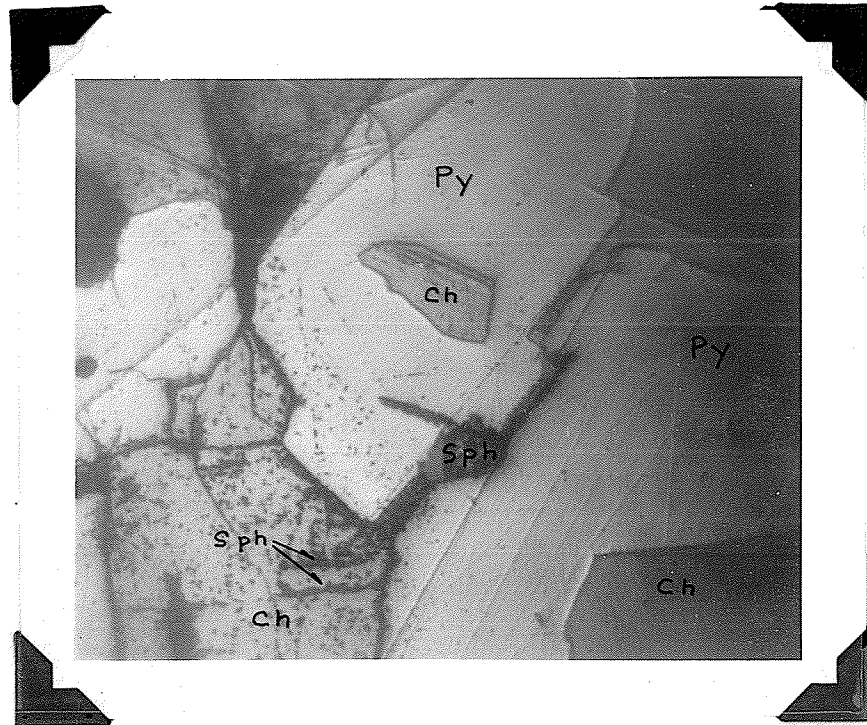
4

X 400

Room Temperature

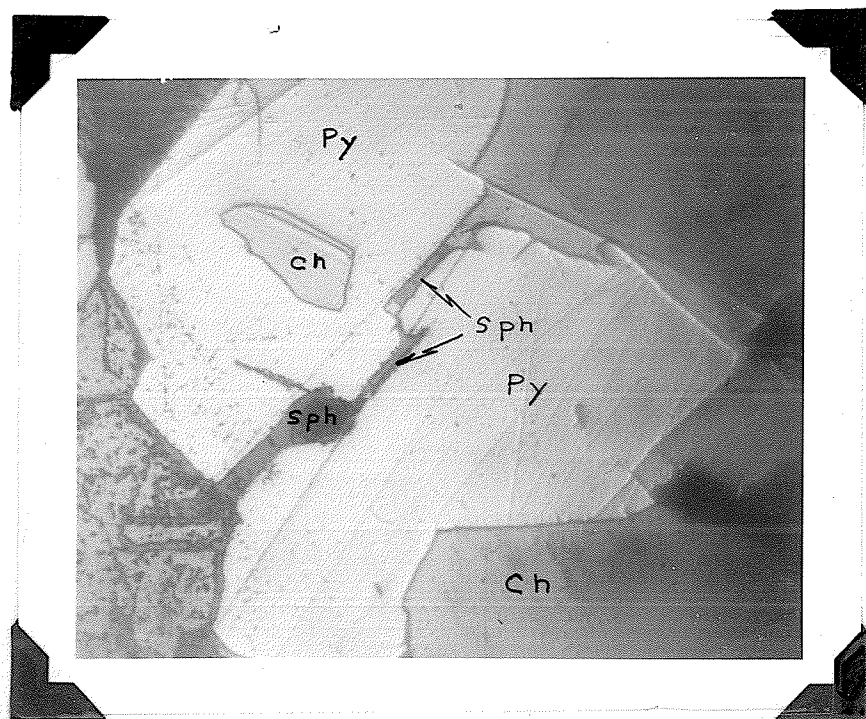
Same area after chilling and Repolishing

PLATE 8
Flin Flon 1



5

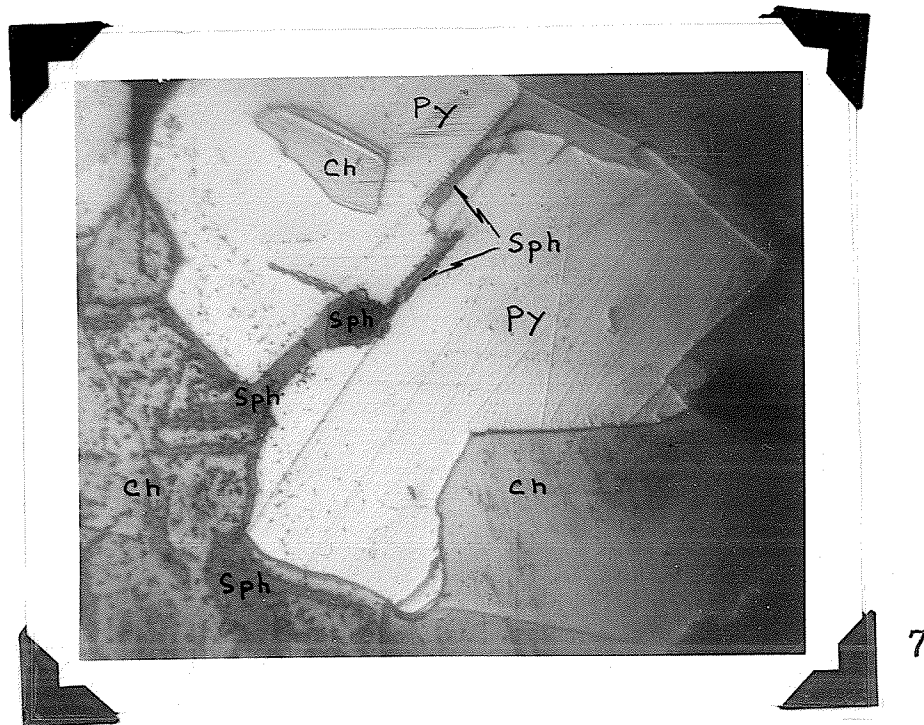
X 400 165 Degrees Centigrade
0.6 Atm. Argon Pressure



6

X 400 196 Degrees Centigrade
0.6 Atm. Argon Pressure

PLATE 9
Flin Flon 1



X 400 273 Degrees Centigrade
0.6 Atm. Argon Pressure

CHAPTER IV

DISCUSSION OF SOLID SOLUTION AND DIFFUSION

The subject of solid solution and diffusion is not new. Auger and Maurice noted the formation of surface films during their sulphide heating experiments (1945, p. 345 - 352). J. S. Dunn (1931, p. 22 - 28) explained the thickening of these films by a diffusion toward the surface of the elements of the mineral itself.

Virginia Ross (1954, p. 741 - 750) in her study of the systems $\text{Cu}_2\text{S} - \text{CuS}$, $\text{Cu}_2\text{S} - \text{Sb}_2\text{S}_3$, $\text{Cu}_2\text{S} - \text{As}_2\text{S}_3$, and $\text{Cu}_2\text{S} - \text{FeS}$ attributed the formation of the intermediate sulphide phases to reactions in the solid state, well below the melting point. These reactions were described as solid solutions. In these solid solutions, "The metallic constituents diffuse as 'ions' through the structure, while the mobility of the sulphur atoms is almost negligible". The equations for the mechanism of this reaction can be found in Virginia Ross' paper and will not be repeated here. Virginia Ross concludes that, "The experiments have indicated that the rates of intermediate phase formation at low temperatures are appreciable in these systems; hence considerable importance should be attached to the role of solid

state diffusion in ore deposits". "The role of solid state diffusion shortly after the deposition of an orebody must be significantly great at the prevailing temperatures, and equilibrium is probably established within a short period. The role of solid state diffusion during thermal metamorphism and the reworking of deposits by solutions should be extensive. In cases where the 'order of solubility' does not appear to be a usable criterion for replacement, solid state diffusion may be responsible for the formation of complex phases."

