SYNTHESIS OF PYRRHOTITE BY HYDROGEN SULPHIDE IN IRON BEARING SILICATES.

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ABSTRACT

This thesis presents the results of a series of experiments in which several common iron-bearing silicates were subjected to heat treatment in an atmosphere of hydrogen sulphide. Pure mineral specimens were crushed and placed in a ceramic boat inside the tube of a Burrell high-temperature furnace. A slowly circulating stream of hydrogen sulphide was passed through the furnace tube. Experiments lasted from 3.5 to 120 hours at temperatures ranging from 640°C to 1085°C. Polished sections of the minerals were prepared before and after treatment. In several cases the reaction products were identified by X-ray powder pictures.

Observations showed that the ferro-magnesian minerals reacted with hydrogen sulphide to form pyrrhotite at temperatures considerably below their melting point. Temperature ranges at which this reaction was initiated were between 835°C and 945°C for hornblende, 670°C and 835°C for biotite, 1000°C and 1055°C for augite, and below 835°C for olivene and epidote.

The possibility of a similar process of "sulphur metasomatism" in nature is considered to be significant in the evaluation of iron sulphide deposits. This reaction of sulphurous vapours with common rock minerals could result in major pyrrhotite deposits without the introduction of metallic elements associated with commercial zones of metallization, and may be an explanation of the non-commercial "pyrrhotite dikes" of the Canadian Shield.

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CHAPTER I

INTRODUCTION

The purpose of this thesis is to consider the synthesis of pyrrhotite by the action of hydrogen sulphide, at high temperature, on iron-bearing silicates. The ultimate goal of this research was to illustrate a possible source for the vast amounts of iron sulphide which constitute the main bulk of many Precambrian zones of metallization. The possibility of a process of leaching the iron from common ferro-magnesian minerals was experimentally examined and qualitatively evaluated. The research was by no means complete, but it does indicate some rather intriguing possibilities in the study of the genesis of natural-occurring pyrrhotite mineralization.

This study of the synthesis of pyrrhotite was considered significant for two reasons. The first has been indicated already. An attempt will be made to give an explanation to an academic problem - the genesis of pyrrhotite. This aspect will be developed further in a later chapter. The second reason was an economic one. In an intensive prospecting program of the Canadian north, mining companies have repeatedly come across magnetic anomalies which, after an expensive ground investigation have proved to be worthless zones of almost exclusively pyrrhotite mineralization. It was hoped that the research involved in this thesis might point to an explanation for

these expensive anomalies. Pyrrhotite dikes, as they are called, suggest the existence of a unique process possibly unrelated to the normal hydrothermal type of metallization. This thesis illustrates the possibility of a process by which the iron in these pyrrhotite dikes was extracted from the wall rock by upward circulating hot vapours or fluids, rich in hydrogen sulphide. Pyrrhotite mineralization could therefore be due to a process of sulphur metasomatism which does not require the addition of metallic elements. Only by reaching an understanding of the genesis of these pyrrhotite dikes will it be possible to contribute to their intelligent evaluation.

The subject matter of this thesis was organized to introduce the problem and to describe the method of research, as well as to present data and conclusions. Chapter II is a review of the literature related to the subject. An attempt was made to determine whether any previous work on the method of pyrrhotite synthesis used by the author had been done. The ideas on metasomatism and volcanic emanations were also reviewed. Chapter III is an account of the experimental procedure. Chapter IV is a discussion of some of the technical aspects involved in carrying out the research. Experimental data and observations are recorded in Chapter V. Chapter VI is a consideration of the possible theory involved in the experimental reaction observed. The summary and conclusions are presented in Chapter VII.

CHAPTER II

REVIEW OF THE LITERATURE

An extensive search of the geological and chemical literature was made by the author before any experimental work was begun. In the first place it was necessary to discover whether any previous studies had been made along the lines of investigation followed in this thesis. Since the problem of pyrrhotite synthesis is largely a chemical one, all the available Chemical Abstracts were referred to under the appropriate headings. The well-known geological journals were also reviewed. The second purpose of the review of the literature was to investigate the nature of the gases present in the earth's crust. Volcanic emanations are the direct evidence of subterranean gases. Pneumatolysis is the process by which minerals are formed due to the action of magmatic gases on rock masses. Both these phenomena were reviewed in order to evaluate the plausibility of a geological process corresponding to the experimental pyrrhotite synthesis carried out in the laboratory.

The history of pyrrhotite synthesis dates back to at least 1825. Hintze[1] records various methods of synthesis by reactions in the dry state. Iron and sulphur combine in various proportions according to the conditions of the

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1. Hintze, C.: Handbuch der Mineralogie, Band 1, Abt. 1, 1904, pg. 650.

experiment. It was recognized early that pyrite lost part of its sulphur upon heating to a red heat in an atmosphere of hydrogen sulphide. Syntheses were carried out by various other means. Combinations of hydrogen sulphide and marcasite, iron and sulphur, iron wire and hydrogen sulphide, hydrogen sulphide and ferrous chloride, and carbon disulphide and iron were heated under varied conditions by different investigators. A reducing atmosphere must be used in order to prevent oxidation of the iron sulphide. The early experiments were very thorough and Doelter[2] lists over 100 pyrrhotite analyses. No mention was found of any experimentor using an iron-bearing silicate as a source of iron in his syntheses. Various explanations for the erratic proportions of iron and sulphur in pyrrhotite were proposed, but not until fairly recently has a picture of the internal structure of pyrrhotite explained this behaviour.

Our knowledge of pyrrhotite has been considerably augmented by a few detailed studies and expecially by some recent crystal structure investigations. A very significant study of pyrrhotite was published in 1912 and 1917 by E.T. Allen and his associates[3]. They studied the reversible

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2. Doelter, C.: Handbuch der Mineralogie, Band 4, 1 Hälfte, pp. 517-523.

3. Allen, E.T., Crenshaw, J.L., Johnson, J., Larson, E.S., Am. Journ. Vol. 33, 1912, pg. 168 and Vol. 43, 1917, pg. 175.

reaction:

$$nFeS_2 \underset{H_2S \text{ atmos.}}{\overset{575^{\circ}C}{\rightleftharpoons}} NFeS(S)_x + (n-x)S$$

The dissociation of pyrite becomes much more rapid at temperatures above 575°C, whereas at a lower temperature the reverse process occurs. Since the system contains a gas phase, the equilibrium temperature is dependent on the pressure. Pressure also affects the composition of the pyrrhotite, the sulphur content increasing with increased pressure. From their study Allen and his co-workers consider pyrrhotite as a mineral-chemical series of which one end-member is troilite (FeS) and the other end-member contains about 6.04% dissolved sulphur. Recent crystal structure study has shown how this variable composition is to be interpreted in terms of atomic arrangement. Hägg and Sucksdorff[4] made an X-ray examination of pyrrhotite. Pyrrhotite belongs to the nickel-arsenide group and its ideal structure consists of six sulphur atoms surrounding each iron atom, and vice versa. Chemical analyses have shown a variation from this one-to-one ratio. Hägg and Sucksdorff, by comparing densities and unit cell measurements, have shown that the number of sulphur atoms per unit cell remains constant whereas the number of iron atoms is below normal in the sulphur-rich varieties. Some of the iron atom positions in the

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4. Hägg, G., and Sucksdorff, I.: Zeitschrift für Phys. Chem. Band 22, 1933, pg. 444.

ideal lattice are therefore vacant in most pyrrhotite samples[5].

