# QUANTITATIVE DETERMINATION OF HEXAGONAL AND MONOCLINIC PYRRHOTITES BY X-RAY DIFFRACTION

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## ABSTRACT

Measurement of the difference in amplitude of components at about 51.75° and 51.40°$2\theta$ (Co K$\alpha$ radiation) of the asymmetric x-ray diffraction peak resulting from partial superposition of strong diffractions from corresponding planes in hexagonal and monoclinic pyrrhotite structures allows rapid quantitative determination of amounts and proportions of these structures in certain sulphide ores carrying at least 3% of either pyrrhotite type. The differences in amplitudes from synthetic mixtures of the pure structures are divided by the amplitudes of a nearby diffraction peak from an internal standard added in constant proportion; and the resulting ratios are plotted against the known proportions of either structure. The plot may be checked against weights of magnetic concentrates of monoclinic pyrrhotites from the ores under study. Determination rates of at least two to three samples per hour with an average error of about ±12% of the amounts present may be readily attained with suitable instrumentation. Economical and relatively precise contouring of sulphide bodies for the amounts and distributions of hexagonal (paramagnetic) and monoclinic (ferromagnetic) pyrrhotites is thus feasible.

## INTRODUCTION

In late 1962 and early 1963 x-ray powder diffraction examinations of magnetic separates from test samples of nickel ore from the Strathcona mine, Sudbury District, revealed varying proportions of two structural types of pyrrhotite. A structural type with hexagonal symmetry showed much less magnetic susceptibility than a type with apparent monoclinic symmetry.

Determinations of proportions of pyrrhotites by magnetic separation in stages seemed feasible. The grain sizes of the two structural types were coarse enough to allow fairly complete separation after grinding to about 80% − 200 mesh. However, the procedure was laborious and also inaccurate because pyrrhotite recoveries calculated from chemical analyses of products contained errors due to incomplete separations and variable concentrations of four iron-bearing sulphides and several iron-bearing oxide and silicate minerals.

In February of 1964, design of an x-ray diffraction method for quantitative determination of amounts and proportions of hexagonal and monoclinic pyrrhotites was begun, and a satisfactory routine method was in use by June of 1964. By December of 1964, more than two

thousand determinations on 1200 samples had been made, and data were available for interpretation (Cowan, 1968; Naldrett and Kullerud, 1967). The methods employed are described below.

## QUANTITATIVE X-RAY POWDER DIFFRACTION

Determination of crystalline phase proportions in mixtures by $x$-ray powder diffraction has been practised for many years, but only a few routine industrial applications have been reported. Those unfamiliar with the principles and practice are referred to standard texts such as Klug and Alexander (1954). Details of practical methods vary considerably with the kind of material and desired accuracy, and we do not propose to review the literature on this. However, a good example of successful application is by Black (1953) on the polymorphs of aluminium hydroxide (and the common mineral impurities) in bauxites. Evaluation of millions of tons of aluminium ore has been aided by this method. This notable success inspired many workers over the next few years to test and use quantitative $x$-ray methods for a variety of phase determinations in rocks, ores, and industrial products. Few have been as successful for a variety of reasons, mostly connected with the difficulty of precisely repeating preparation of samples of materials that are not in such a randomly-oriented and a uniformly cryptocrystalline state as in bauxite.

Quantitative $x$-ray diffraction depends on the precise measurement of the relative intensities of selected $x$-ray diffraction spectra produced by particular crystalline phases present in mixtures. These intensities, with suitable corrections for matrix and other effects, are functions of the amounts of the crystalline phases present. The instrument used in the present study was a Norelco $x$-ray diffractometer, purchased in 1955, fitted with a gas-filled proportional counter feeding a ratemeter and Brown recorder through a modified 1958 model electronic circuit panel.

Difficulties in standardization of sample preparation, presentation methods and a variety of interferences from the complex powder diffraction patterns of low symmetry crystalline phases are the major obstacles to precision which have to be overcome in establishing quantitative methods for determination of mixtures of several phases. Anisotropy of grain dimensions, cleavage, differential hardness and malleability of phases may result in undergrind, yielding irregular diffraction responses; or overgrind, yielding diffraction broadening through structural deformations which reduce effective crystallite-size below 500 Å. Fibrous and platy grains result in preferred orientation on the pressed surfaces of dry sample mounts. Moisture adsorption by fine mineral powders after

grinding may lead to complex changes of phase, porosity, and density at ambient laboratory temperatures. All these factors affect reproducibility, and tend to discourage the investigator with ambitions to develop quantitative methods by x-ray powder diffraction. However, considerable progress in increasing the accuracy of this kind of analysis has been made in the past so that now the method can be used with some confidence if the net effect of a number of variables is minimized.

Most workers control many of the variables through the internal standard method. The physical characteristics of the internal standard, such as grain and crystallite size, and its crystal structure should be such that one of its major diffraction spectra should be of similar shape characteristics, and adjacent to, a major diffraction spectrum of the unknown. The amount of standard added should be adjusted to yield approximately the same intensities for the two diffraction spectra measured. Silicon metal, metallic nickel powder, fluorite, and quartz have been used successfully as internal standards for quantitative analyses of pyrrhotite, pyrite, and other sulphides. Suitable fluorite was at hand, and therefore was used in the technique described below.

Sample preparation included mixing thoroughly the internal standard with the sample after grinding separately to yield a powder 100% less than 40 microns in size, and at least 80% between 1/10 micron and 15 microns. The mixture was presented for x-ray diffraction in such a way that its irradiated surface contained a consistently random distribution of grains. Packing and then scraping with a non-magnetic spatula or glass slide, to present a flat and relatively random surface in the cylindrical sample tray provided for the Norelco rotating holder, has been for us the most satisfactory practical method. Other methods have been found to provide greater intensities, or more consistent randomness, but for speed, convenience, and adequate reproducibility of results, this simple mounting method has proved acceptable.