Solid Solution and Diffusion as an Explanation of Micro-
textures in Sulphide Ores

Edwards states (1954, p. 86) that extensive mutual solid solutions of the order-disorder type are possible between ZnS , FeS , $CuFeS_2$, Cu_2FeSnS_4 , Cu_5FeS_4 , Cu_3SbS_3 , Cu_3AsS_3 . "These minerals crystallize with a zinc blende structure, in which the metal atoms lie in a face centred cubic lattice, and the sulphur atoms are arranged in a similar lattice." In the experiments on specimens of Flin Flon ore described in this paper, the preferred inter-reaction of sphalerite with chalcopyrite was evident. The interreaction of sphalerite and pyrite was distinct, but

not as extensive as that of sphalerite and chalcopyrite. This may be explained in part by the following from Edwards, "Chalcopyrite (CuFeS_2) has a very similar structure (to sphalerite), in which the Zn atoms are replaced by alternate Cu and Fe atoms, but the unit cell of chalcopyrite is twice as large as that of sphalerite, the difference in size of the Cu and Fe atoms compared with the Zn atoms causes the tetrahedral arrangement of the metal atoms in CuFeS_2 to be slightly irregular, so that CuFeS_2 is tetragonal, but with its angles very close to those of the cubic system". The differences between FeS and FeS_2 may account for the relative reluctance of Zn to enter the structure of pyrite (FeS_2) while FeS enters readily into the sphalerite structure. Edwards states, "Clearly there is opportunity for extensive isomorphous substitution of Cu, Fe, Sn, and Zn for one another in these structures, that is for solid solution between these minerals. The possible relationships are more complex still in that tetrahedrite (Cu_3SbS_3) and tennantite (Cu_3AsS_3) also have the zinc-blende structure". Rates of unmixing of the several precipitate minerals, and their segregation, varies with temperature and concentration, so that though one solute mineral may begin to precipitate before another, the unmixing of the latter may be completed first".

Conclusions of the Boundary Migration Experiments

1. The use of the vacuum heating stage to study the effects of heating on sulphide ore textures is feasible, but refinements in technique and modifications of the equipment must be made if studies at higher temperatures than those mentioned previously are to be undertaken.
2. Swelling and splitting of specimens is due to heating, a result similar to that attained by Zurbrigg (1941, p. 36).
3. Microtextures developed as a result of boundary migration or migration of mineral material, closely resemble those recorded as typical of replacement type sulphide ore deposits.
4. The comparatively low temperatures at which the boundary or textural changes took place are most important. These temperatures are hundreds of degrees below those postulated for mineral deposition.
5. The presence of a temperature gradient within the heating stage, and the definite increase of sphalerite in the cooler portions of the specimen (the face under observation) with rising temperature, suggests that the sphalerite may have migrated from the high temperature

portions of the specimen to portions where the temperature was lower. This conclusion is enlarged later in this thesis.

CHAPTER V

DIFFUSION EXPERIMENTS

The discovery of a temperature gradient within the heating stage led to two conclusions. The first, that the furnace element must be re-designed to eliminate the thermal gradient if boundary migration, exclusive of surface migration, was to be studied, and experiments were to be conducted at higher temperatures without vaporization. The second, that the thermal gradient might be used to advantage. In the second case, the mechanism of solid state diffusion might be observed if material could be forced to migrate from the upper, hotter parts of the specimen into a thin slice of a different mineral located in the lower, cooler part of the heating stage. Evidence of this type of migration was exemplified in the extensive veining of chalcopyrite by sphalerite in specimen Flin Flon 1. Comparison of the polished face before and after heating showed more sphalerite at the polished surface after heating than in the original unheated surface.

In the publications of the International Geological Congress, XXI Session, Norden 1960, Dr. J. E. Gill published an interesting article on the results of heating specimens of CuS and FeS in an atmosphere of sulphur. The CuS and

FeS were held in contact during the heating period. Recently, MacDougall, Meikle, Guy-Bray, Saull, and Gill have published a more extensive paper on the same subject (1961, p. 362). It was thought that a similar experiment might be carried on at the University of Manitoba using naturally occurring sulphide ore minerals in the vacuum heating stage, rather than purified compounds. Specimens of this type were called "two part specimens". Minerals selected for this work were chalcopyrite and sphalerite. Care was taken that the chalcopyrite did not contain any sphalerite, and that the sphalerite was free from chalcopyrite. The chalcopyrite was selected from the Sudbury suite, the sphalerite from the Tri-State suite in the University of Manitoba collection. Both parts of the specimens were examined under the reflecting microscope to determine their purity.

It was planned to place the two-part specimens in the heating stage, introduce the thermal gradient, and observe the lowest face of the specimen. If the foreign material of the upper part of the specimen could migrate across the interface between the two specimen parts and through the thin lower part to the lowest face, the mechanics of the diffusion could be observed and photographed.

These experiments proved to be only partially successful as difficulty was encountered with vaporization. Transfer in the vapor state was evident. However, the study was concerned with solid diffusion transfer between the two parts of the specimen, not with vapor transfer.

The first two diffusion experiments encountered immediate difficulty (two-part specimens 1 and 2). The selection of coarse grained sphalerite from the Tri-State district was unfortunate because in both these experiments the upper sphalerite portions of the specimens shattered. The first shattered at 177 degrees centigrade, the second at 172 degrees centigrade. Expansion due to heating was apparently too great or too fast, and the specimens shattered along cleavages. This breakage was so violent that in the second case the quartz specimen table was cracked.

These first two diffusion experiments showed that some other type of sphalerite specimen must be used for the upper part of the two-part specimens. Sphalerite from Many Mine, Flin Flon district, has all the characteristics lacking in Tri-State ore in that it is fine grained, hard, and easily shaped. However, Mandy ore has a considerable chalcopryrite content. Considering this, Mandy specimens could be used only as the upper parts of two-part specimens. Sphalerite diffusing downward would be noticeable in the

lower chalcopyrite slice, but chalcopyrite would not. The maximum temperature achieved in this series of experiments was approximately 329 degrees centigrade, at 91 Cm. Hg. pressure.

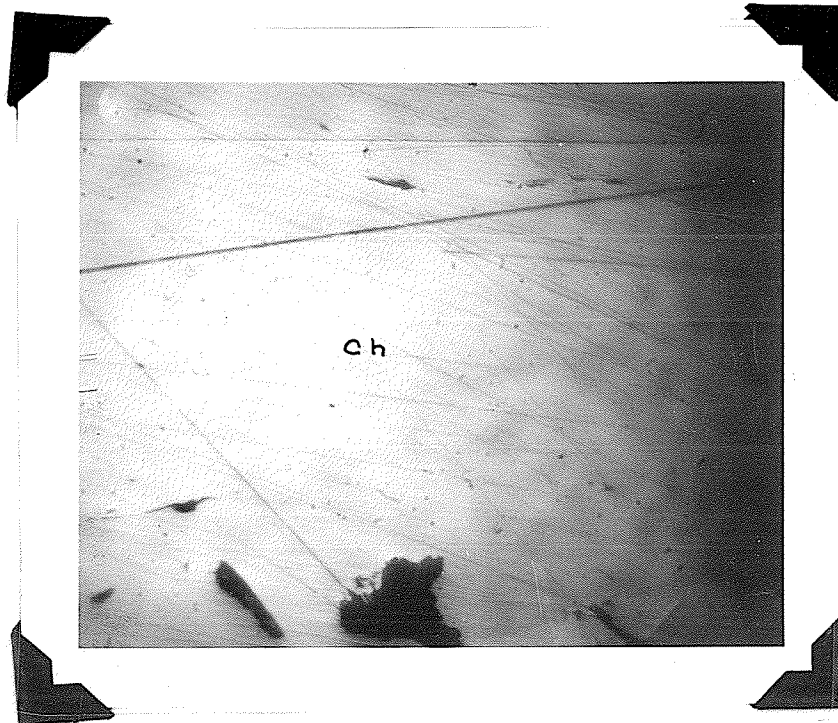
One of the notable features of the diffusion experiments was the development of cracks in the lower (chalcopyrite) portion of the specimens. With the exception of inert argon gas, nothing was introduced into the heating stage once the heating process had begun. Therefore, the cracking of the lower portion was due entirely to the rise in temperature. Similar results were observed by H. F. Zurbrigg in work done under the direction of J. E. Hawley at Queen's University (1941, p. 34). The fractures seen in the present experiments developed in the central areas of the specimen face, not at the edges. With increasing temperature, the cracks extended, sometimes developing as a series of en echelon fractures which joined the main fractures as they extended. In some places, small en echelon fractures developed as branches from the main fracture. Photomicrographs 1 and 2 (Plate 10), taken of 'Two-Part Specimen 3' show a 'before and after' comparison of fracture development.

The diffusion experiments produced negative results as far as diffusion was concerned. Material sub-

limed from the hotter areas of the specimen across the interface and onto the lower cooler part, but it did not diffuse through the thin lower mineral slice. Some vaporization accompanied this transfer, and it is implied that the transfer was effected by this means. Prior to placing the specimen in the heating stage, all surfaces of the two parts of the specimen were polished, studied, and selected areas photographed. Thus a comparison of these areas could be made before and after the experiment, even though it was not possible to observe all surfaces during the heating process. Photomicrographs 1 and 2 (Plate 11), taken of specimen 'Two-Part Specimen 4' illustrate the condition of the specimen interface after the experiment. The light patches, denoted by the symbol Ch_a , seen in the pictures are apparently chalcopyrite. Microchemical tests affirmed this, but the presence of original chalcopyrite in the section renders this identification somewhat dubious. The material suspected of being chalcopyrite was so diffuse that it was impossible to collect enough of it for an X-ray analysis. However, differences between the diffused material suspected of being chalcopyrite, and original chalcopyrite in the specimen are obvious in the photomicrograph, and still more obvious during personal observation.