The two preceding paragraphs have made brief reference to the experimental work on the laboratory analyses and synthesis of pyrrhotite. This work has shown that when iron is subjected to a sulphur (or hydrogen sulphide) atmosphere at temperatures above 575°C pyrrhotite tends to be formed. The reactions occurred between compounds of both the elements under consideration. It therefore remains to be demonstrated, as far as this thesis is concerned, that the iron of some of the common rock-forming ferro-magnesian minerals is available for reaction with the sulphur of hydrogen sulphide.

The focus of our search shifts from artificial surroundings of the chemical laboratory to the true geological environment of gaseous reactions in the earth's crust. The thesis, if geologically significant, suggests that some pyrrhotite occurrences are the result of the actions of hydrogen sulphide gas on rocks containing ferro-magnesian minerals. Various geologists have evoked a theory of this nature -sulphur metasomatism- to explain pyrrhotite mineralizations.

Turner and Verhoogen[6] summarize the discussion

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5. Bragg, W.L.: Atomic Structure of Minerals, 1937, pg. 65.

6. Turner and Verhoogen: Igneous and Metamorphic Petrology, 1951, pg. 493.

as follows:

> "Disseminations of pyrite and pyrrhotite through skarns and magnesian-iron silicate rocks formed by metasomatism, or through sericite quartzites produced at lower temperatures by alkali metasomatism of quartzofeldspathic rocks, has been attributed to reaction between iron-bearing silicates (e.g. chlorite or biotite) and magmatically derived hydrogen sulphide. It has been suggested by Goldschmidt that the commonly observed association of graphite and sulphides in rocks of this kind is due to reaction between ferruginous silicates and volatile compounds of carbon and sulphur such as carbon disulphide and carbon dioxide. - - - Local deposits of metallic sulphide ores are commonly associated with rocks that have been affected on a broader scale by any of the above mentioned types of sulphur metasomatism."

V.M. Goldschmidt[7] defines metasomatism as a process of enrichment of the rocks which "takes place by definite chemical reactions between the original minerals and enriching substances". He cites a case where Vogt has described deposits of pyrite in slates near intrusive rocks as an example of sulphur metasomatism by reactions between chlorite or biotite rich in iron and hydrogen sulphide.

From the above references it can be concluded that the formation of pyrrhotite by the action of hydrogen sulphide on iron silicates is entirely within the realm of geologic possibility and has in fact been proposed to explain field relationships.

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7. Goldschmidt, V.M.: On the Metasomatic Processes in Silicate Rocks, Econ. Geol. Vol. 17, 1922, pp. 105-123.

It was essential to demonstrate that hydrogen sulphide is present in the gases which are active in various phases of magmatic activity not necessarily related to ore deposits. Volcanic emanations are the external manifestations of the gases present in the earth's crust and constitute the only direct evidence for an investigation of these gases.

Rankama and Sahama[8] indicate the significance of volcanic emanations in the problem of magmatic gases and their genesis:

> "During magmatic differentiation the most readily volatile constituents become concentrated in pneumatolytic and hydrothermal deposits. Little is known of the concentration of the volatiles in a melt or in its derivatives until they rise to the earth's surface along cracks and fissures surrounding the magma basin."

Analysis of volcanic emanations were found to reveal several features which are significant to the thesis problem.

1. Hydrogen sulphide is almost invariably present in considerable quantities during some phase of fumarolic activity. Zies[9] gives tables emphasizing the considerable volume of the hydrogen sulphide escaping from the Katmai fumaroles in Alaska.

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8. Rankama and Sahama: Geochemistry, pg. 184

9. Zies: The Valley of Ten Thousand Smokes, I and II, 1929, Nat. Geog. Soc. Contributed Tech Papers I Katmai Series No. 4

2. Hydrogen sulphide and the other sulphur compounds have their definitely established position in the sequence of events involved in fumarolic activity. This order of appearance was more or less established in 1858 by Deville and Leblanc and was modified by F.W. Clarke[10]. In most of these considerations the presence of water results in the oxidation of the hydrogen sulphide except at greatly lowered temperatures. At depth the reactions might well be modified by other effects, such as pressure and preponderance of reducing gases.

To try to fit the formation of pyrrhotite by the action of hydrogen sulphide on iron silicates into the scheme of gas activity evidenced by volcanic emanations, we must try to trace the possible reactivity of the gases throughout their course of travel. Rankama and Sahama[11] (like most investigators of the chemistry of ore-formation) believe that the pneumatolytic and hydrothermal emanations are first acid in reaction due to the presence of numerous volatile acids. These acids (including hydrogen sulphide) are neutralized in reactions with the surrounding rocks and the solutions may become alkaline in a later stage. The complex chemistry involved will permit only a tentative

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10. Clarke, F.W.: Data of Geochemistry, 5th Ed., 1924, pp. 261-292.

11. Op. cit., pg. 184.

postulate that this early acid reaction may include a more or less widespread sulphur metasomatism depending on the type of magma involved.

The conclusions, or generalizations, which were made after a review of the literature are threefold:

1. No experimental investigations of the nature of the present research have been previously performed.

2. Various theories on sulphur metasomatism show that the reactions attempted by the author in the laboratory are in harmony with the ultimate geologic criterion which is field observations.

3. Hydrogen sulphide is frequently present in volcanic emanations and could therefore well be an active agent of a process of sulphur metasomatism.

CHAPTER III

METHOD OF RESEARCH

To determine whether pyrrhotite could possibly be formed by the action of hydrogen sulphide on iron-bearing silicates, an extremely simple procedure was followed in the laboratory. Mineral, and sometimes rock, samples were placed inside the combustion tube of a high-temperature furnace and a slow stream of hydrogen sulphide was permitted to flow through the tube while the furnace was brought to the desired temperature. The specimen was removed after treatment and examined by making polished sections, and in some cases, X-ray powder photographs.

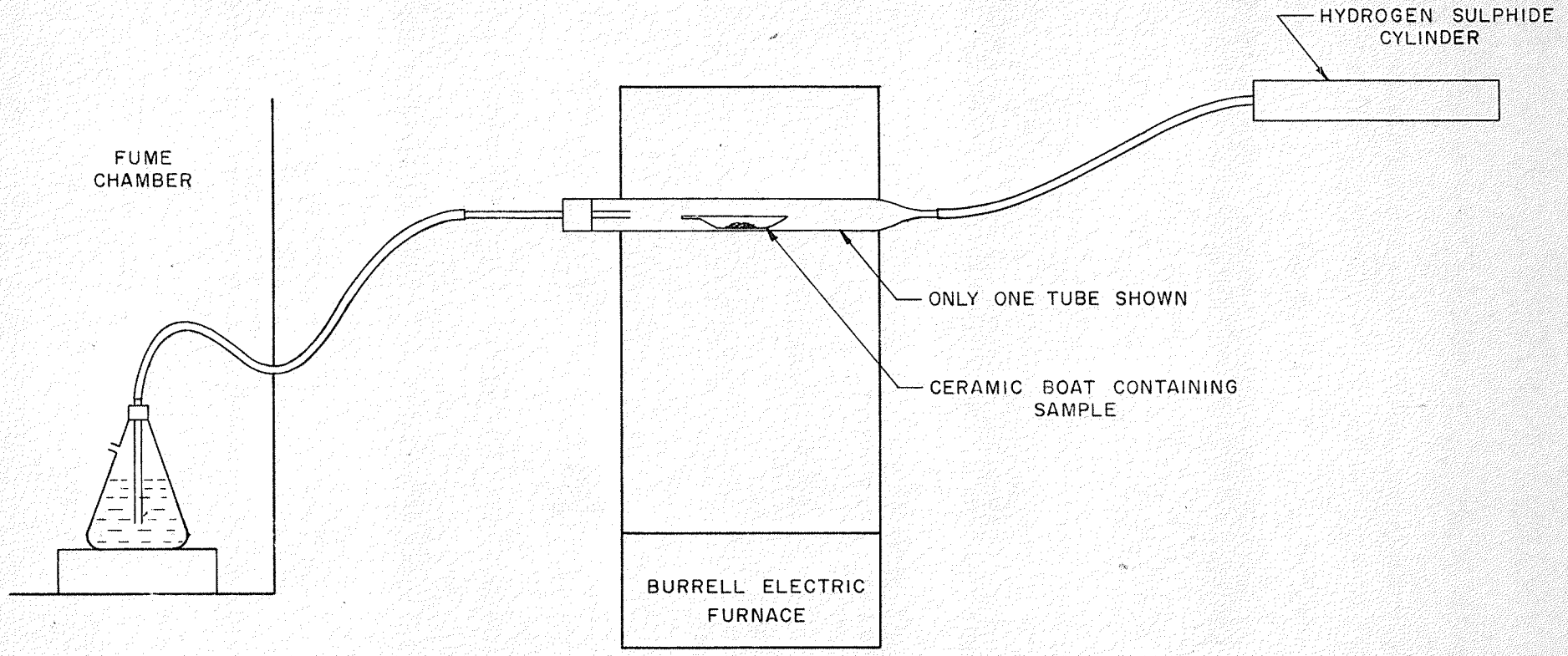
The apparatus used while carrying out the problem consisted of the following:

1. Burrell Tube Furnace, Model T-29 and accessories.
2. Pressure Cylinder containing hydrogen sulphide.
3. Apparatus for the preparation and examination of polished sections of the powdered sample.
4. Leeds and Northrup Potentiometer and Thermocouple.

Figure 1 is a sketch of the apparatus during a typical experimental procedure.

The research procedure can be outlined as follows:

1. Preparation of the specimen.
   a. Select a pure mineral sample.
   b. Crush mineral to + 200 or + 100 mesh.



SCHEMATIC DIAGRAM
OF THE APPARATUS USED THROUGHOUT THE PRESENT RESEARCH

FIGURE 1

c. Examine specimen for purity and separate out any possible magnetic fraction.

d. Place a small amount of the powdered mineral (5 to 10 gms.) in a porcelain boat.

2. Treatment of the specimen

a. Slide the porcelain boat containing the mineral sample into the combustion tube. (See Fig. 1)

b. Start the flow of hydrogen sulphide through the tube expelling the air from the apparatus.

c. Switch the furnace on with the secondary voltage dials set at a value above that necessary for the desired temperature.

d. Maintain a slow flow of hydrogen sulphide throughout the experiment.

e. When the desired temperature is reached, maintain it for a specified time, keeping a record of any temperature variations.

f. Switch the furnace off and continue the hydrogen sulphide flow until the furnace has cooled.

g. Remove the specimen from the cooled combustion chamber.

3. Examination of the treated specimen.

a. Examine under the binocular microscope for sulphide formation, fusion, discolouration and any other possible effects.

b. Prepare a polished section of the mineral specimen. The most successful technique for this is outlined in a later chapter.

c. Examine the polished section of the mineral under the metallographic microscope.

d. Take an X-ray powder picture of the treated specimen (if considered necessary).

4. Recording of the results.

Only a qualitative evaluation of the results could be made and recorded.

The method outlined above was followed with a few exceptions. An attempt was made to use a nitrogen atmosphere for both the heating and cooling stages of the experiment. A polished rock specimen (instead of a powdered mineral) was used during one run. The results of these variations will be recorded later.

During the course of the experimentation numerous difficulties were encountered, many of which were inherent in the apparatus and hence purely mechanical. Temperature controls were difficult to maintain without constant regulation. The flow of hydrogen sulphide tended to be erratic and dangerous leakages remained a problem at all times. Since the experiments generally lasted for at least eight hours, it was necessary to organize this time so as to be able to check the apparatus constantly. The furnace, along with the

rest of the apparatus, had not been used previously and much time was consumed in misruns, attempted calibrations, and mechanical adjustments of the apparatus. In order to summarize these operational problems, the author has inserted the following chapter.

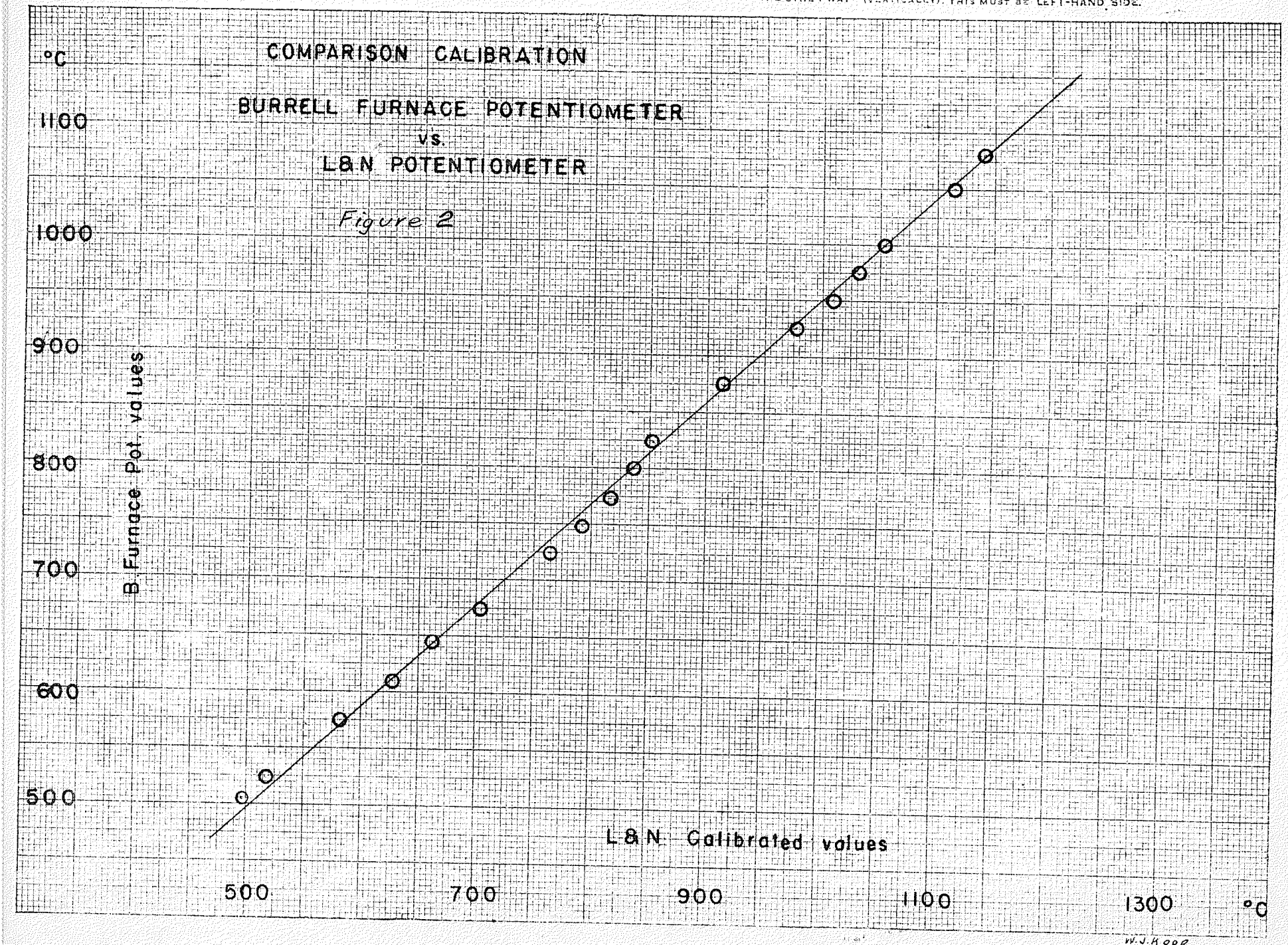
CHAPTER IV

TECHNICAL ASPECTS AND OPERATIONAL PROCEDURE

This chapter, as already indicated, is intended as a purely practical operations guide for any possible further research on the present problem. The great amount of time spent on eliminating difficulties in technique and assembling and checking the apparatus warrants a brief discussion.