The grinding method requires especially careful attention for relatively soft minerals such as sulphides. "Shatterbox" type automatic grinding, employing heavy slugs in hard alloy grinding chambers, while admirable for rapid reduction to micron sizes, apparently destroys crystalline continuity in certain crystal structures, and the resulting line-broadening invariably reduces resolution of closely spaced diffraction spectra. We used 80% less than 100 mesh samples as discharged from a plate pulverizer, and employed routine ore-sample "bucking" procedure to cut out 2 gm portions, which were then ground by hand in a mullite mortar, with or without acetone or alcohol. Less than two minutes was usually sufficient to reduce the ore sample to an impalpable powder. The ore powder packs well, and gives sharp diffraction resolutions accompanied

by quite reproducible intensities. We have also found that with such samples, the rotating sample holder improves reproducibility about 10–25%, with little or no reduction in effective resolution, as compared with the stationary type.

## $X$-Ray Diffraction Characteristics of Pyrrhotites

Much has been written on the $x$-ray crystallography and chemistry of pyrrhotite over the forty-four years since Ålsen (1925) proposed a niccolite-type structure and a composition near FeS. Hägg and Sucksdorf (1933) compared pyrrhotite and troilite structures, proposed a defect structure to account for non-stoichiometry of pyrrhotite, and described a supercell in hexagonal synthetic compounds. Byström (1945) measured several pyrrhotites from Sweden and showed conclusively that some possessed monoclinic structures and were deficient in iron. Buerger (1947) proposed another superstructure type for two natural pyrrhotites. In 1948, I discovered a third superstructure in non-magnetic, euhedral, artificial material (Graham, 1949). Grønvold and Haraldsen (1952) determined compositions of material showing simple hexagonal structures, proving that the more iron-deficient artificial structures were monoclinic, and that the latter compared favourably in lattice dimensions with Byström's natural monoclinic pyrrhotites.

Interpretation of the very complicated detailed crystal chemistry of the pyrrhotites continues in many laboratories. Several articles, notably those of Andresen and Torbo (1967), Arnold (1966), Corlett (1967), Morimoto and Nakazawa (1968) and Fleet (1968$a$ and $b$), should be consulted in the originals. All these have appeared since the abstract of the present work was submitted in March of 1966, pending oral presentation of the research as a paper to the September 1966 meeting of the Mineralogical Association of Canada. Only the 1966 article by Arnold relates a method for quantitative determination of proportions in mixtures of pyrrhotites, however.*

Mention of two-phase intergrowths of pyrrhotite in the literature, according to Carpenter and Desborough (1964), began with Scholtz (1936), and continued through Kuovo et al. (1963). These authors

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*In the spring of 1965, after completion of the analytical campaign of June to December 1964 on Strathcona ore samples, Dr. Arnold visited the author's laboratory and discussed the quantitative determination of pyrrhotites in natural mixtures, both by microscopy and by $x$-ray diffraction. Dr. Arnold's quantitative $x$-ray method, described in his 1966 article, differs from the ratio method described here only in the choice of ratio to be plotted against proportion of pyrrhotites. It is therefore equally valid for determination of relative proportions in mixtures, but for determination of absolute proportions in ores, the procedures described in the present article are required.

described pyrrhotites from Griqualand, Africa, and Finland respectively, Von Gehlen (1963) described intergrowths in pyrrhotite from Dracut, Connecticut, and Ramdohr (1960) mentioned them in his textbook. Other authors among the large number that have discussed these intergrowths are listed in the references. Most refer to the hexagonal phase as *troilite*. Until direct determinations of element proportions are available, and can be related conclusively to structure, this treatment of Strathcona material will refer to *hexagonal, low-susceptibility pyrrhotite*, and *monoclinic, high-susceptibility pyrrhotite* as the main iron sulphide phases present.

Pyrrhotites from the Falconbridge and Hardy mines, Sudbury area, were shown by P. G. Thornhill in an unpublished report early in 1952 to yield x-ray diffraction doublets with equally intense components, where single peaks would be expected from hexagonal structures. Doublets from Falconbridge pyrrhotite were also observed by me in 1955, and were attributed to monoclinicity. No evidence of mixed pyrrhotites had been detected in routine x-ray diffraction examinations of samples from other mines of our Company, and few, to our knowledge, had been reported from the Sudbury District until the Strathcona samples were submitted for study as related above (Hawley, 1962).

Optical detection of pyrrhotite phase intergrowths in freshly-polished surfaces is often difficult. Even after staining, etching, or the application of a magnetic colloid, quantitative measurement of proportions by point-count or other optical method is tedious and unreliable. The main reasons are the extreme irregularity of certain of the finer intergrowths and differential effects of orientation of grains upon the surface reactivities of the same structural types. X-ray diffraction was therefore the sole remaining physical technique known to provide unequivocal identification, and which could possibly be adapted for usefully quantitative measurements. Calibration would depend on partial magnetic separations, chemical analyses, and computations of modal compositions.

In developing the x-ray method, a number of assumptions concerning the compound nature of the diffraction were adopted. The first and most important is that only two types of pyrrhotite are present in important quantities in the Strathcona deposit. So far as is presently known, this assumption is justified by the subsequent results, but is by no means established as fact.

The second important assumption involves the relative intensities and resolution of the major composite diffractions from atomic planes in the two closely similar crystal structures. With monochromatic cobalt K$\alpha$ radiation, self-filtered by the iron in the sample, strong multiple diffractions appeared from samples of mixed pyrrhotites. The hexagonal

pyrrhotites yielded single peaks at about 51.35°2$\theta$ ($d$ = 2.066 Å), while monoclinic pyrrhotites separated from the same samples gave doublets, measured at about 51.75°2$\theta$ ($d$ = 2.015 Å) and 51.40°2$\theta$ ($d$ = 2.064 Å). So far as could be determined with the materials and equipment at hand, the hexagonal peak was about twice the height of one peak of the doublet, for the same weight percent of the two concentrates separated from the same sample by magnetic methods.

It was therefore assumed that the slight distortion of atomic positions from the strictly hexagonal lattice array, resulting in monoclinic symmetry, had not changed greatly the total intensity diffracted from analogous planes in the hexagonal structures. The six equally-spaced planes of the hexagonal pyramid, responsible for the strong single diffraction from the hexagonal pyrrhotite, correspond in the monoclinic type to the planes of two monoclinic pyramids ($hkl$) and ($hk\bar{l}$), and two monoclinic orthopinacoids ($h0l$) and ($h0\bar{l}$), with multiplicities of two and one respectively. Each peak of the monoclinic doublet is thus composed of two diffractions, each from an orthopinacoid paired with a pyramid of nearly equivalent spacing.*

The total intensity of the doublet is approximately equivalent to that of the single hexagonal diffraction, as observed above. Suitable compromises in instrumental settings can minimize the effect of lack of coincidence of the monoclinic diffractions, and resolution of the monoclinic peaks into a quadruple peak can be avoided.