PLATE 10

Fracture Development Resulting from Heating



1

X 400

Room Temperature



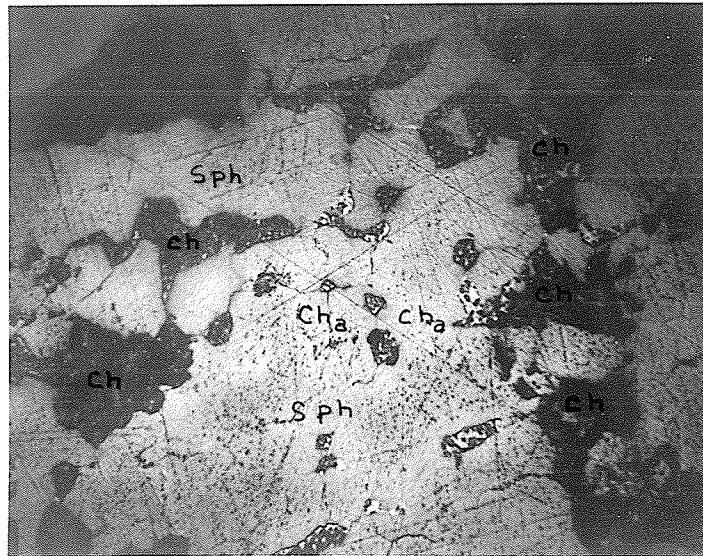
2

X 400

132 Degrees Centigrade

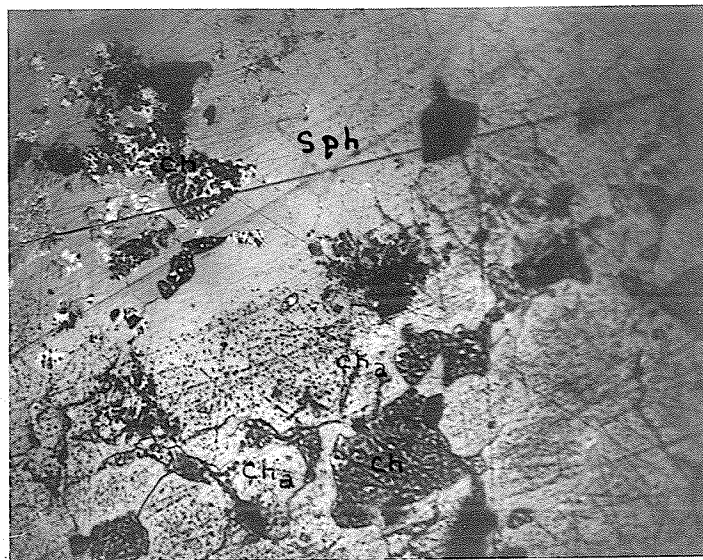
The foregoing experiment was repeated with mixed sphalerite-chalcopyrite from Mandy Mine as the lower part, and clean chalcopyrite from Garson Mine, Sudbury, as the upper part of the specimen. This arrangement was called a reverse two-part specimen. Heating of reverse two-part specimens resulted in unexpected but spectacular results. At 185 degrees centigrade in argon gas at 95 Cm. Hg. pressure chalcopyrite blebs in the lower sphalerite portion of the specimen turned a brownish flesh colour. At 252 degrees centigrade reaction rims between chalcopyrite and sphalerite were noted. Yellow material appeared to diffuse outward from the chalcopyrite into the sphalerite. After five hours and twenty-five minutes of continuous heating, during which time the specimen was subjected to gradual rise in temperature, a maximum temperature of 343 degrees centigrade was attained. The heating was stopped at this point and the heating stage allowed to cool. When the stage was opened, and the two parts of the specimen extracted, the top of the upper chalcopyrite plug was seen to have been re-crystallized to a deep blue material. This material occurred as octohedral crystals which were visible to the naked eye. X-ray analysis showed the blue crystals to be cubo-octohedral bornite (see Appendix A). Nothing was introduced during the course of the experiment except inert argon at a pressure of 95 Cm. Hg. Inspection of the stage

PLATE 11

Diffusion of Chalcopyrite on Sphalerite
(Reverse Two-Part Specimen 4)

X 400

Room Temperature



X 400

Room Temperature

interior revealed very little sublimed sulphur adhering to the interior surfaces. No condensation had occurred on the quartz window during the experiment. The bornite crystals were definitely a surface feature, probably formed as a breakdown product of chalcopyrite under heat. Lack of sulphur vaporization in this transformation is probably due to the fact that the formation of bornite from chalcopyrite requires a slight excess of sulphur. The formation of the bornite took place at a temperature below 321 degrees centigrade under an argon pressure of 95 Cm. Hg. This reaction rendered the specimen very crumbly and it was of no further use because it could not be repolished for study.

A third feature of significance was the development of thermal breakdown phenomena in the chalcopyrite portions of the two-part specimens. Chalcopyrite used in the diffusion experiments had of necessity to be free from any sphalerite. Therefore, specimens from Garson Mine, Sudbury, were selected. These were difficult to shape because the specimen was composed of large crystals which fractured along cleavages during shaping on the grinder. Originally, very few traces of bornite were visible in the polished face of the chalcopyrite. However, as the heating progressed, blades and blebs of pink-cream

material appeared in the chalcopyrite. At 182 degrees centigrade, laths of pink-cream colour appeared all over the face of the section. The appearance of these laths was almost instantaneous. At 199 degrees centigrade the laths were enlarged, and their colour had acquired a blue cast. Secondary blades and blebs, forming at acute angles to the primary exsolved blades, were noted at 204 degrees centigrade. The colour of both primary and secondary blades and blebs was definitely bluish-red at this temperature. The secondary blades were parallel to each other. With increasing temperature, the secondary blades thickened and lengthened, in some places growing together to form vein-like structures. Small "barbs" growing from previously exsolved features (both primary and secondary) were noted at 324 degrees centigrade. These were not parallel, nor aligned in any particular direction. Junctions of primary and secondary features did not have the pinched appearance, so common to exsolution features, but instead had a swelled look similar to that found with vein crossings. No further change was noted on heating to 301 degrees centigrade when the experiment was terminated. Photomicrographs of these features are found on plates 12 and 13.

Development of distinct thermal breakdown phenomena during the diffusion experiments pointed the way to

investigation of this subject using the heating stage. A short series of three experiments was carried out on chalcopyrite specimens from the Garson Mine.

Experiment 1

In the first of these experiments, thermal breakdown features developed at 121 degrees centigrade with the development of pink laths. At a slightly higher temperature the specimen shattered. Shattering and its cause have been dealt with previously.

Experiment 2

In the second experiment the specimen was heated to a maximum temperature of 144 degrees centigrade. Thermal breakdown phenomena similar to those previously described were noted at 135 degrees centigrade. The maximum temperature was reached one hour and fifteen minutes after heating began. This temperature was maintained for some time in the hope that an equilibrium had been reached. The temperature was then allowed to drop slowly.

Experiment 3

The third experiment achieved the same results as the first two.

Photomicrographs of the features are found on Plate 14, page 68.

Two hours and 45 minutes after the temperature had been allowed to drop from the maximum, the temperature was 110 degrees centigrade. There was no apparent change in the microtexture from that created by heating. However, it is believed that the time allowed for cooling may not have been long enough, and the cooling rate slow enough to permit any textural change with decreasing chemical activities.

Several faults are to be found with this experiment. The small capacity of the cooling water reservoir placed a serious limitation on the lengths of time devoted to heating and cooling. A larger reservoir would eliminate this by requiring only intermittent observation. The maximum temperature was possibly not held long enough so that the chance that equilibrium was not attained was great.

One unexplained feature of the thermal breakdown phenomena is the fact that they are apparently surface features. Repolishing of specimens in which these features developed removed almost all traces of them. The sharp contrast between the blades and chalcopyrite precludes any surface migration. This can be demonstrated with a comparison of photomicrographs 1 - 4, Plates 2 - 4, showing true

surface migration in Bathurst, N.B. ore with Plates 12 - 14, showing thermal breakdown in Garson ore.

The appearance of thermal breakdown features as surface phenomena may be due to higher temperature at the surface of the specimen than within it. In all probability then, the reaction takes place more easily at the surface than in the interior of the specimen. If it had been possible to maintain the reaction temperature for an extended period of time, the thermal breakdown features might have developed internally also.

CHAPTER VI

STUDY OF THERMAL BREAKDOWN PHENOMENAExperiment Sudbury 3

Experiment Sudbury 3 was conducted on a specimen of pure chalcopyrite from Garson Mine. As before, difficulty was encountered in shaping the specimen because of its coarsely crystalline nature. The experiment was performed in an identical manner to those previously described. A maximum argon pressure of 95 Cm. Hg. was used.

Primary pale rose-cream coloured thermal breakdown blades first appeared at 104 degrees centigrade. Photomicrograph 1 (Plate 12) exposed at this temperature, illustrates a few of these.