Temperature Problems

The maintenance of a fiarly consistent temperature and its accurate measurement was necessary. Several calibrations were attempted using pure metal freezing curves. A considerable discrepancy between the furnace temperature readings and the known melting points was found. The variations did not appear to follow a very consistent pattern and as a result it was considered necessary to acquire a more reliable Leeds and Northrup Potentiometer and Thermocouple. A series of comparison calibrations were run with the previously calibrated Leeds and Northrup Thermocouple inserted in one of the combustion tubes. Figure 2 is a graph indicating the accurace Leeds and Northrup values in comparison to the values observed on the Burrell potentiometer dial. All the temperature readings given throughout this thesis



have been corrected according to this graph. The Leeds and Northrup Potentiometer was calibrated by running a series of freezing curves, plotting temperatures against time. The accuracy was found to be within two degrees in every case. This accuracy was sufficient for the present research, especially since the load fluctuations on the A.C. source caused frequent small temperature irregularities. As indicated by the data tables, it was impossible to maintain a desired temperature and in each case the greatest variation was recorded. This situation might possibly be remedied by the insertion of a rheostat which, if carefully controlled, could vary the power input so as to be able to keep the exact desired temperature. For the purpose of this research such exactitude was unnecessary, considering the length of time required to attain temperature stability without constant readjustment.

A few precautions - most of them probably obvious - had to be taken. Because hydrogen sulphide is inflammable, all the air was circulated out of the combustion tube before any heat was applied. To prevent an explosion, it was necessary to cool the furnace before opening the combustion tube to remove the sample. The voltage readings on the dials of the furnace had to be watched closely because even the finest adjustment caused considerable temperature fluctuation. Ceramic boats had to be cooled slowly in the combustion chamber to prevent cracking.

Operational Procedure

Most of the experiments were run for less than eight hours. There were two reasons for this. In the first place it was somewhat hazardous to leave the hydrogen sulphide flowing overnight, due to the danger of leakage and possible ignition in the hot combustion tube. The second reason was that the extent of the reaction and the amount of pyrrhotite formed appeared to be unaffected by an increase in time. Thus with a reasonably short experimental time, it was possible to conduct a "run" during a single day. The fume chamber draught was poor and throughout the year hydrogen sulphide gas could be detected in various parts of the building. An improved system would be required if a more intensive experimentation schedule were to be attempted. By inserting the specimen in the morning and regulating the temperature throughout the day, it was possible to have the furnace cooled and the hydrogen sulphide valve closed before night.

It was necessary to maintain a very slow flow of hydrogen sulphide through the combustion tube of the furnace. The screw valve which is part of the hydrogen sulphide cylinder was of insufficient sensitivity and considerable difficulty was experienced in regulating the proper flow. A generator with a sensitive needle valve would have been a definite improvement. An attempt to use a Kipp

Generator was unsatisfactory. This type of generator might introduce foreign iron into the system. Another variation attempted was to use a nitrogen atmosphere during the heating and cooling stages of the experiments. This refinement did not appear to be warranted for the present stage of experimentation especially because little is known about the possible hazards of mixing nitrogen and hydrogen sulphide at extremely high temperatures.

Polished sections of the mineral samples were examined before and after treatment in the furnace. Several techniques of mounting the powdered mineral in bakelite were attempted. The most satisfactory method however was found to be one using leucite. The procedure was as follows:

1. Mix a small amount (approximately 1/8" in a 25 ml. beaker) of finely powdered leucite with the crushed mineral.

2. Pour the mixture into the mould, spreading it over the bottom. Fill the mould to the required level with leucite powder.

3. Heat the mould to 100° at 2000 pounds pressure.

4. Increase the pressure to 3500 pounds and retain this pressure until the temperature reaches 125°. At this temperature switch the heater off and allow to cool under pressure.

5. Grind and polish the transparent leucite

section on the Graton-Vanderwilt Polishing Machine.

The sections made in this manner proved very satisfactory for the detection of pyrrhotite on or inside the mineral sample.

CHAPTER V

EXPERIMENTAL DATA AND OBSERVATIONS

The details of all the significant experiments were recorded in Table 1 which appears on page 23. This table shows some of the difficulties which were encountered. An "Average Maximum Temperature" (the desired experimental temperature) was often exceeded during the course of the experiment. This is a weakness which could be overcome by closer supervision and technical adjustments of the apparatus. For the present research this difficulty was not considered to be too harmful. The column headed "Total Operating Time" records the number of hours that the furnace was switched on. The difference between this total and the "Duration of the Average Maximum Temperature" indicated the time required to heat the furnace to the desired temperature. Brief observations were noted under "Comments and Results". The remainder of this chapter will consider some of the individual minerals separately.

It wasobserved from the first few experiments that pyrrhotite was formed by the reaction of hydrogen sulphide with all of the iron-bearing silicates providing the temperature was high enough (usually within a few hundred degrees of their melting temperatures). Further experiments were then carried out to determine the lower limits to which this process of pyrrhotite formation was

TABLE 1 SUMMARY OF EXPERIMENTAL DATA

No.	Date	Total Operating Time	Maximum Recorded Temp.	Average Maximum Temp.	Duration of Average Maximum	Specimen Untreated Treated	X-Ray	Comments and Results
1	12/12/51	7.5 hrs.	1115°C	1085°C	3.5 hrs.	2A Hortonolite 2B Dunite		Abundant pyrrhotite formed
2	19/12/51	10.0	1065°C	1055°C	5.5	3A Augite 3B 4A Biotite 4B	3B 4B	Small amount pyrrhotite Pyrrhotite abundant on cleavage
3	4/1/52	9.0	1065°C	1055°C	5.0	5A Serpentine 5B 6A Epidote 6B	6B	Minor pyrrhotite 5-10% pyrrhotite on grains
4	8/1/52	10.0	1080°C	1055°C	6.5	7A Hornblende 7B 8A Quartz 8B	7B	Up to 10% pyrrhotite on grains No metallic minerals formed
5	10/1/52	12.0	1075°C	1035°C	8.0	5A Serpentine 5B[1] 2A Hortonolite 2B[1] Dunite		No visible change Pyrrhotite formed in and on grains
6	12/1/52	7.0	1055°C	1035°C	3.0	As above		As above
7	14/1/52	8.0	1065°C	1035°C	4.0	As above		As above
8	15/1/52	10.5	1030°C	1025°C	9.0	As above		As above
9	17/1/52	12.0	1020°C	1000°C	9.0	7A Hornblende 7B[1] 4A Biotite 4B[1]		Small amount pyrrhotite on cleavage 20% pyrrhotite on cleavage
10	18/1/52	11.0	1030°C	1010°C	8.0	As above		As above
11	19/1/52	8.0	1045°C	1010°C	5.0	As above		As above
12	21/1/52	8.0	980°C	970°C	5.0	9A Magnetite 9B 8A Quartz 9B	9B	Completely reduced to pyrrhotite Fresh surface, no metallic minerals
13	22/1/52	8.5	1025°C	980°C	5.5	10A Chlorite 10B		Minor amount pyrrhotite
14	23/1/52	80.5	670°C	660°C	80.0	Hornblende and pyrrhotite at opposite ends vacuum tube		No evidence of pyrrhotite transfer to hornblende
15	28/1/52	8.0	835°C	835°C	5.0	6A Epidote 6C 7A Hornblende 7C		No visible change No sulphides formed
16	29/1/52	10.0	945°C	945°C	6.5	6A Epidote 6C 7A Hornblende 7D		Occasional pyrrhotite specks Very minor pyrrhotite
17	30/1/52	11.0	1010°C	1000°C	7.5	6A Epidote 6E 7A Hornblende 7E		Sulphides throughout To 5% pyrrhotite on grains

