

**SYNTHESIS OF PYRRHOTITE BY HYDROGEN
SULPHIDE IN IRON BEARING SILICATES.**

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by

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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.

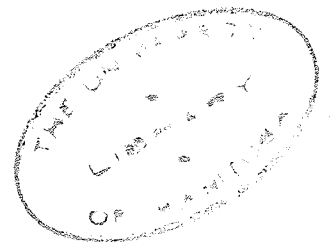


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CHAPTER I

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. Hintze¹ records various methods of synthesis by reactions in the dry state. Iron and sulphur combine in various proportions according to the conditions of the

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

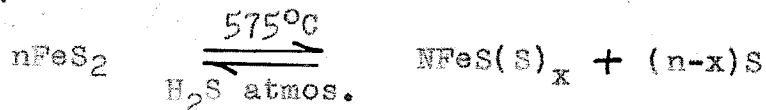
experiment. It was recognized early that pyrite lost part of its sulphur upon heating to a red heat in an atmosphere of hydrogen sulphide. Syntheses were carried out by various other means. Combinations of hydrogen sulphide and marcasite, iron and sulphur, iron wire and hydrogen sulphide, hydrogen sulphide 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 Doelter² lists over 100 pyrrhotite analyses. No mention was found of any experimenter 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 especially by some recent crystal structure investigations. A very significant study of pyrrhotite was published in 1912 and 1917 by E.T. Allen and his associates³. They studied the reversible

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:



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 Sucksdorff⁴ 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

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

ideal lattice are therefore vacant in most pyrrhotite samples⁵.

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 Verhoogen⁶ summarize the discussion

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. Goldschmidt⁷ 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.

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