Adjustment of diffractometer scan-rate and slit-system, and careful attention to degree of grind thus yields an asymmetric doublet from mixed pyrrhotites, the degree of asymmetry of which is a measure of the amount of hexagonal pyrrhotite present, relative to the amount of monoclinic pyrrhotite, and the total area under the compound is proportional to the sum of the concentrations of both pyrrhotites.

Since the diffractometer properly set yields Gaussian-type curves at diffraction positions, the amplitudes of the diffraction peaks can be used as direct measures of proportions of the responsible lattice-spacings in the sample. Regular Gaussian curves partially superposed can be completed subjectively, and the amplitudes of the components can be measured

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*From this argument, it is seen that the distortion from hexagonal to monoclinic symmetry may take place by slight parallel displacement of originally strictly hexagonal arrays of lattice points (0001) occupied by iron atoms, in the direction [$\bar{1}$00] of the monoclinic lattice. This is an effect which might be expected if enough iron deficiency allows crimping of the structure through development of a higher degree of covalent bonding. Increased bond strength may also explain the observed lower surface reactivity of monoclinic pyrrhotite compared to that of the hexagonal variety. This lower reactivity to etch reagents (especially to acid potassium dichromate) is inexplicably the reverse of that recorded by Arnold (1966), although checked by adsorption of magnetic colloid to the more magnetic monoclinic pyrrhotite.
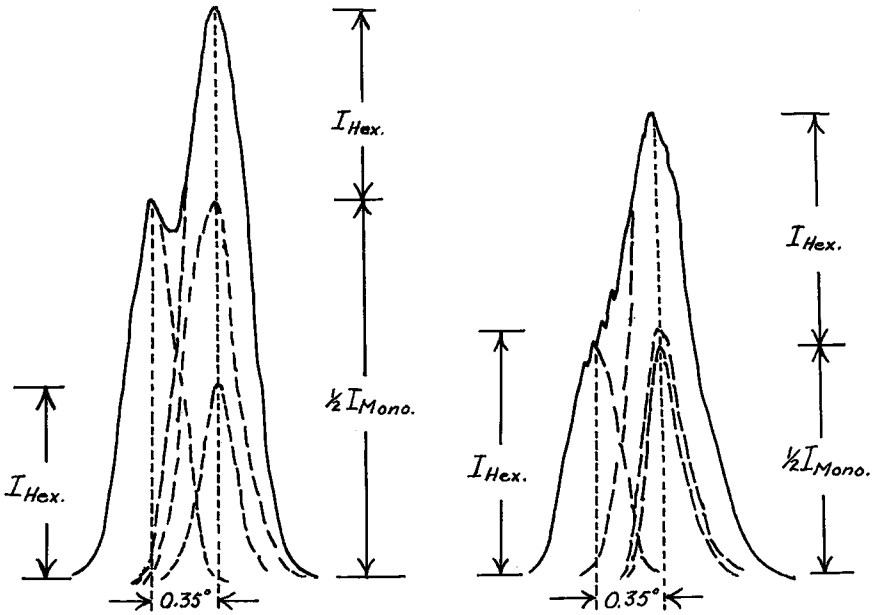
FIG. 1. Examples of interpretation of diffraction profiles traced from actual charts. $2\theta$ of $CoK\alpha$ increasing from right to left.
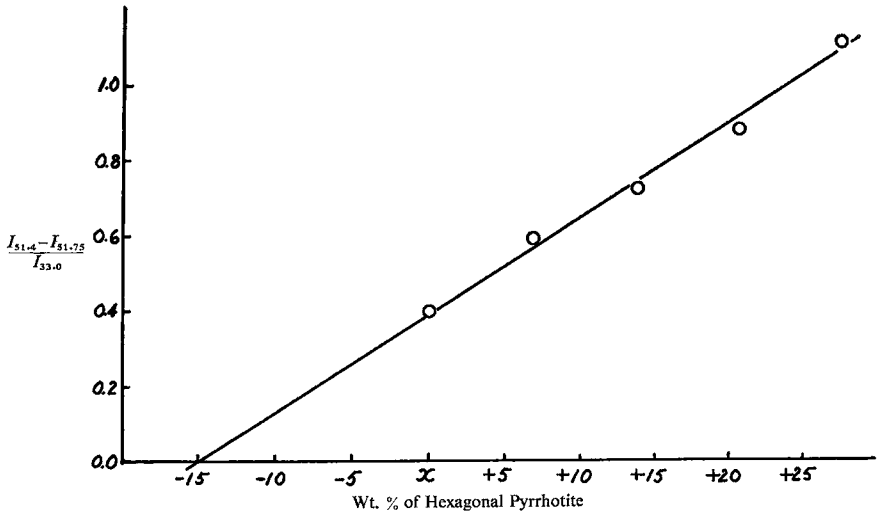


FIG. 2. Plot of the ratio of the differences between peak amplitudes of the pyrrhotite doublet divided by the peak amplitude from internal standard $CaF_2$, as a function of the unknown total % of hexagonal pyrrhotite in the test samples ($x+5$, $x+10$, $x+15$, ...). See Table 1, last column, for the data.

rapidly. Thus the difference in amplitude is proportional to the amount of hexagonal phase, the amplitude of the lower peak is proportional to half of the amount of monoclinic phase, and the sum of the amplitudes of both peaks is proportional to the total pyrrhotite present. An example of the procedure for measurement is shown in Fig. 1.