No.	Date	Total Operating Time	Maximum Recorded Temp.	Average Maximum Temp.	Duration of Average Maximum	Specimen Untreated Treated	X-Ray	Comments and Results
18	31/1/52	8.0	860°C	835°C	5.0 hrs.	4A Biotite 4C 11A Limonite 11B		Traces Reduced to pyrrhotite on surface
19	4/2/52	9.0	1065°C	1055°C	5.0	A2A Hortonolite A2B 11A Limonite 11C	A2B	To 25% pyrrhotite on some grains Grains coated with pyrrhotite
20	6/2/52	6.0	860°C	835°C	3.0	A2A Hortonolite A2C F87A Metasediment F87B		Rare pyrrhotite Scattered pyrrhotite on biotite
21	7/2/52	4.0	835°C	830°C	2.0	As above		As above
22	8/2/52	8.0	945°C	945°C	5.0	A2A Hortonolite A2D 3A Augite 3C		Minor pyrrhotite on most grains No change visible
23	10/2/52	8.0	1010°C	1000°C	5.0	A2A Hortonolite A2D 3A Augite 3D		Minor pyrrhotite No trace of pyrrhotite
24	12/2/52	8.0	915°C	890°C	5.0	3A Augite 3E 10A Chlorite 10C		No visible change No change
25	15/2/52	102.0	670°C	640°C	100.0	Epidote and pyrrhotite at opposite ends vacuum tube		No transfer of pyrrhotite to epidote
26	4/4/52	123.0	680°C	670°C	120.0	4A Biotite 4D		No visible change
27	17/4/52	3.5	1040°C	1025°C	3.5	A2A Hortonolite A2F		Used nitrogen atmosphere No pyrrhotite
28	28/4/52	9.5	1025°C	1010°C	5.0	7A Hortonolite 7F 7A Hornblende 7G		Misrun
29	7/5/52	8.0	1085°C	1065°C	5.5	7A Hornblende 7H 7A Hornblende 7J		Small amount pyrrhotite as above. Used nitrogen while heating and cooling.

active. The experimental time was also varied to determine how this would affect the extent to which the reaction progressed.

1. Hornblende.

Formula: $(OH)_2(Ca,Na,K)_{2-3}(Mg,Fe,Al)_5(Si,Al)_2Si_6O_{22}$

Melting Temperature: 1025-1085°C[12]

Atomic Structure: Double silicon-oxygen chains

The following experimenta were carried out using hornblende samples:

Exp.No.	Sample No.	Aver.Max.Temp.	Time (hr)	Observations
15	7C	835°C	5.0	No visible change
16	7D	945°C	6.5	Trace of pyrrhotite
17	7E	1000°C	7.5	Up to 5% pyrrhotite
9-11	7B[1]	1010°C	22.0	Small amount pyrrhotite on cleavage
4	7B	1055°C	6.5	To 10% pyrrhotite
29	7H	1065°C	5.5	Less than 5% pyrrhotite

Results: The data given above indicate that at high temperature hydrogen sulphide will react with hornblende to form pyrrhotite. There was a very slight indication that the reaction is more extensive at higher temperatures but Experiment 29 would appear to deny this. Increased

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12. Grout, F.F.: Petrography and Petrology, 1932, pg. 152.

time had no noticeable effect on any aspect of the pyrrhotite formation. As would be expected, the pyrrhotite was formed at the more accessible outer margin and along the cleavage.

2. Biotite.

Formula: $K(Mg,Fe)_3(AlSiO_{10})(OH)_2$

Melting Temperature: 1130-1230°C[13]

Atomic Structure: Sheets of silicon-oxygen tetrahedra.

Data:

Exp. No.	Sample No.	Aver.Max.Temp.	Time (hr)	Observations
2	4B	1055°C	5.5	5-10% pyrrhotite
9-11	4B[1]	1000°C	22.0	To 5% pyrrhotite
18	4C	835°C	5.0	Trace pyrrhotite
26	4D	670°C	120.0	Unaltered biotite, no pyrrhotite

Results: The heat treatment of biotite in an atmosphere of hydrogen sulphide resulted in a reaction to form pyrrhotite at temperatures above about 835°C. The reaction was found to be more extensive at higher temperatures as seen in the above table. A 120-hour experiment at 670°C failed to produce any pyrrhotite. As in the case of hornblende, the pyrrhotite formed along the cleavage. (See Photomicrograph Plate 2). The biotite showed evidence of partial fusion (or reaction products ?) at temperatures

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13. Grout, F.F.: Op. cit. pg. 152.

above 1000°C. The X-ray powder photograph (Table 3) of 4B gave a fairly weak pyrrhotite pattern with no evidence of biotite. The thermal disintegration of the biotite was therefore indicated.

3. Augite.

Formula: $Ca(Mg,Fe)(Si_3O_2)_2\left((Al,Fe)_2O_3\right)_x$

Melting Temperature: Diopside 1391°C other pyroxenes 925-1400°C[14]

Atomic Structure: Single silicon-oxygen chains.

Data:

Exp. No.	Sample No.	Aver.Max.Temp.	Time (hr)	Observations
2	3B	1055°C	5.0	Small amount pyrrhotite. X-ray shows augite.
22	3C	945°C	5.0	No change visible
23	3D	1000°C	5.0	No change visible
24	3E	890°C	5.0	No change visible

Results: Experiments indicated that pyrrhotite will form by the reaction of hydrogen sulphide with an augite sample at temperatures above about 1055°C. Experimental time was 5.0 hours throughout. The possibility of a time factor will be discussed later. An X-ray powder picture of sample 3B (Table 2) indicates that the mineral structure did not break down. Photomicrograph Plate 1 shows a typical polished section of the augite grains after treatment.

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14. Grout, F.F.: Op. cit. pg. 152.

4. Hortonolite. (From hortonolite dunite sample collected by Dr. H.D.B. Wilson.)

Formula: $(Mg,Fe)_2SiO_4$ (Iron-rich olivene)

Melting Temperature: Assuming Fe:Mn ≡ 38:22 melting range is from 1300-1550°C.

Atomic Structure: Separate silicon-oxygen groups.

Data:

Exp. No.	Sample No.*	Aver.Max.Temp.	Time (hr)	Observations
1	2B	1085°C	3.5	Abundant pyrrhotite formed
5-8	2B[1]	1035°C	24.0	Pyrrhotite on surface and interior
19	A-2B	1055°C	5.0	Abundant pyrrhotite
20-21	A-2C	835°C	5.0	Trace pyrrhotite on some grains
22	A-2D	945°C	5.0	Minor amounts pyrrhotite
23	A-2E	1000°C	5.0	Minor amount pyrrhotite

*Samples designated 2 are ground-up rock (hortonolite dunite) specimens with magnetite removed. A-2 samples are pure hortonolite separated by the use of heavy liquids (Clerici solution).