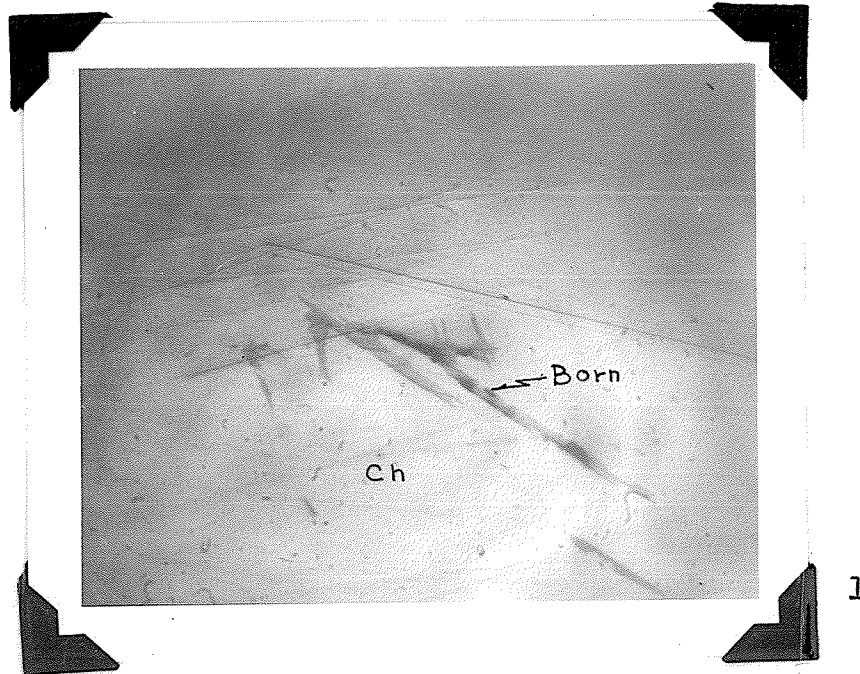
Photomicrograph 2 (Plate 12) shows the same area as that photographed in photomicrograph 1. This photomicrograph was exposed at 135 degrees centigrade. Note that the blades have darkened somewhat in colour, and that they have thickened slightly. With increasing temperature, the junctions between blades showed a pronounced swelling, and the largest of the primary blades began to extend in the direction of its original development.

Photomicrograph 3 (Plate 13), exposed at 173 degrees centigrade, illustrates lineal extension and broadening of the blades. This photograph and photomicrograph 4 (Plate 14) (Experiment Two-Part 4), exposed at 159 degrees centigrade, show the type of junction developed between thermal breakdown blades.

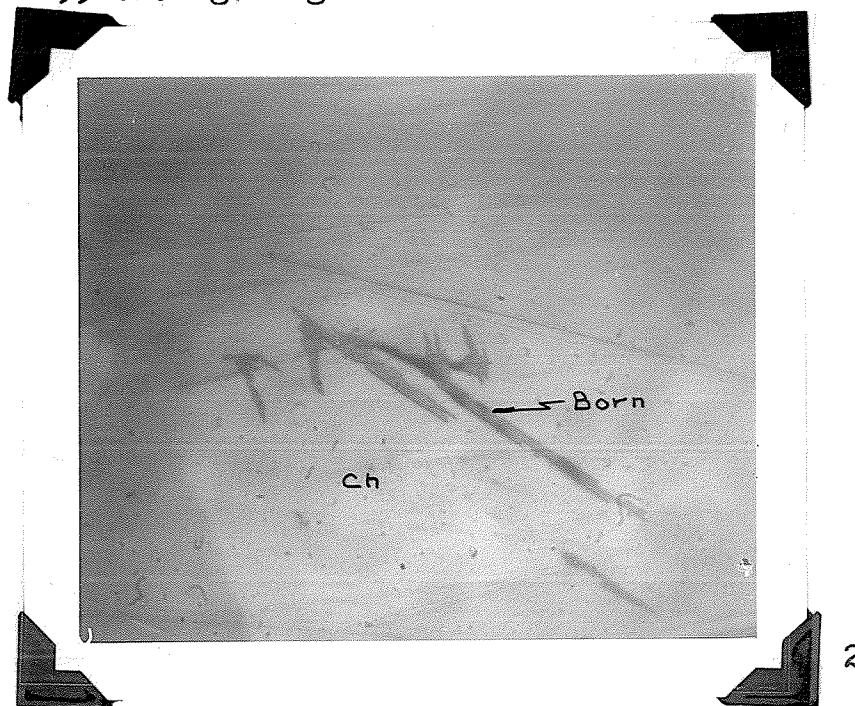
The thermal breakdown material was identified as bornite using the reflecting microscope and microchemical tests.

PLATE 12

Growth of Thermal Breakdown Features - Sudbury 3

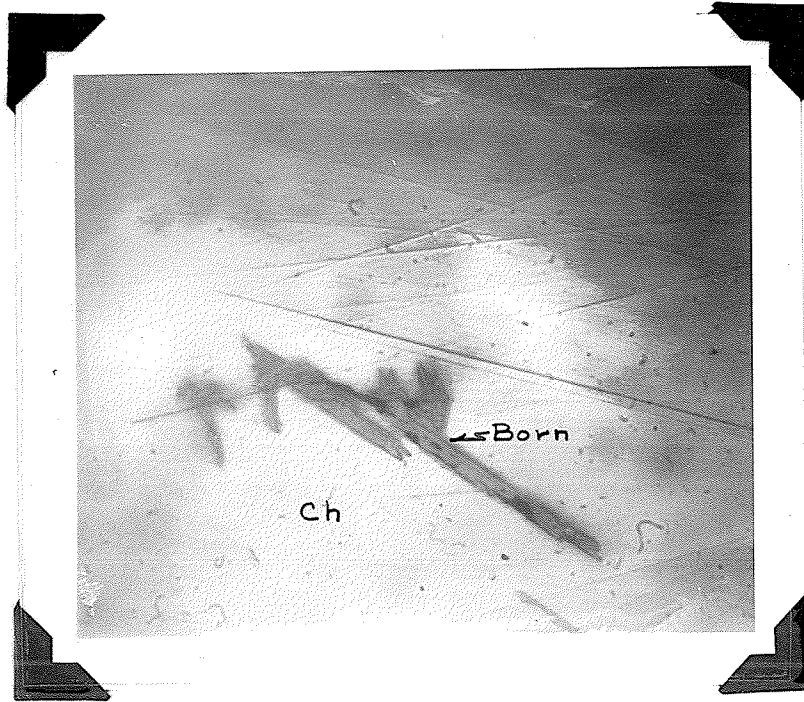


X 400 104 Degrees Centigrade
95 Cm. Hg. Argon Pressure



X 400 135 Degrees Centigrade
95 Cm. Hg. Argon Pressure

PLATE 13
Sudbury 3



3

X 400

173 Degrees Centigrade

PLATE 14

Illustration of Junctions of Primary and Secondary Thermal
Breakdown Features - Sulphide Sandwich 4



X 400

Conclusions Resulting from the Diffusion and Thermal
Breakdown Experiments

1. Diffusion down a thermal gradient, away from areas of high activity, has been shown by previous workers (Gill 1960, pp. 209-217). In the present study, using the 'Two Part' type specimens, any evidence of this type of solid diffusion was concealed by material transported in the vapor state across the interface between the two parts of the specimen. In each experiment, either chalcopyrite or sphalerite was deposited at the interface on the upper polished surface of the lower, cooler part of the specimen. Some vaporization accompanied this deposition. It is believed that deposition of this material, chalcopyrite or sphalerite, depending on the arrangement of the layers of the specimen, resulted from vapor transport or sublimation.
2. Bornite began to form from the chalcopyrite at temperatures as low as 104 degrees centigrade. These thermal breakdown phenomena occurred as blades and laths. With increasing temperature, these joined in a manner unusual to exsolution. These junctions widened or swelled as the temperature rose. Primary blades continued to elongate with temperature rise, in places contacting blades in line with them.

Investigation of the Relative Capabilities of Migration of
Selected Sulphide Minerals

Throughout the entire series of experiments it was apparent that some sulphide minerals migrate easier than others. This ability is apparently a function of the relative capabilities of the two adjoining minerals for a solid solution reaction. These capabilities are dependent on temperature, pressure, and concentration of the mineral constituents, as shown later. Solid solution of any pair, or group, of sulphide minerals, one within the other, may be responsible for many of the ore textures. Therefore, the abundance of the minerals, relative to each other, of the solid solution pair or group must be taken into account in consideration of the possible resulting microtexture. G. M. Schwartz reached the following conclusion as a result of his study of the bornite-chalcopyrite intergrowths, "The texture resulting from the breakdown of a solid solution of bornite and chalcopyrite depends on which mineral is in excess, the rate of cooling is also an important factor".

Many paragenetic sequences have been worked out for as many ore deposits. But what of the effect of metamorphism on the microtextures of ores? These microtextures form the basis for the postulation of the para-

genetic sequences. Early work with the vacuum heating stage showed the differences in the migration capabilities of the limited number of minerals observed, and the effect of their relative concentrations. The next step was to increase this number in the hope that textures as seen in orebodies could be represented. Perhaps in this could be found a partial answer to some problems of paragenesis. This work was based on the assumption that the materials for the formation of the ore minerals were introduced into the ore zone at the same time. Perhaps the textures of sulphide ores are due to the degree of unmixing at the particular temperature, pressure, and relative concentration existent when the deposit was formed.