QUANTITATIVE PROCEDURES

Calibration plots (Figs. 2, 3, 4, 5, 8) were estimated by eye and drawn from data points of synthetic mixes of relatively pure non-magnetic and magnetic pyrrhotites prepared by Franz Isodynamic separation of ore samples. The methods and procedures used for these plots are described in detail in the Appendix. The plots were checked by running unknowns
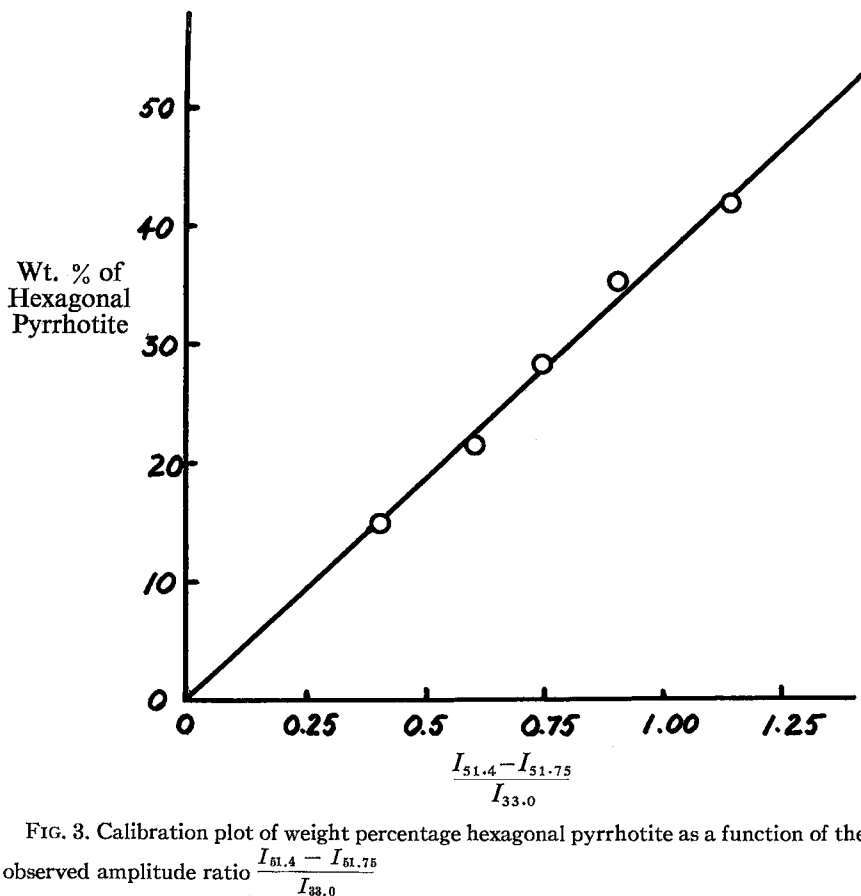


FIG. 3. Calibration plot of weight percentage hexagonal pyrrhotite as a function of the observed amplitude ratio $\dfrac{I_{51.4} - I_{51.75}}{I_{33.0}}$
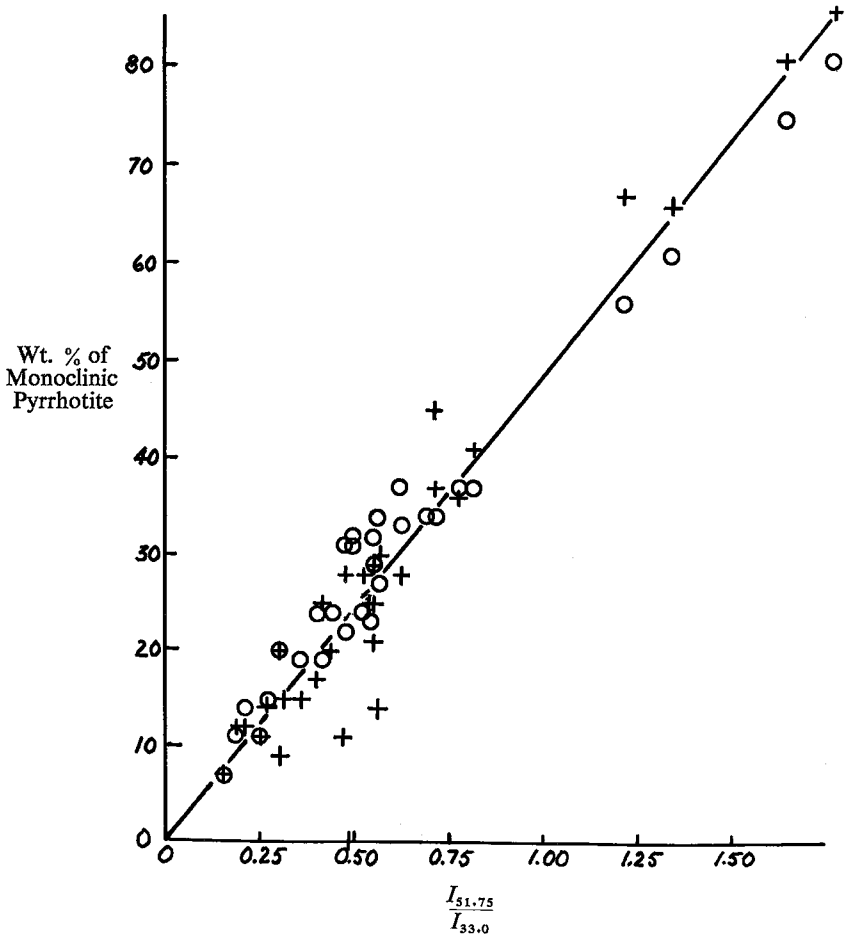
FIG. 4. Calibration plot of weight percentage monoclinic pyrrhotite as a function of the observed amplitude ratio $I_{51.75}/I_{33.0}$. Open circles are points calculated by subtracting the weight percentage of hexagonal pyrrhotite (Fig. 3) from the total pyrrhotite (Fig. 8). Crosses are points located by using sulphur assays to calculate total pyrrhotite, then subtracting the percentage of hexagonal pyrrhotite obtained using Fig. 3 to yield percentages of monoclinic pyrrhotite by difference.