Results: Experiments indicate that at temperatures above about 835°C pyrrhotite will form by the reaction of hydrogen sulphide on iron-rich olivene. Photomicrograph Plate 5 shows the distribution of the pyrrhotite throughout the olivene. X-ray powder pictures indicate that the olivene suffered a thermal breakdown, during the heat

treatment, to pyrrhotite and enstatite (?). X-ray data are presented in Tables 5 and 6. Partial fusion of sample A-2B resulted in a glassy residue which may have been a reaction product.

5. Epidote.

Formula: $H_2O \cdot 4CaO \cdot 3(Al,Fe)_2O_3 \cdot 6SiO_2$

Melting Temperature: Data not available

Atomic Structure: Undetermined[15]

Data:

Exp.No.	Sample No.	Aver.Max.Temp.	Time (hr)	Observations
3	6B	1055°C	5.0	5-10% pyrrhotite on fractures. X-ray shows enstatite
15	6C	835°C	6.5	Minor amount pyrrhotite
17	6E	1000°C	7.5	Fairly abundant pyrrhotite

Results: At temperatures above about 945°C pyrrhotite will form by the reaction of hydrogen sulphide with epidote under the conditions of the experiment. Photomicrograph Plate 3 shows the epidote sample after treatment. Table 4 presents data indicating mineralogical changes involved during the reaction process.

6. Other Minerals.

Minerals not containing iron were subjected to experimental conditions. Serpentine and quartz were

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15. Bragg, W.L.: Atomic Structure of Minerals, 1937, pg. 47.

used to test possible introduction of iron into the reaction system. In all these attempts iron sulphide was not detected and hence the pyrrhotite was actually formed by the extraction of iron from the ferro-magnesian minerals.

Experiment 13 indicated that pyrrhotite was formed from chlorite by reaction at 980°C for 5.5 hours.

Samples of magnetite (Experiment 12) and limonite (Experiment 18) showed more or less complete reduction to pyrrhotite.

7. Treatment of Rock Samples.

A sample of unmineralized Falcon Lake metamorphosed graywacke (F87 - quartz, feldspar, biotite) was subjected to temperatures of about 1000°C for ten hours. A thin section of the treated specimen showed that the biotite became almost completely opaque and was largely replaced by pyrrhotite (Photomicrograph Plate 6).

TABLE 2 X-Ray Powder Data

Substance: Augite sample 3B (after treatment)

Film Number: 818

Radiation/Filter: Fe/Mn

Centre reading: 46.7

I	R	S = θ	d (meas.)	Published values d (Augite)
1	64.1	17.4	3.23	3.26 (50)
10	65.5	18.8	2.99	2.99 (100)
10	69.1	22.3	2.55	2.56 (85)
.5	71.3	24.6	2.32	2.29 (50)
.5	72.3	25.6	2.24	2.20 (50)
2	73.6	26.9	2.14	2.13 (75)
.5	74.8	28.1	2.05	2.04 (75)
.5	75.3	28.6	2.02	2.00 (60)
2	80.0	33.2	1.76	1.74 (75)
6	83.1	36.3	1.63	1.62 (100)
1	85.8	39.1	1.53	1.53 (60)
1	86.6	39.9	1.51	1.51 (60)
2	89.2	42.5	1.43	1.43 (100)
1	89.8	43.1	1.41	1.41 (85)
1	93.1	46.4	1.33	1.33 (85)
1	95.2	48.5	1.29	1.28 (85)
.5	96.4	49.7	1.27	1.27 (50)
.5	97.0	50.3		
.5	103.9	57.2	1.15	1.15 (50)
6	110.2	63.5	1.08	1.08 (100)
4	111.2	64.5	1.07	1.07 (100)

TABLE 3 X-Ray Powder Data

Substance: Biotite sample 4B (after treatment)

Film Number: 777

Radiation/Filter: Fe/Mn

Centre reading: 38.8

I	R	S = θ	d (meas.)	Published values d (Pyrrhotite)
5	58.2	19.4	2.91	2.98
7	60.0	21.2	2.67	2.64
8	61.4	22.6	2.51	
9	66.3	27.5	2.09	2.06
7	77.6	38.8	1.54	
	88.2	49.6	1.27	1.29
10	94.9	56.1	1.16	1.11

Note: The above pattern is probably a weak pyrrhotite pattern. The biotite reflections are entirely absent indicating complete breakdown of the atomic structure of the biotite during the heat treatment.

TABLE 4 X-Ray Powder Data

Substance: Epidote sample 6B (after treatment)

Film Number: 781

Radiation/Filter: Fe/Mn

Centre Reading: 45.4

I	R	S = θ	d (meas.)
10	62.5	17.0	3.30
9	63.2	17.8	3.16
9	64.6	19.2	2.94
3	67.1	21.6	2.62
.5	68.4	23.2	2.45
7	73.3	27.9	2.06
1	77.5	32.1	1.82
6	79.9	34.5	1.70
4	84.5	39.1	1.53
.5	89.8	44.4	1.38

Note: The above pattern differs from that of untreated epidote (visual comparison and measurement) and has affinities with that of some of the pyroxenes.

TABLE 5 X-Ray Powder Data

Substance: Hortonolite sample A2 - A (untreated)

Film Number: 780

Radiation/Filter: Fe/Mn

Centre reading: 45.5

I	R	S = θ	d (meas.)
5	56.0	10.6	5.25
2	59.4	14.1	3.96
3	61.2	15.7	3.57
5	63.9	18.5	3.04
9	65.4	19.9	2.84
7	67.6	21.9	2.59
9	68.2	22.5	2.52
5	69.3	23.8	2.39
4	70.2	25.7	2.23
1	71.7	26.2	2.19
10	78.5	33.0	1.77
1	80.3	34.8	1.69
1	81.0	35.5	1.66
1	81.5	36.0	1.64
1	82.1	36.6	1.62
5	82.6	37.1	1.60
1	85.0	39.5	1.52
2	85.4	39.9	1.51
2	88.3	42.8	1.42
1	90.3	44.8	1.37
2	92.0	46.5	1.33
1	106.0	60.5	1.11
2	108.0	62.5	1.09
8	112.4	66.9	1.05
4	104.8	59.3	1.12
1	116.1	70.6	1.02
2	125.3	79.8	0.98

TABLE 6 X-Ray Powder Data

Substance: Hortonolite sample A2 - B (after treatment)

Film Number: 784

Radiation/Filter: Fe/Mn

Centre reading: 45.2

I	R	S = θ	d (meas.)	
10	63.0	17.8	3.16	
10	64.4	19.1	2.95	
10	64.9	19.8	2.85	
	66.8	21.6	2.62	
	67.9	22.5	2.52	
	75.3	28.1	2.05	
	75.1	29.9	1.94	Note absence of
	82.3	37.1	1.60	1.77 - strongest
4	84.6	39.4	1.52	Hortonolite line
5	86.2	41.0	1.47	
	87.7	42.5	1.43	
1	89.5	44.3	1.38	
	92.3	47.1	1.32	
	93.8	48.6	1.29	
4	95.1	49.9	1.26	
5	98.2	53.0	1.21	
5	100.9	55.7	1.17	
	106.6	61.4	1.10	
	110.3	65.1	1.06	
	112.4	67.2	1.05	
	121.8	76.6	0.99	
5	118.2	73.0	1.01	

CHAPTER VI

THEORETICAL CONSIDERATIONS

A theoretical consideration of high-temperature mineral-gas systems is necessary because of the scarcity of factual data on the subject. The thermal study of minerals may indicate the physical chemistry of the reactions involved in the formation of pyrrhotite under the present experimental conditions. It was found experimentally that hydrogen sulphide will react with iron-bearing silicates at relatively high temperatures. Simple thermal disintegration of the minerals may be taking place at these temperatures. The X-ray patterns exhibited by treated specimens (except augite) do indeed record structural breakdown of the atomic pattern. This aspect and also the speculative nature of the suggested hypothesis of pyrrhotite genesis necessitates a theoretical digression.