Experiments were made to attempt to determine the relative ease of migration of a limited number of pairs of the sulphide minerals. Effect of relative concentration was taken into consideration. Many sulphide minerals can occur together, but the number of pairs of minerals studied was limited by the time available. The following pairs of minerals were selected:

pyrrhotite - sphalerite

galena - sphalerite

galena - pyrrhotite

chalcopyrite - sphalerite

The selection of these mineral pairs was based on the availability of specimens, mineral assemblage, and representation of deposits of different types.

As mentioned previously, it was necessary to redesign the heating stage element. Early work had shown the presence of a thermal gradient within the stage which was undesirable for this work. The relationship of the minerals to each other was the object of the experiments, not the reactions of the minerals to a thermal gradient. A drafting of the redesigned element is shown in Figure 2, page 12. The lowest groove in the original ceramic wire holder is cut at a distance of three mm. from the bottom of the holder which is supported by a hollow ceramic cylinder whose floor measures about 2.5 mm. in thickness. Thus the polished specimen face is approximately 5.5 mm. from the nearest heating coil. To improve this condition, the element holder was wired together with heat resistant wire, and one end was ground flat on the steel lap. This shortened the distance from the lowest coil groove to the bottom of the coil holder. The suspension cylinder was eliminated, and the element holder cemented directly into a suspension collar in such a manner that the distance from the lowest heating coil to the specimen face would be reduced to a minimum. Sauereisen low expansion cement was used for this

purpose. The distance from the bottom of the element holder to the thermocouple and specimen table must be carefully estimated. If this distance is misjudged, and the element holder is allowed too long a suspension, there is risk of breaking the quartz specimen table and crushing the thermocouple insulation as the stage is bolted together. With the new furnace element design, the distance from the lowest heating coil to the specimen face is approximately 3 mm. and most of the specimen then lies within the heating portion of the stage. Vaporization of the upper part of the specimen, at higher temperatures than those recorded is thus eliminated. However, vaporization may still take place if the temperature of the specimen is raised above the vaporization temperature, at the chosen operating pressure, of the minerals in the specimen.

Pyrrhotite - Sphalerite

Experiment Sullivan 1

The textural relationship of galena and sphalerite was not studied in any of the previous heating experiments. Work with Tri-State sphalerite specimens had not achieved any useful results because of fracturing of the specimens. The fine grained ore from Sullivan, British Columbia, appeared to have a suitable texture for heating stage

experimentation. However, shaping these specimens was a major problem because the Sullivan ore available was very friable. New shaping methods were tried. Efforts to drill out a specimen with a brass tube and carbide cutting compound succeeded only in drilling a hole in the hand specimen, with only chips to represent the cylindrical specimen. The original shaping method described on page 23 proved best. Sullivan specimens shaped by this method never measured more than 1 Cm. in height, but were successfully polished and treated in the heating stage. The Sullivan suite at the University of Manitoba contains several samples consisting of sphalerite, galena, gangue, and bands of pyrrhotite. Edwards (1954, p. 84) regards pyrrhotite as common to high temperature lead-zinc ores. Bateman notes (1958, p. 540) that pyrrhotite occurs in the lower orebody at Sullivan. Advantage of the presence of pyrrhotite was taken by cutting the specimens to include the pyrrhotite bands.

Photomicrograph 1 (Plate 15) illustrates the original Sullivan microtexture. No apparent change in texture occurred as the temperature of the specimen was raised to 136 degrees centigrade.

At 163 degrees centigrade the pyrrhotite turned a

slightly darker brown-yellow-bronze, relative to its original colour.

Photomicrograph 2 (Plate 15) exposed when the temperature of the specimen had reached 171 degrees centigrade, shows the darkened pyrrhotite and a fracture developing in the centre of the section. Not discernable in the photomicrograph is the gradation of pyrrhotite from the normal brown-bronze to shades of gray.

Photomicrographs 3 and 4 (Plate 16) were exposed at specimen temperatures of 216 and 233 degrees centigrade respectively. The developing gray colour of the pyrrhotite is shown, but not clearly, because the colour change from brown-bronze to gray shows only as a darkening of gray on the black and white film used. At 216 degrees centigrade a definite brown cast was noted in the formerly gray sphalerite. Note in photomicrographs 3 and 4 (Plate 16) that the intensity of the gray colour of the pyrrhotite closely matches that of the brown-gray of the sphalerite.

Microchemical tests for zinc, performed on both the solid solution end products, gave positive results. X-ray analysis of material which was originally pyrrhotite, made after the specimen had been heated, indicated that this material was in part, and in some cases largely, composed of sphalerite.

X-ray data on the solid solution products are given in Appendix A.

Discussion

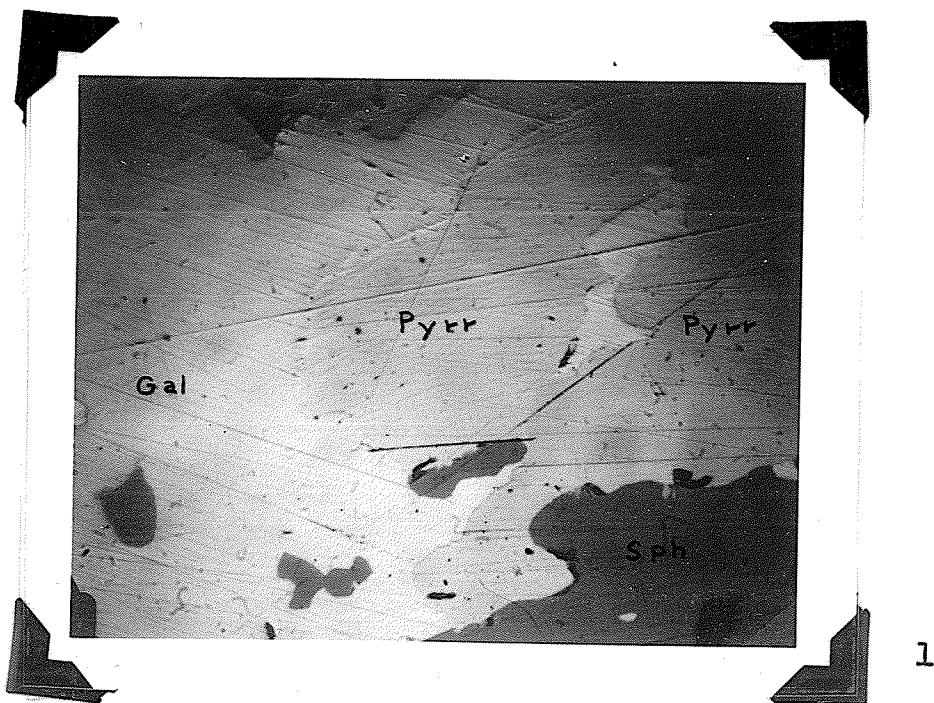
An interchange or substitution of Fe and Zn has occurred between pyrrhotite and sphalerite. Fe substitutes easily for Zn sphalerite solid solutions. According to Edwards (1954, p. 86), extensive solid solutions of the order-disorder type are possible between ZnS and FeS. These, and other solid solutions, have been explained previously on pages 45-47. In the case in question, specimens 'Sullivan 1 and 2', the sphalerite has been enriched in Fe, while the pyrrhotite was enriched in Zn. The end products are then two gray-brown coloured Fe-Zn solid solutions. The solid solution of pyrrhotite and sphalerite occurs approximately at 177 degrees centigrade at a pressure of 91 Cm. Hg.

Galena - Sphalerite

No apparent reaction took place between galena and sphalerite, or between galena and pyrrhotite at these temperatures and pressures.