both by x-ray diffraction and by magnetic separation methods, and comparing the results (Figs. 6, 7). Various forms of these plots were used depending on the relative precision required; the internal standard method given in the accompanying appendix is of course the most reliable. Triplicate determinations were used to attain an average error of about ±10% of the amount present in important groups of test
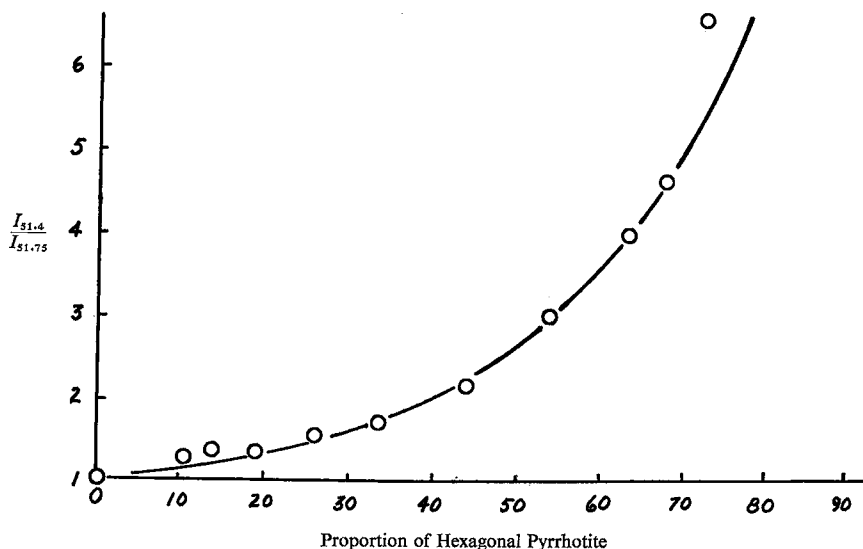
Fig. 5. Calibration plot of ratio of amplitudes $I_{51.4}/I_{51.75}$ as a function of weight ratio of hexagonal pyrrhotite in synthetic mixtures of hexagonal and monoclinic pyrrhotites.

samples. Table 1 shows as an example the effect of additions of a sample containing 84% hexagonal pyrrhotite to a sample containing an unknown minor proportion ($x$ weight per cent) of hexagonal pyrrhotite, to establish the calibration plot for hexagonal pyrrhotite.

The most rapid procedure used assay information already derived from composite drill core samples, each representing an average of several feet of pyrrhotite-pentlandite-chalcopyrite ore. The assay rejects were simply ground by hand for a minute or two, mounted, and scanned on the diffractometer over $2\theta$ angles from 51.0° to 52.5° at the rate of 1/2° per minute. The ratio of the amplitudes of the individual diffractions in the doublet gave a ratio of hexagonal to monoclinic pyrrhotite from the appropriate calibration (Fig. 5). The sulphur equivalents of the nickel and copper assays were subtracted from total sulphur in the same sample to yield sulphur associated with iron in pyrrhotite (both pentlandite and chalcopyrite have about 1/3 sulphur by weight and a nickel or copper to iron to sulphur ratio of about 1:1:1). The effects of low proportions (<2%) of pyrite were neglected. Application of the hexagonal mono-clinic ratio to the assay-computed total pyrrhotite gave the absolute proportion of hexagonal pyrrhotite appropriate to that sample, with an average error of about 15% of the amount present. The percent hexagonal pyrrhotite was in turn weighted by footage for computation of total
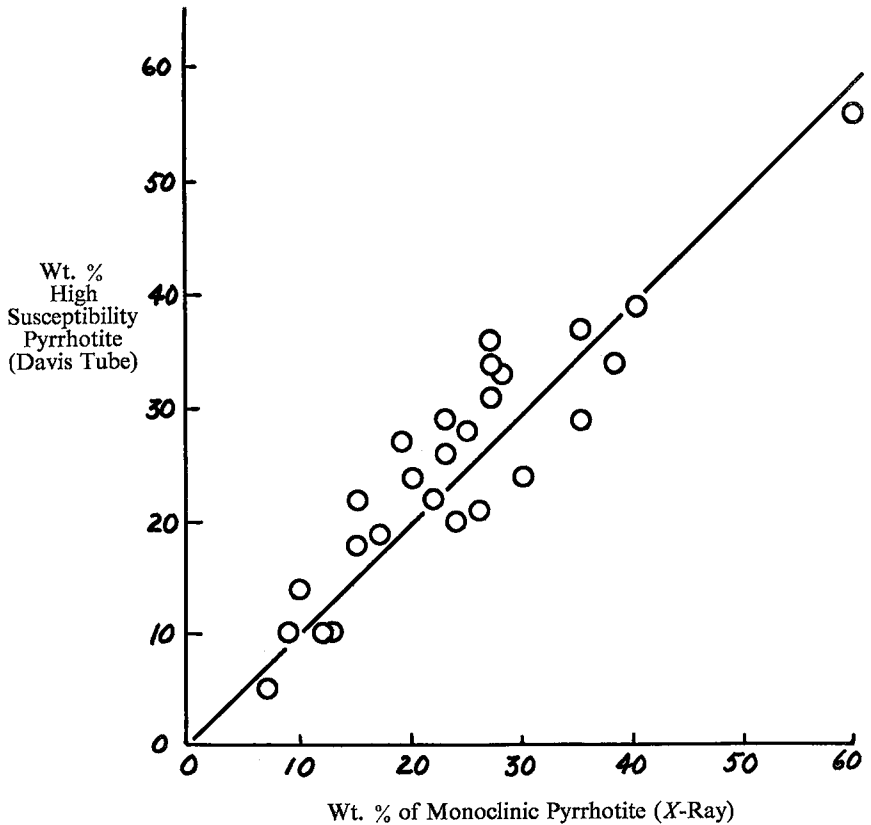
FIG. 6. Correlation plot of weight percentage of high susceptibility (monoclinic) pyrrhotite magnetically separated at low flux densities from ore samples by Davis tube manipulation, as a function of percentage monoclinic pyrrhotite determined using Fig. 4. Data are from Table 2, columns 5 and 6.

hexagonal pyrrhotite represented by the samples. Tables 2 and 3 give comparisons of some of the results selected at random from some of the early data which had been checked by magnetic separations and calculations from assays.