The subject of structural disintegration of minerals at high temperatures had not received much attention until fairly recent refinement of X-ray techniques. A review of the literature did however indicate that as early as 1884 Doelter and Hussak[16] determined that green hornblende broke down into magnetite

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16. Doelter, C. and Hussak, E.: Uber die Einwirkung geschmolzener Magmen auf Verschiedene Mineralin: Neues Jahr für Min., Geol., und Pal., Band 1, pp. 18-44 (1884).

plus augite, or olivene, at a high temperature. Wittels[17], in 1937, by means of differential thermal analyses, discovered the temperature of structural disintegration of some amphiboles. Disintegration was indicated by peaks (endothermic reactions) on his thermographic curves. Breakdowns occurred between 925°C and 1125°C and one of the products of disintegration was usually hematite or magnetite. The present experiments (see page 25) show that at, and above, the temperature of 945°C (lower limit of reaction is between 835°C and 945°C) pyrrhotite will form by the action of hydrogen sulphide on hornblende. Wittels' experiments suggest that the iron for the formation of pyrrhotite is made available for reaction with hydrogen sulphide simply as the result of thermal structural disintegration. The following is an example of a reaction at high temperature produced by Wittels.

$$\text{Hornblende} + {}^{3}/_{2}\ O_2 + \Delta H \rightarrow \text{polyaugite} + \text{plagioclase} + \text{hematite} + H_2O$$

In an atmosphere of hydrogen sulphide the hematite would be immediately reduced to pyrrhotite. It is possible that in all of the present experiments performed by the writer, structural breakdown of the iron-bearing silicates was

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17. Wittels, M.: The Structural Disintegration of Some Amphiboles, Am. Min. pp. 28-36, 1937.

necessary in order for the pyrrhotite-forming reactions to take place. X-ray analyses verified this breakdown, with the exception of augite.

The temperature of pyrrhotite-forming reactions was never found to be lower than 835°C (biotite and hortonolite). This is a high temperature, even in terms of igneous reactions, since contact metasomatism probably takes place at temperatures from 400°C. to 800°C. The temperature of an intruding siliceous magma ranges from 500°C to 1100°C. The possibility of a process of pyrrhotite genesis in nature paralleling the conditions of the experiment would therefore appear to be rather remote. The conditions attained during deep-seated dynamic and regional metamorphism of basic rocks (e.g. "greenstone" and graywacke) could however quite conceivably be accompanied by a high temperature sulphur gas stage.

The complexity of Precambrian areal geology illustrates amply the intimate association of regional metamorphism and igneous activity which could result in such a gas phase at least locally. This gas phase need not necessarily be accompanied by the mineralogical changes of an advanced stage of regional metamorphism in the usual sense. Permeable zones would channel the gases and the resultant pyrrhotite occurrence and other associated phenomena would be restricted along these zones.

Field observations by the writer in the West Hawk Lake area have shown that the pyrrhotite "dikes" of the area always trend parallel to the bedding and foliations of the country rock. Most of the mapped "dikes" or zones of pyrrhotite mineralization do, in fact, occur at a contact zone between meta-sediments and meta-volcanics. Mineralogical changes along these zones are unique for this series of rock formations and have been discussed by L.S. Binda[18].

Several theoretical postulations can be made as to the significance of the experimental process of pyrrhotite genesis demonstrated by this thesis.

1. The availability of the iron in iron-bearing silicates. It has been demonstrated that, given the required conditions of temperature and sulphurous atmosphere, the metallic element iron could be extracted from ordinary rock-forming iron-bearing minerals in the solid state. The parallel process in nature has not been established, but the possibility of the process has been proved.

2. Pyrrhotite-forming processes might occur within a magma prior to complete consolidation. Late magmatic sulphurous gases (if present) would react with basic iron-bearing silicates, which have already been crystallized,

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18. Binda, L.S.: Petrology of the Archaean Sediments in the West Hawk Lake Area, M.Sc. Thesis, Sept. 1953.

to form pyrrhotite. The observed presence of abundant pyrrhotite in some phases of hortonolite dunites could be explained by this process. It is not within the scope of this thesis to speculate on the presence of such a gas at a sufficiently early stage of consolidation.

3. A non-metalliferous gas phase of a magma could form iron-bearing sulphide dikes by a process of wall-rock leaching. This process would (except for pressure) more or less duplicate the conditions of the present experiments. The pressure release necessary to enable such a gas phase to escape is not unfeasible in the thermally and tectonically active zone of igneous intrusion. Some fairly obvious mineralogical associations and changes might be detectable in the vicinity of this metallization process which would assist in distinguishing these uneconomic iron-sulphide zones from commercial prospects.

CHAPTER VII

SUMMARY AND CONCLUSIONS

A very simple experimental procedure was followed to examine the high temperature reactivity of various rock-forming, iron-bearing silicates in an atmosphere of hydrogen sulphide. Rock and mineral specimens were treated in a high-temperature Burrell Tube Furnace through which a stream of hydrogen sulphide was passed. Polished sections of the powdered specimens were made before and after treatment. X-ray powder pictures were made of significant samples.

Summary of Observations

The experimental data has been briefly summarized in Table 1, appearing in Chapter V. It was observed that the various iron-bearing silicates reacted with hydrogen sulphide at high temperatures. Examination under a metallographic microscope showed that pyrrhotite was being deposited around and within the minerals. Minerals with well developed cleavage (e.g. biotite) showed pyrrhotite blebs along this cleavage. X-ray investigation of samples after treatment indicated that the atomic structure of the minerals subjected to the heat treatment usually suffered thermal disintegration. Augite was a notable exception to this observation. The fact that

pyrrhotite was formed without structural breakdown of the augite specimen indicates that temperatures exceeding the "thermal disintegration temperature" are not necessary for this method of pyrrhotite synthesis.

Variations in the experimental procedure pointed out two interesting aspects. The time of heat treatment was increased (e.g. Experiments 9 to 11 and 26) in order to evaluate the significance of the time factor. With the limited experimental data the increased time appeared to have no visible effect on the reaction. A second variation is recorded in Experiment 20 where a meta-sedimentary rock specimen was used instead of a mineral sample. The highly selective nature of the reaction was emphasized by the polished section (Photomicrograph Plate 6) which showed the biotite partially replaced by, and surrounded with, pyrrhotite while the non-iron-bearing minerals remained clear.

Conclusions

The series of experiments described in this thesis have demonstrated that hydrogen sulphide will react with iron-bearing silicates at high temperature to form pyrrhotite. No study was made of the nature of the reaction nor of any possible by-products. The geological significance of this demonstration is that, in the earth's crust, an originally non-metallic sulphur

gas phase could, by reaction with common wall-rock minerals, produce iron sulphide. This process of sulphur metasomatism may be a major metallization agent in the "pyrrhotite-dike" occurrences of certain areas such as West Hawk Lake in the Precambrian Shield of Manitoba.

ILLUSTRATIONS

The magnification, except where noted, is approximately 300 times.

Plate 1

Photomicrograph of a polished section through an augite grain after treatment (Sample 3B of Experiment 2) showing scattered minute pyrrhotite blebs throughout. There is a slight tendency for the pyrrhotite to occur in rows, possibly along cleavage directions.