PLATE 15

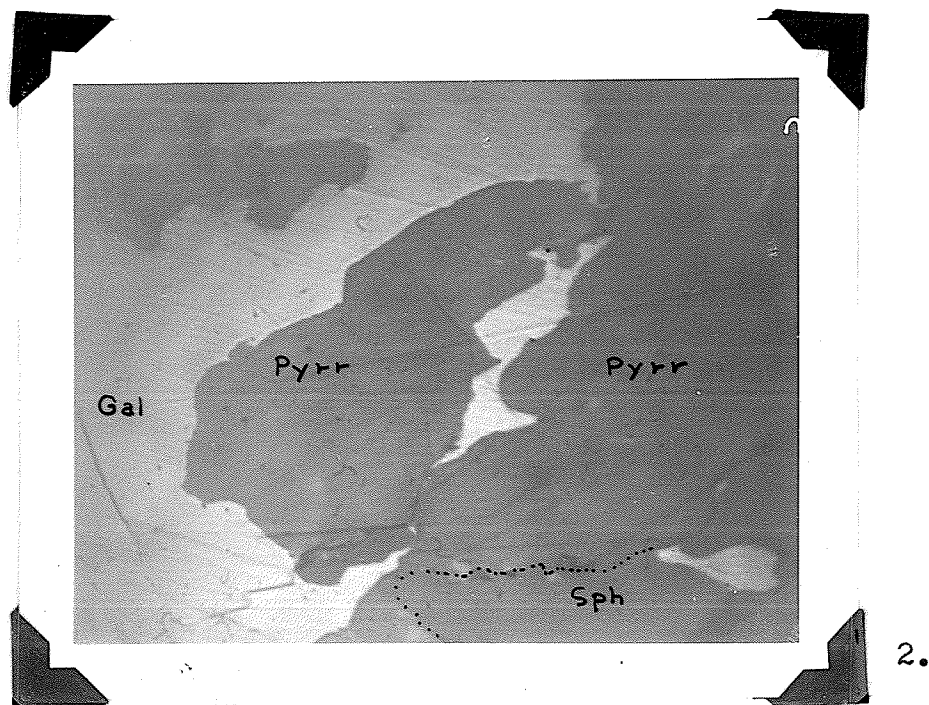
Solid Solution of Pyrrhotite and Sphalerite - Sullivan 2



X 400

Room Temperature

Original Microtexture



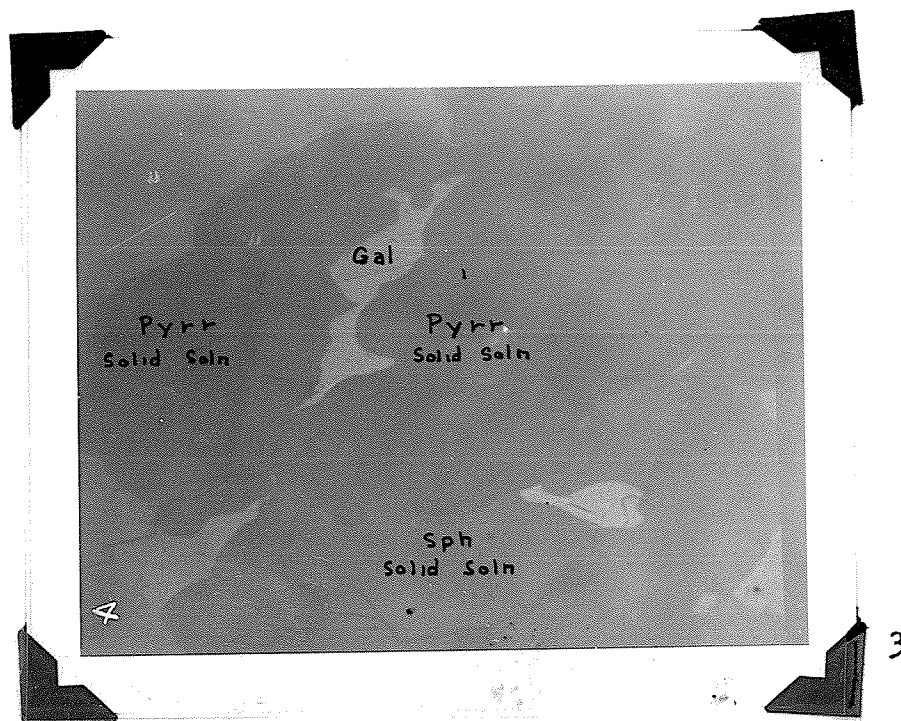
X 400

171 Degrees Centigrade

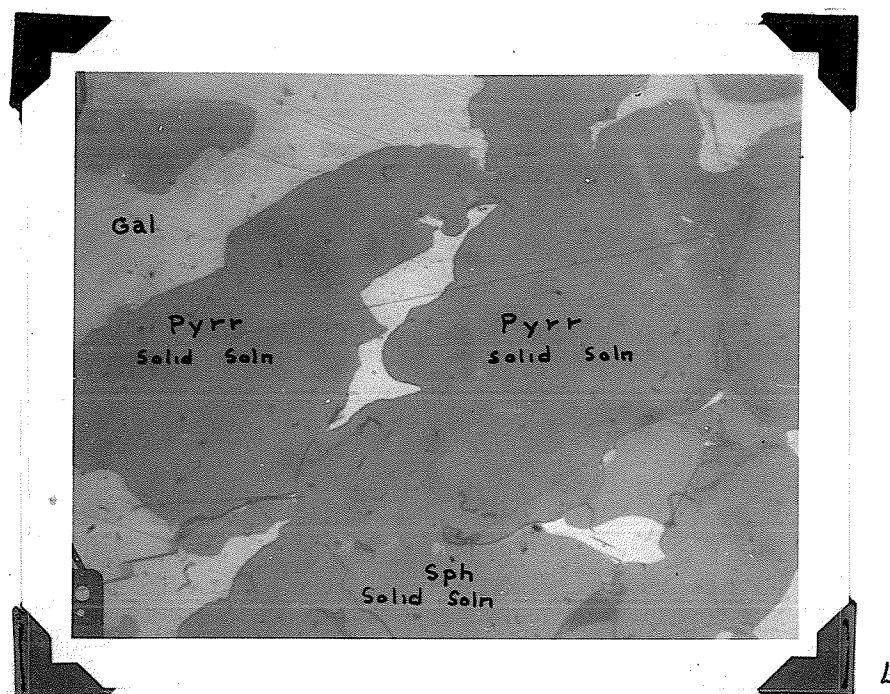
95 Cm. Hg. Argon Pressure

PLATE 16

Sullivan 2



X 400 216 Degrees Centigrade
95 Cm. Hg. Argon Pressure



X 400 233 Degrees Centigrade
95 Cm. Hg. Argon Pressure

Chalcopyrite - SphaleriteExperiment Mandy 1

In previous experiments of the boundary migration type, samples from the Flin Flon Mine were used. These samples contained disseminated chalcopyrite up to 50% of the total sulphide content. For the experiments on relative migration capability, specimens with sphalerite content up to 70% of the sulphides were used in an attempt to illustrate the effect of relative concentration of constituents on the migration reaction.

Photomicrograph 1 (Plate 17) illustrates the original microtexture of the specimen. As the specimen was heated, there was no apparent change in the polished face until the specimen temperature had reached 163 degrees centigrade. At this temperature a faint yellow reaction rim was noticed in sphalerite near grains of chalcopyrite. This reaction was too faint to be recorded photographically.

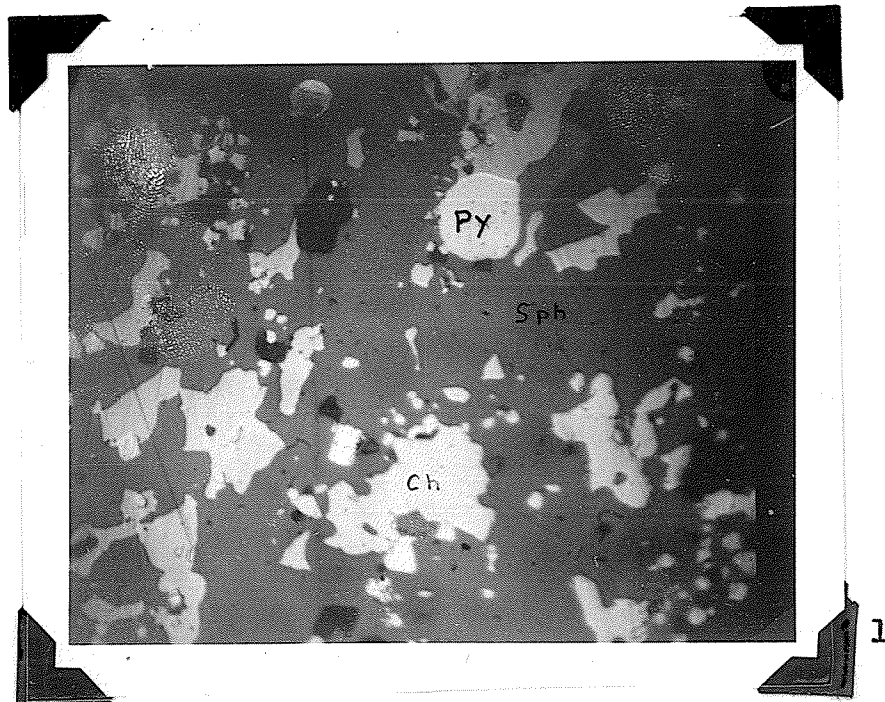
At 199 degrees centigrade, faint yellow "flames" in sphalerite were clearly seen. Note centre area, photomicrograph 2 (Plate 17). The chalcopyrite appeared to be diffusing outward into the sphalerite from the preexistent blebs of chalcopyrite. Note fractures.

At 252 degrees centigrade chalcopyrite was diffused through large areas of sphalerite. See Photomicrograph 3 (Plate 18), note particularly the central area of the photo.