With the above procedure, and two operators, the maximum speed of analysis of twelve samples per hour could be attained for short periods, and an average speed of five to seven samples per hour could be maintained over periods of weeks. Sensitivity estimated from the results indicated that a usable result for proportion of hexagonal pyrrhotite could be determined to one significant figure in samples containing as little as five percent total pyrrhotite.
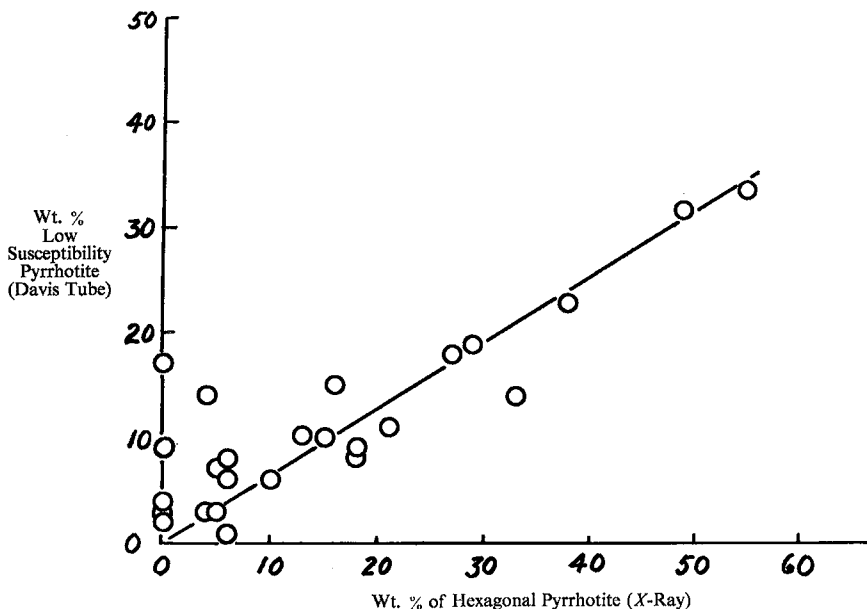
FIG. 7. Correlation plot of weight percentage of low susceptibility (hexagonal) pyrrhotite obtained as Davis tube separates, as a function of percentage hexagonal pyrrhotite determined using Fig. 3. Data are from columns 2 and 3, Table 2.

## CONCLUDING REMARKS

The present application of x-ray powder diffraction technique was assisted in several ways by much background data in the scientific literature on methods and upon the specific properties of the minerals to be determined. It can be used therefore as an example of the utility of basic research on mineralogical properties and investigative techniques, in the assembly of information eventually vital to efficient mineral extraction and processing.

The procedures outlined for quantitative pyrrhotite phase determinations have allowed the contouring of an important ore-body for concentrations of high- and low-susceptibility iron sulphides (which differ chemically by a maximum of only four atomic per cent in elemental composition), in the presence of at least four other iron-bearing phases, two of which are sulphides. The variability of the amounts and distributions of the pyrrhotite types, both locally and on a large scale, when combined with exact elemental distributions determined by microprobe, will probably contribute to our knowledge of the history of ore deposition
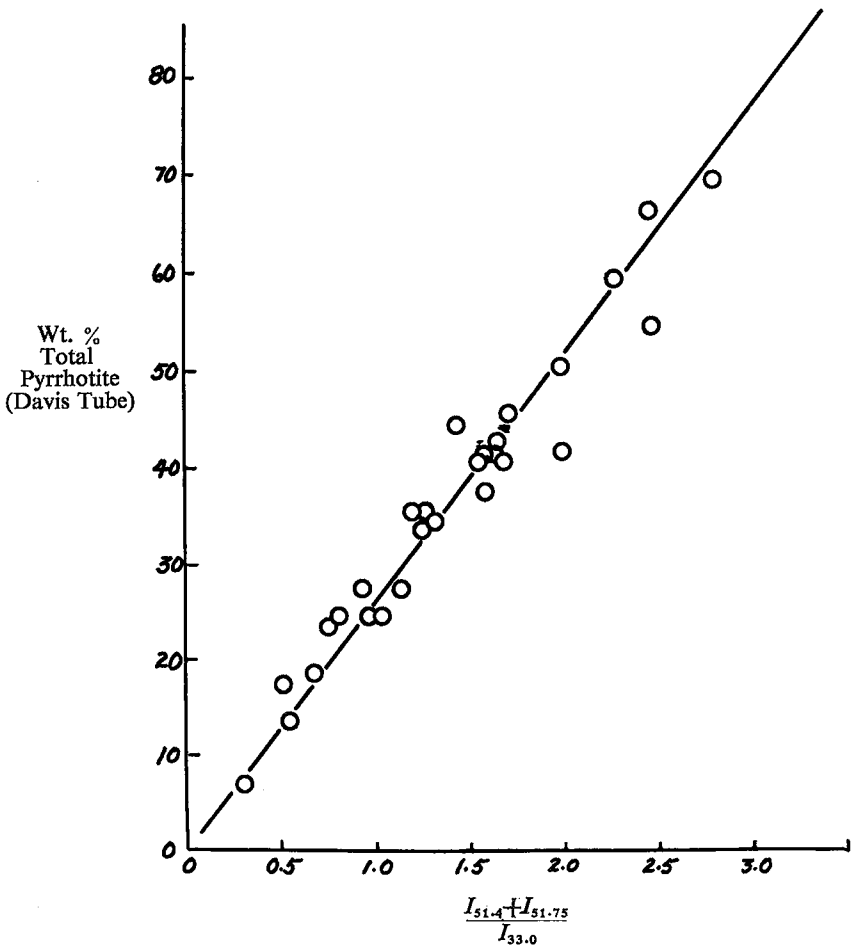
FIG. 8. Calibration plot of weight percentage total pyrrhotite in ore samples separated magnetically at low and high flux densities by Davis tube as a function of the peak amplitude ratio $\dfrac{I_{51.4} + I_{51.75}}{I_{33.0}}$ Data are from Table 3.

in the area. We have made no attempt to interpret, from the physical chemistry of the solid-state reactions responsible for the appearance of two pyrrhotites, the reasons for this variability but we hope to do so in the future.