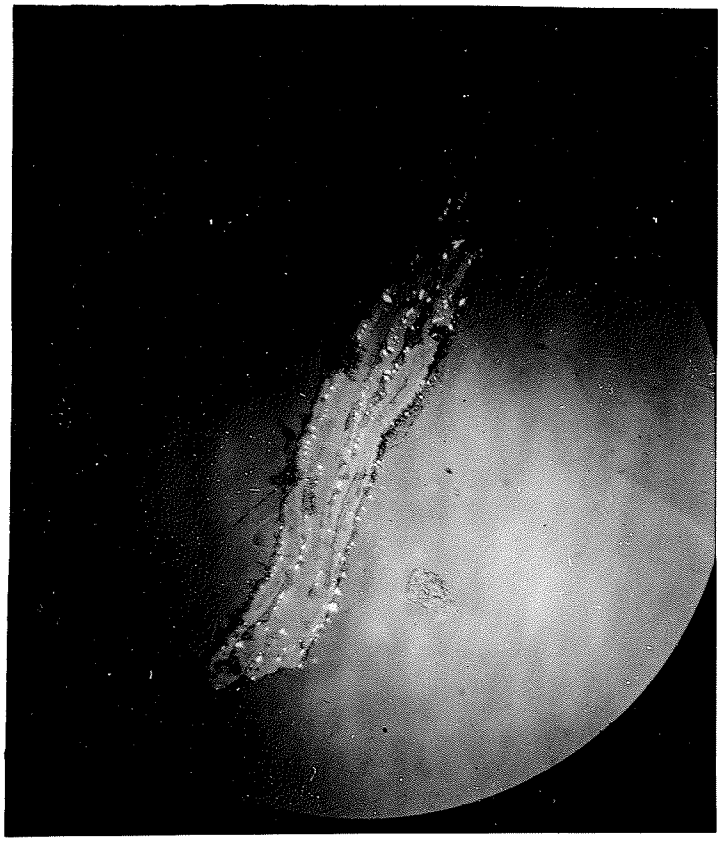

Plate 2

Photomicrograph showing a biotite grain after heat treatment (Sample 4B of Experiment 2) in an atmosphere of hydrogen sulphide. Note the very abundant pyrrhotite along the well developed cleavage planes. The X-ray powder photograph of this sample showed very strong pyrrhotite reflections.

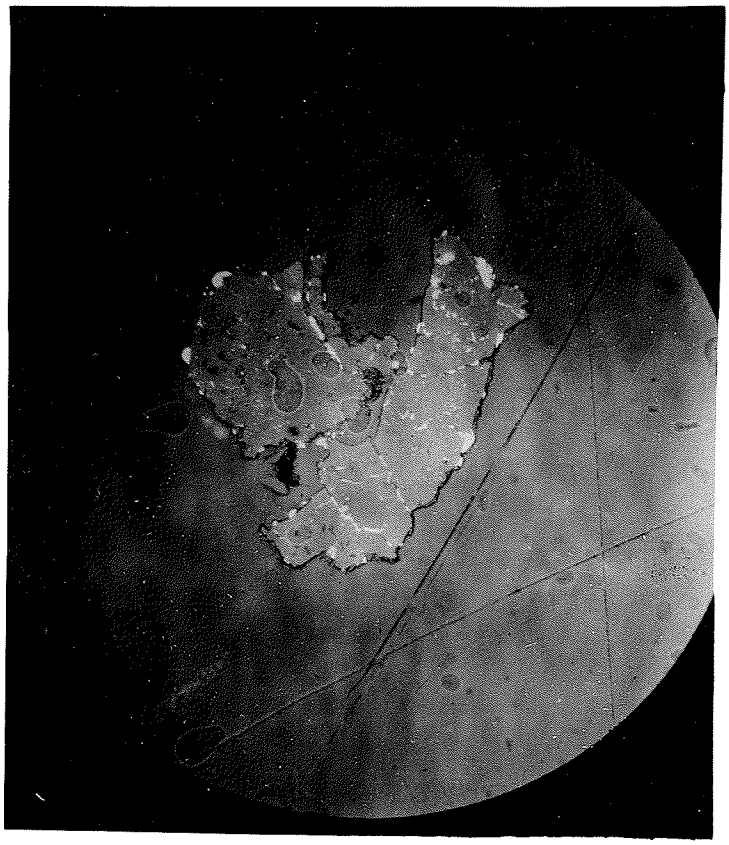

Plate 3

Photomicrograph of a grain of epidote after heat treatment showing pyrrhotite formed by the reaction of the epidote with the atmosphere of hydrogen sulphide. The pyrrhotite occurs mainly on the rim of the grains and along minute fractures. (Sample 6B of Experiment 3)

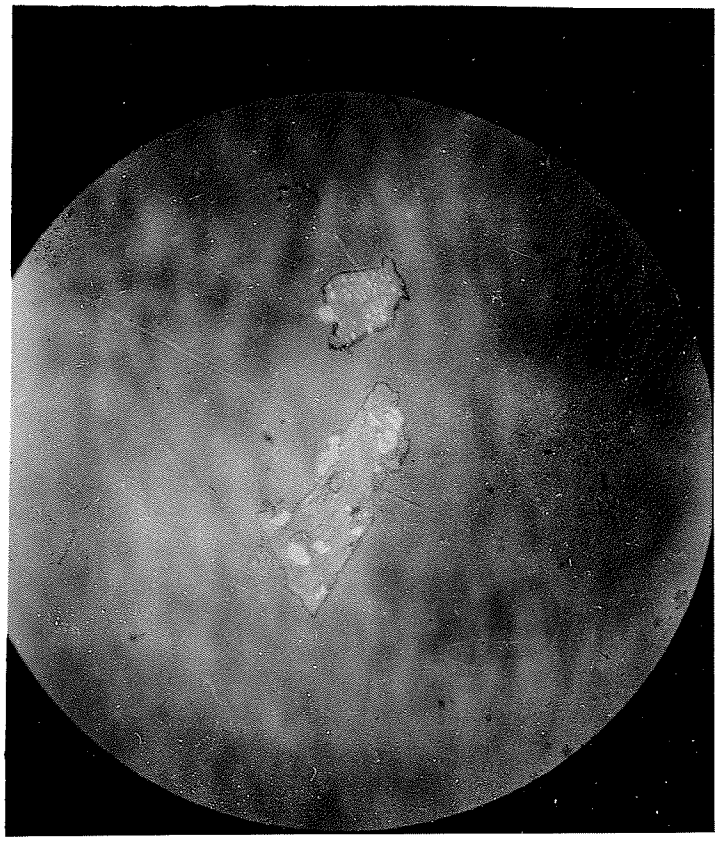

Plate 4

Photomicrograph of hornblende grains after treatment (Sample 78 of Experiment 4) showing scattered well defined blebs of pyrrhotite. X-ray powder photographs of the hornblende sample before and after treatment were completely different indicating that the atomic structure suffered a breakdown.

Plate 5

Photomicrograph of a hortonolite grain after treatment at 1055°C (Sample A2B of Experiment 19). Pyrrhotite is very abundant throughout the grain and forms a layer along part of the edge.

Plate 6

Magnification 23 times.

Photomicrograph of a polished section of a sample of metasediment (Sample P87B of Experiment 20) showing abundant pyrrhotite specks on the surface of the biotite. The biotite of the rock specimen reacted in a similar manner as the mineral specimen (see Plate 2) and the pyrrhotite formed in a highly selective manner only on the iron-bearing silicate.

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