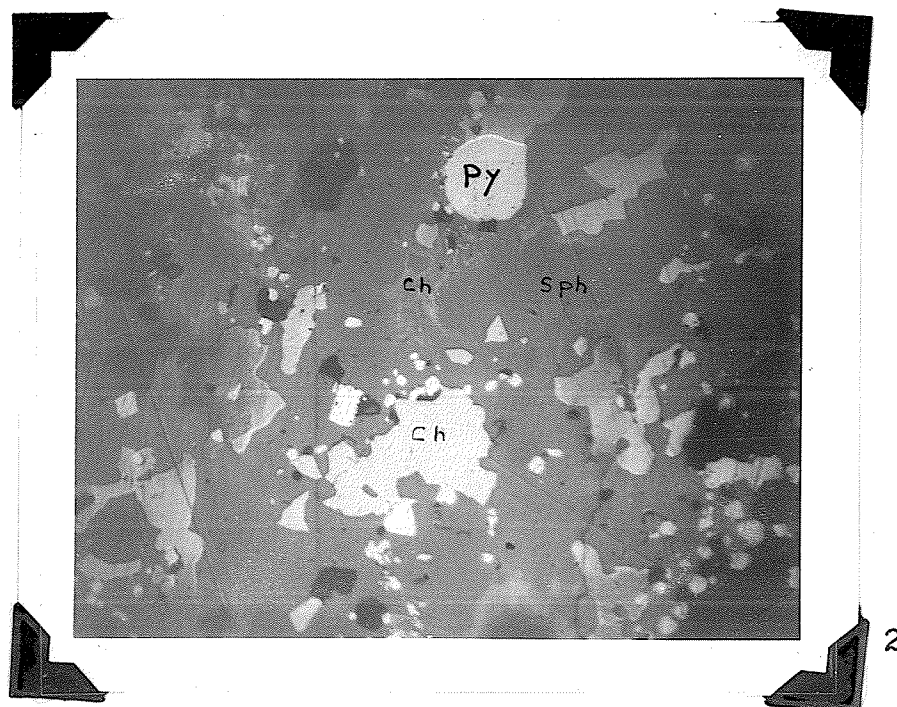
In this experiment, the chalcopyrite migrated more easily than the sphalerite; the opposite result to that obtained with specimens having higher chalcopyrite content than sphalerite content. This was shown in experiment 'Flin Flon 1'. This illustrates that in work with the vacuum heating stage, as well as in previous studies by other workers, the relative ease of migration of each of the minerals within the other is dependent also on the relative concentration of the minerals in the specimen as well as the temperature and pressure. That is the amounts of the minerals present determine which is the solvent, and which the solute of the solid solution. This supports the work of M. J. Buerger on "Intergrowths of Bornite and Chalcopyrite". "The texture resulting from the breakdown of a solid solution of bornite and chalcopyrite depends on which mineral is in excess, and the rate of cooling is also an important factor."; and with Edwards, "Rates of unmixing of the several precipitate minerals and their segregation, vary with temperature and concentration".

PLATE 17

Effect of Concentration on Migration - Mandy 1



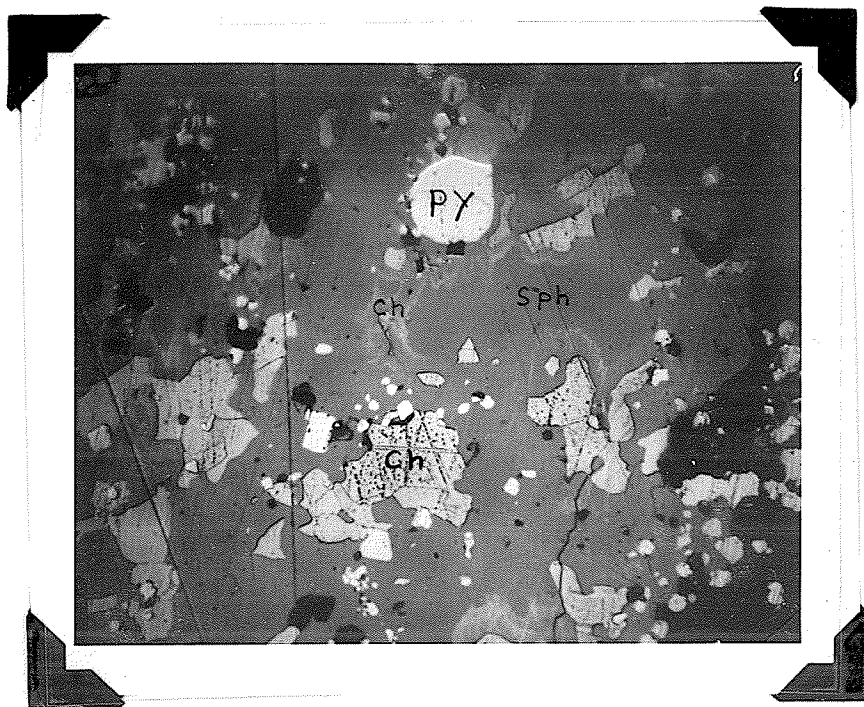
X 400 Room Temperature
Original Microtexture



199 Degrees Centigrade X 400

PLATE 18

Mandy 1



3

X 400

252 Degrees Centigrade

95 Cm. Hg. Argon Pressure

Experiment Anaconda Caribou 3

This was a study of the sphalerite-galena reaction; pyrite and gangue were also present in the specimen.

The temperature of the specimen was raised to 435 degrees centigrade with no reaction. A pressure of 91 Cm. Hg. argon was used.

At a temperature of 213 degrees centigrade minute surface migration of sphalerite onto galena was noticed.

The following mineral relationships were presented earlier in this thesis, and are not repeated here:

galena - pyrrhotite - sphalerite
pyrite - chalcopyrite - sphalerite
chalcopyrite - sphalerite - galena.

CHAPTER VI

SUMMARY AND CONCLUSIONS

In the use of the vacuum heating stage for the study of sulphide ore microtextures, refinements in both technique and equipment were required before the potential of the equipment for use with sulphides could be approached. Suggestions for the modification of the equipment and refinement of technique have been made.

Early experiments showed the existence of two types of mineral migration: (a) Surface migration, and (b) True boundary migration. The effect of small increases in argon pressure on vaporization and surface migration was notable. Virtually all vaporization and surface migration was eliminated by an increase of 0.75 - 1 atmosphere pressure.

With further investigation, the second type of migration was discovered. This was the migration or alteration of the mineral grain boundaries, as distinct from surface migration. This second type of migration forms microtextures characteristic of replacement. Because nothing was added to the specimens during the course of the experiments, the materials for the formation of these

textures must have been present in the specimens themselves and only heat was needed to effect the changes. Such would be the case in thermal metamorphism of an orebody. The effect of metamorphism on microtextures of sulphide ores has been a matter of speculation. Perhaps with this equipment further information in this direction may be attained.

Boundary migration has been explained in terms of diffusion and solid solution between adjacent grains in the specimen. The importance of relative concentration of the constituent minerals of the solid solution on texture formation has been noted. The low temperatures at which boundary migration took place were unexpected.

Chalcopyrite exhibited more activity than sphalerite in specimens in which sphalerite was dominant. Sphalerite showed more activity than chalcopyrite in specimens having a chalcopyrite content greater than that of sphalerite. However, even in cases where chalcopyrite was the minor constituent, the ease with which migration took place was less than that in the opposite case. Thus, while relative concentration of the two minerals is an extremely important factor, it appears that sphalerite is more mobile than chalcopyrite. This is in direct contrast to the field evidence.

Vaporization of specimen parts other than the polished face, and the condition of the early specimens after heating indicated the presence of a thermal gradient in the heating stage. Two things were clear, firstly the furnace element must be redesigned if continued work at higher temperatures was to be carried out. Secondly, studies of the behavior of diffusion of mineral material in a thermal gradient might be undertaken. It was hoped that observations could be made of the diffusion process. This work was only partially successful. Sublimation occurred. This migration was away from hot areas of the heating stage, toward cooler areas. Solid state diffusion was not observed. The failure in this respect was due to two factors. The first, was the necessity of constant surveillance of both the specimen and cooling water reservoir. It was impossible to maintain a vigilance for the lengths of time which might be required for solid state diffusion at temperatures below the vaporization temperatures of the minerals in the specimens. The second was the vaporization of the upper portions of the specimens during heating. This was due to the temperature gradient. Temperature recordings were taken at the lower, cooler end of the specimen. A lag in the heating rate in this area might indicate a need for an increase in the current to the element. The immediate result would be vaporization of the upper sections of the

specimen nearest the element coils.

Several things were learned from the diffusion experiments. Grossly crystalline sphalerite and chalcopyrite ores are unsuitable for work with the vacuum heating stage, as these specimens shatter during heating. Internal fracturing of chalcopyrite specimens occurred; this phenomena was observed by Zurbrigg at Queen's University in 1937. Fracturing of this latter type is due entirely to heating.

Bornite found at the top of chalcopyrite specimens when removed from the heating stage was formed by thermal breakdown and sublimation of chalcopyrite. In 1901, A. N. Winchell suggested that bornite was formed as a volatilization product. Bornite is commonly found in the flues of copper smelters. The current work agrees with this finding.