Proper application of quantitative x-ray powder diffraction analysis, a relatively neglected tool, can provide useful information on major phase proportions in average or individual samples of rocks, (Bristol

TABLE 1. ADDITIONS TO BULK SULPHIDE CONCENTRATE RUN #1, DEEP ORE ZONE (LAB #4407)

| Desired Wt. % Add'n. (to 1.5 gm.) | Addition #4396 (84% Hex. Po) | Add'n. for 20% CaFe$_2$ (Int. Stand.) | Wt. Sample After Add'ns. Po Only | Calc. Wt. Hex. Po Added | Assumed Total Hex. Po (x = 15%) | Calc. Wt. % Hex. Po (x = 15%) |
|---|---|---|---|---|---|---|
| x + 0% | 0.0000 gm | 0.3750 gm | 1.5000 gm | 0.0000 gm | 0.2250 gm | 15.0% |
| x + 10 | 0.1667 | 0.4167 | 1.6667 | 0.1400 | 0.3650 | 21.9 |
| x + 20 | 0.3750 | 0.4688 | 1.8750 | 0.3150 | 0.5400 | 28.8 |
| x + 30 | 0.6430 | 0.5357 | 2.1430 | 0.5401 | 0.7651 | 35.7 |
| x + 40 | 1.0000 | 0.6250 | 2.5000 | 0.8400 | 1.0650 | 42.6 |

| Actual Wt. % Add'n. (x = 15%) | $I$(obs)* (51.4°) | $I$(obs)* (51.75°) | Obs. Difference $I_{51.4} - I_{51.75}$ | $I$(obs)* (33.0°) | Ratio Diff. $I_{33.0}$ |
|---|---|---|---|---|---|
| x + 0% | 10.6 | 7.9 | 2.7 | 6.8 | 0.40 |
| x + 6.9 | 12.6 | 8.4 | 4.2 | 7.0 | 0.60 |
| x + 13.8 | 12.9 | 7.5 | 5.4 | 7.3 | 0.74 |
| x + 20.7 | 13.4 | 6.8 | 6.6 | 7.3 | 0.90 |
| x + 27.6 | 13.9 | 6.0 | 7.9 | 6.9 | 1.14 |

*Average of six measurements each.

TABLE 2. CORRELATION OF % HEXAGONAL AND % MONOCLINIC PYRRHOTITES WITH LOW AND HIGH SUSCEPTIBILITY PYRRHOTITES (DAVIS TUBE)

| Sample No. | Wt. % Hex. Po | Wt. % Low S | Diff. | Wt. % Mon. Po | Wt. % High S | Diff. | Total Po X-Ray | Total Po Mag | Diff. |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 18 | 7 | +11 | 19 | 27 | −8 | 37 | 34 | +3 |
| 2 | 21 | 11 | +10 | 27 | 33 | −6 | 48 | 46 | +2 |
| 3 | 10 | 6 | +4 | 17 | 19 | −2 | 27 | 25 | +2 |
| 4 | ~3 | 5 | ~2 | 12 | 10 | +2 | 15 | 14 | +1 |
| 5 | 6 | 7 | −1 | 13 | 10 | +3 | 19 | 19 | 0 |
| 6 | 33 | 14 | +19 | 27 | 36 | −9 | 70 | 51 | +21 |
| 7 | 18 | 9 | +9 | 27 | 31 | −4 | 45 | 38 | +7 |
| 8 | <3 | 3 | +3 | 26 | 21 | +5 | 26 | 25 | +1 |
| 9 | 38 | 23 | +15 | 15 | 22 | −7 | 53 | 43 | +10 |
| 10 | 16 | 15 | +1 | 21 | 22 | +1 | 37 | 36 | +1 |
| 11 | 49 | 32 | +17 | 23 | 29 | −6 | 72 | 60 | +12 |
| 12 | 55 | 34 | +21 | 24 | 20 | +4 | 79 | 54 | +25 |
| 13 | 15 | 10 | +5 | 28 | 33 | −5 | 43 | 42 | +1 |
| 14 | <3 | 2 | −2 | 7 | 5 | +2 | 7 | 7 | 0 |
| 15 | <3 | 9 | −9 | 59 | 56 | +3 | 59 | 67 | −8 |
| 16 | 6 | 8 | −2 | 9 | 10 | −1 | 15 | 18 | −3 |
| 17 | <2 | 2 | −2 | 20 | 24 | −4 | 20 | 25 | −5 |
| 18 | 6 | 6 | 0 | 35 | 37 | −2 | 41 | 42 | −1 |
| 19 | 29 | 19 | +10 | 30 | 24 | +6 | 59 | 42 | +17 |
| 20 | 27 | 18 | +9 | 15 | 18 | −3 | 42 | 35 | +7 |

TABLE 3. DETERMINATIONS OF PYRRHOTITE IN CORE SAMPLE REJECTS (INTERNAL STANDARD METHOD)

| (1) Wt. % Hex. Po (Fig. 3) | (2) Wt. % Mon. Po (Fig. 4) | (3) Wt. % Total Po (1) + (2) | (4) Wt. % Total Po (Fig. 8) | (5) Wt. % Total Po (Calc.) |
|---|---|---|---|---|
| 0 | 22 | 22 | 23 | 32 |
| 6 | 42 | 48 | 51 | 54 |
| 1 | 59 | 60 | 64 | 59 |
| 5 | 51 | 56 | 58 | 54 |
| 0 | 20 | 20 | 20 | 24 |
| 0 | 44 | 44 | 44 | 48 |
| 0 | 39 | 39 | 41 | 41 |
| 1 | 37 | 38 | 41 | 46 |
| 11 | 58 | 69 | 70 | 65 |
| 13 | 57 | 70 | 71 | 65 |
| 0 | 22 | 22 | 25 | 31 |
| 9 | 47 | 56 | 56 | 54 |
| 1 | 32 | 33 | 35 | 36 |
| 2 | 8 | 10 | 10 | 12 |
| 3 | 13 | 16 | 17 | 20 |
| 8 | 38 | 46 | 46 | 44 |
| 4 | 50 | 67 | 66 | 64 |
| 4 | 17 | 21 | 22 | 23 |
| 13 | 30 | 43 | 41 | 38 |
| 0 | 9 | 9 | 9 | 12 |
| 12 | 23 | 35 | 33 | 37 |
| 33 | 39 | 72 | 65 | 66 |
| 3 | 20 | 23 | 23 | 25 |
| 7 | 22 | 29 | 29 | 31 |
| 34 | 28 | 62 | 56 | 53 |

1968), ores (Petruk 1964), and process materials, more rapidly than most other means. In contrast to chemical analysis, quantitative physical analysis by this method yields information bearing on the relationships and chemical bonding of elements in the crystalline compounds of mixtures, as well as the proportions of both elements and compounds, and thus gives another dimension to our knowledge of these materials.