Development of thermal breakdown phenomena in chalcopyrite during the diffusion experiments led to the study of thermal breakdown in chalcopyrite specimens from Garson Mine, Sudbury. Noteworthy in these experiments is the divergence in appearance of the thermal breakdown bornite blades from that of the ideal exsolution type. In some cases, the junction of these blades with each other is expanded. This is directly opposed to the classical

concept of the joining of exsolution phenomena. The elongation of blades with increase in temperature also occurred. Development of blebs or lumps, growing from the primarily appearing blades resembled incipient veins. The fact that these features occurred only at the surface can be explained by the presence of higher temperature at the surface of the specimen than within it. Reactions therefore take place more easily at the surface than internally. Failure of the thermal breakdown features to disappear with dropping temperature is explained by reduced activities with decreasing temperature. This is in accord with Buerger's findings in the study of bornite-chalcopyrite intergrowths.

The effect of small increases in temperature on the microtextures of sulphide ores has been demonstrated by studies with the vacuum heating stage and metallographic microscope. It appears then, on the basis of these studies, that, in some cases, microtextures are not an accurate guide to the paragenesis of the sulphide ores, particularly if there is a suggestion of thermal metamorphism.

The prominent feature of the entire series of experiments was the difference in migrational capability of the minerals studied. This capability is a function of the degree and ease of solid solution, at a certain temperature and pressure, between two adjacent mineral grains. The

solid solution is dependent on temperature and the relative concentration of the constituents, that is, which mineral of the pair or assemblage is the most abundant within the specimen. Work with the vacuum heating stage has shown that, in the specimens studied, microtextures are dependent on the diffusion or solid solution reactions between adjacent minerals. These microtextures are a basis for the determination of ore paragenesis. Study of the migrational capabilities of a limited number of minerals was undertaken. The following is a list of these minerals in order of increasing migrational capability:

Galena

Pyrite

Pyrrhotite

Chalcopyrite

Sphalerite.

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APPENDIX A

X-RAY POWDER DATA

Bornite

Film Number A-487

Radiation/Filter Fe/Mn

Camera radius 114.6 mm.

X-ray powder data for bornite and chalcopyrite are given in the table below, where they are compared with the data given by the A.S.T.M. Card Index for X-ray diffraction identification. A number of extra lines on the bornite pattern can best be accounted for by the presence of chalcopyrite as an impurity in the sample taken. The print of this X-ray powder photograph is shown in Plate 19.

Bornite A-487	Bornite A.S.T.M. #3-1077	Chalcopyrite A.S.T.M. #9-423
I d	I d	I d
4 3.29	3 3.31	
6 3.15	3 3.15	
5 3.073		10 3.03
1 2.835	$\frac{1}{2}$ 2.82	
5 2.728	3 2.74	
1 2.666		$\frac{1}{2}$ 2.63
3 2.50	3 2.51	

I	d	I	d	I	d
1	2.098	$\frac{1}{2}$	2.12		
10	1.929	10	1.94		
4	1.885			4	1.865
1	1.846			8	1.854
3	1.646	1	1.65		
2	1.61			6	1.591
1	1.574	$\frac{1}{2}$	1.58		
1	1.53	$\frac{1}{2}$	1.54		
1	1.48	$\frac{1}{2}$	1.47		
1	1.424	$\frac{1}{2}$	1.43		
1	1.366	$\frac{1}{2}$	1.37		
1	1.261	$\frac{1}{2}$	1.27		
1	1.224			1	1.214
1	1.203			3	1.205
4	1.116	3	1.12		

Sullivan #1 and 2

Film Number A-571 Sullivan #1
A-572 Sullivan #2

Radiation/Filter Fe/Mn

Camera Radius 114.6 mm.

Both Sullivan #1 and 2 were originally samples of pyrrhotite, sphalerite, galena and gangue. The original pyrrhotite was X-rayed to see if any change had taken place in it during heating. Specimens for X-ray analysis were obtained by scratching the sample with a needle and mounting

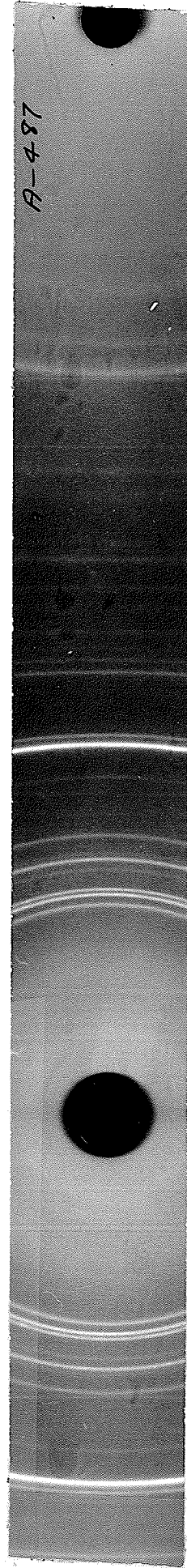
the powder on glass rods. Because of the very small amount of material available it was impossible to obtain a pure specimen.

X-ray powder data for Sullivan #1 and 2 are given in the table below, where they are compared with the data given by the A.S.T.M. Card Index for galena, and sphalerite, and by Erd, Evans, and Richter (1957) for pyrrhotite. Sullivan #1 is composed of sphalerite and galena. Sullivan #2 is composed mainly of galena and pyrrhotite with minor sphalerite. One extra line appears at 3.09 A which corresponds to the strongest line of sphalerite. Three lines present on the pattern at 9.5 A, 4.12 A, and 3.72 A could not be accounted for. The prints of these X-ray powder photographs are shown in Plate 20.

Sullivan #1		Sullivan #2		Galena		Sphalerite		Pyrrhotite	
A-571		A-572		A.S.T.M. #5-0592		A.S.T.M. #5-0566		Erd, et al. 1957	
I	d	I	d	I	d	I	d	I	d
		5	9.5					4	5.75
		5	4.12						
		$\frac{1}{2}$	3.72						
6	3.41	8	3.41	8	3.42				
10	3.12	6	3.09			10	3.12		

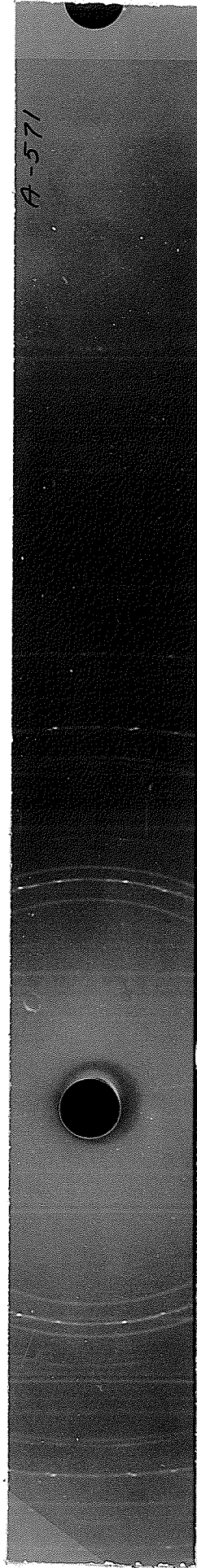
I	d	I	d	I	d	I	d	I	d
7	2.96	10	2.96	10	2.96			8	2.97
								4	2.84
						1	2.70		
1	2.64	8	2.64					9	2.64
								4	2.27
4	2.09	5	2.09	6	2.09				
4	2.06	10	2.06					10	2.06
9	1.91					5	1.91		
1	1.79	4	1.78	3	1.79				
1	1.71	9	1.72	2	1.71			8	1.71
8	1.63					3	1.63		
		$\frac{1}{2}$	1.61					2	1.60
								6	1.42
		7	1.32	2	1.32			4	1.32

PLATE 19

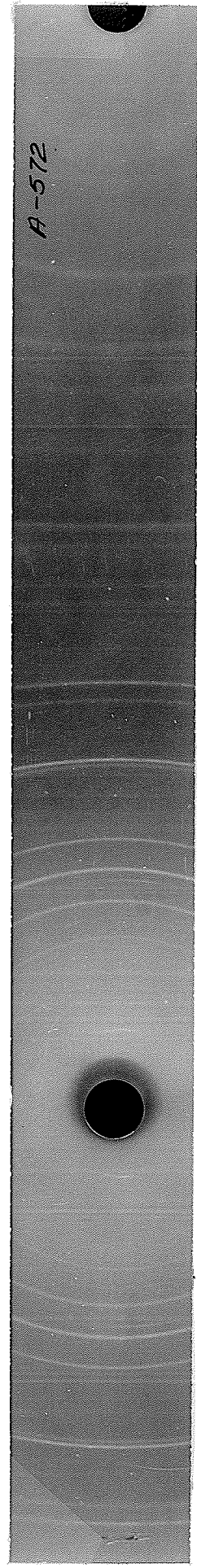


X-Ray Powder Photograph for Bornite

PLATE 20



Sullivan #1



Sullivan #2

X-Ray Powder Photographs for Sullivan #1 and 2.