APPENDIX

OUTLINE OF PROCEDURES FOR QUANTITATIVE DETERMINATION OF
PYRRHOTITE TYPES BY X-RAY POWDER DIFFRACTION

A. *Preparation of Standards for Synthetic Mixes of Pyrrhotite Types*

(1) Establish presence of two pyrrhotite phases in a large sulphide sample by qualitative x-ray scan. Prepare and stain polished section and examine under ore microscope to ensure grain size will permit mechanical separation.

(2) Crush and grind carefully, avoiding overgrinding and overheating (which may cause oxidation), to appropriate grain size for free milling of pyrrhotite phases.

(3) Prepare deslimed size fraction of about 100 gm by screening (−200 +325 mesh gave good results with Strathcona material).

(4) Clean sample of residual gangue by heavy liquid, flotation or other means.

(5) Carefully remove any magnetite by low intensity magnetic separation methods, avoiding pyrrhotite loss.

(6) Using residual magnetic flux only on the Franz Isodynamic Separator (no magnet current) and appropriate end and side slopes, separate high magnetic susceptibility pyrrhotite. Check for purity using x-ray diffraction, and repeat if necessary.

(7) Increase magnetic flux in small steps, until all possible high susceptibility (monoclinic) phase has been removed. Check each product by x-ray diffraction.

(8) When the monoclinic ($2\theta = 51.75°$) peak has disappeared, separate remaining pyrrhotite from paramagnetic and nonmagnetic residual minerals as completely as possible by further manipulation of the separator.

(9) Check both products for purity by reflection microscopy in polished grain mounts. Assess proportions (if any) of adulterants remaining by point counting after staining, or magnetic colloid adsorption, and make adjustments in weights for mixtures accordingly.

B. *Preparation of Calibrations from Standard Samples: Addition Method*

(1) Select high purity hexagonal pyrrhotite concentrate (>80% hexagonal and <5% monoclinic) as in A(9) above.

(2) To 1.5 gm portions of sample carrying a high proportion (>80% est.) of monoclinic pyrrhotite and low proportion (<20% est.) of hexagonal pyrrhotite, make a series of additions of hexagonal pyrrhotite concentrate. (An example is in Table 1).

(3) Compute theoretical additions in terms of weight % hexagonal pyrrhotite in final mix, assuming a series ($x = 5, 10, 15, \ldots$) of proportions of hexagonal pyrrhotite in the original sample.

(4) To each of these mixes, add internal standard as in C(4).

(5) Irradiate samples and interpret results as in C(5) to C(7). Make repeat runs at least five times on newly mounted samples to increase precision of the mean.

(6) Make addition plot as in Fig. 2 and repeat using the computed percentages of hexagonal pyrrhotite for $x = 5, 10, 15, \ldots$, and extrapolate each plot to cut the abscissa.

(7) Interpolate best fit figure for actual percentage of hexagonal pyrrhotite in original sample (15% in Fig. 2).

(8) Recompute actual percentages of hexagonal pyrrhotite in the series of mixes.

(9) Plot calibration from these figures, as in Fig. 3.


C. *Preparation, Irradiation and Interpretation*

(1) Crush and grind ore sample to ~90% less than 100 mesh, as in A(2).

(2) Cut representative samples of 1.5 gm.

(3) Grind to impalpable powder by hand under acetone, or (with care) dry.

(4) Mix 1.5 gm thoroughly with internal standard (10% by weight nickel powder, or 20% by weight fluorite, or 15% by weight silicon powder in terms of final sample weight, all of which yield appropriate peak heights for nickel ores). Use mechanical shakers, but do not overheat or overgrind. Internal standard should have approximately the same grain size distribution as unknown sample, to avoid segregation effects during mixing and mounting, and should not be ground with the unknown sample, as differential grinding may ensue.

(5) Pour excess sample into sample tray mounted on platform scales. Use consistent pressure of about 20 lb. on the piston to pack the sample. Carefully scrape excess sample from tray using edge of a glass slide or a non-magnetic spatula, leaving a uniform surface.

(6) Irradiate sample using rotating holder on the $x$-ray diffractometer. Scan over appropriate angular range at not more than $1/2°$/minute, adjusting counting rates and time constants to yield sufficiently smooth curves on the chart for interpretation. Our usual settings on the Norelco unit are: Cobalt $K\alpha$ radiation

(unfiltered) at 30 KV and 9 ma, 320 C/S for full-scale deflection, time-constant 4.

(7) Resolve the superimposed diffraction peaks on the chart by eye and then measure amplitudes (I) above background of the peaks at 51.4° and 51.75° and subtract. Measure amplitude of internal standard peak (either nickel at 52.2°, fluorite at 33.0° or silicon at 56.3°), depending on which standard is in use, and divide into above result.

(8) Read per cent hexagonal pyrrhotite from calibration plot prepared from synthetic mixes (Fig. 3).

(9) Add amplitudes of the 51.4° and 51.75° peaks and read total pyrrhotite from the calibration plot previously prepared from synthetic mixes (Fig. 8).

(10) Repeat steps (5) to (9) for increased precision of the mean.

D. *Preparation of Calibration curves from Standard Samples:*
*Ratio Method*

(1) Prepare mixes of high purity hexagonal and monoclinic concentrates to yield suitable range of known percentages.

(2) Mount and irradiate as in C(5) and C(6).

(3) Complete superimposed diffraction peaks by eye.

(4) Divide amplitude of the 51.4° peak by amplitude of the 51.75° peak.

(5) Plot as hyperbolic function % Hex Po $= f(I_{51.4}/I_{51.75})$.

E. *Preparation of Calibration Plots for Total Pyrrhotite*

(1) Prepare and irradiate a number of mixes carrying known amounts of pyrrhotites, adding common gangue or other ore minerals as in C(1) to C(6).

(2) Compute $\dfrac{I_{51.4°} + I_{51.75°}}{I_{Stand.}}$ , plot against known proportions of pyrrhotite in any available samples and derive the best-fit curve.

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