THE AMERICAN MINERALOGIST, VOL. 47, JANUARY-FEBRUARY, 1962

MEASUREMENT OF THE METAL CONTENT OF NATURALLY OCCURRING, METAL-DEFICIENT, HEXAGONAL PYRRHOTITE BY AN *X*-RAY SPACING METHOD[1]

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ABSTRACT

It is shown on the basis of fourteen chemically analyzed pyrrhotites that the metal content of metal-deficient natural pyrrhotites may be measured to ± 0.25 atomic per cent using an experimentally derived *x*-ray determinative curve, provided the combined concentration of nickel, cobalt, and copper in solid solution is less than about 0.6 per cent by weight.

INTRODUCTION

Ramsdell (1927) and Grønvold and Haraldsen (1952) have shown that the cell dimensions of synthetic hexagonal pyrrhotites decrease regularly with decreasing iron-to-sulfur ratio. An *x*-ray determinative curve relating $d(102)$[3] to iron content has been established employing this relationship (Arnold, 1956). This curve, determined experimentally over the composition range 50.0 to 46.0 atomic per cent iron, is shown graphically in Fig. 1 and is expressed by the equation $Y = -0.0182 + 0.0767X - 0.00069X^2$, where Y represents $d(102)$ in Å and X represents the metal content of pyrrhotite expressed in atomic per cent. The metal content of synthetic pyrrhotites containing less than 0.06 per cent by weight nickel, cobalt, copper, and manganese in solid solution may be measured to about ± 0.13 atomic per cent by this method.

The valid application of the *x*-ray determinative curve to hexagonal, metal-deficient natural pyrrhotites is shown by demonstrating the similarity between the $d(102)$ versus composition relationship for natural and synthetic pyrrhotites.

The *x*-ray spacing method is a rapid, convenient and reasonably accurate way of measuring the metal content of hexagonal, natural pyrrhotites. It has the advantage over chemical analytical methods in that pyrrhotite separations of high purity need not be achieved to obtain accurate results, provided the *x*-ray reflections of admixed phases do not interfere with those to be measured. The chief disadvantage of the *x*-ray method is that it cannot measure the amount of iron only in pyrrho-

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[3] Abbreviated Miller-Bravais indices are used throughout this paper, that is $(102) = (10\bar{1}2)$.

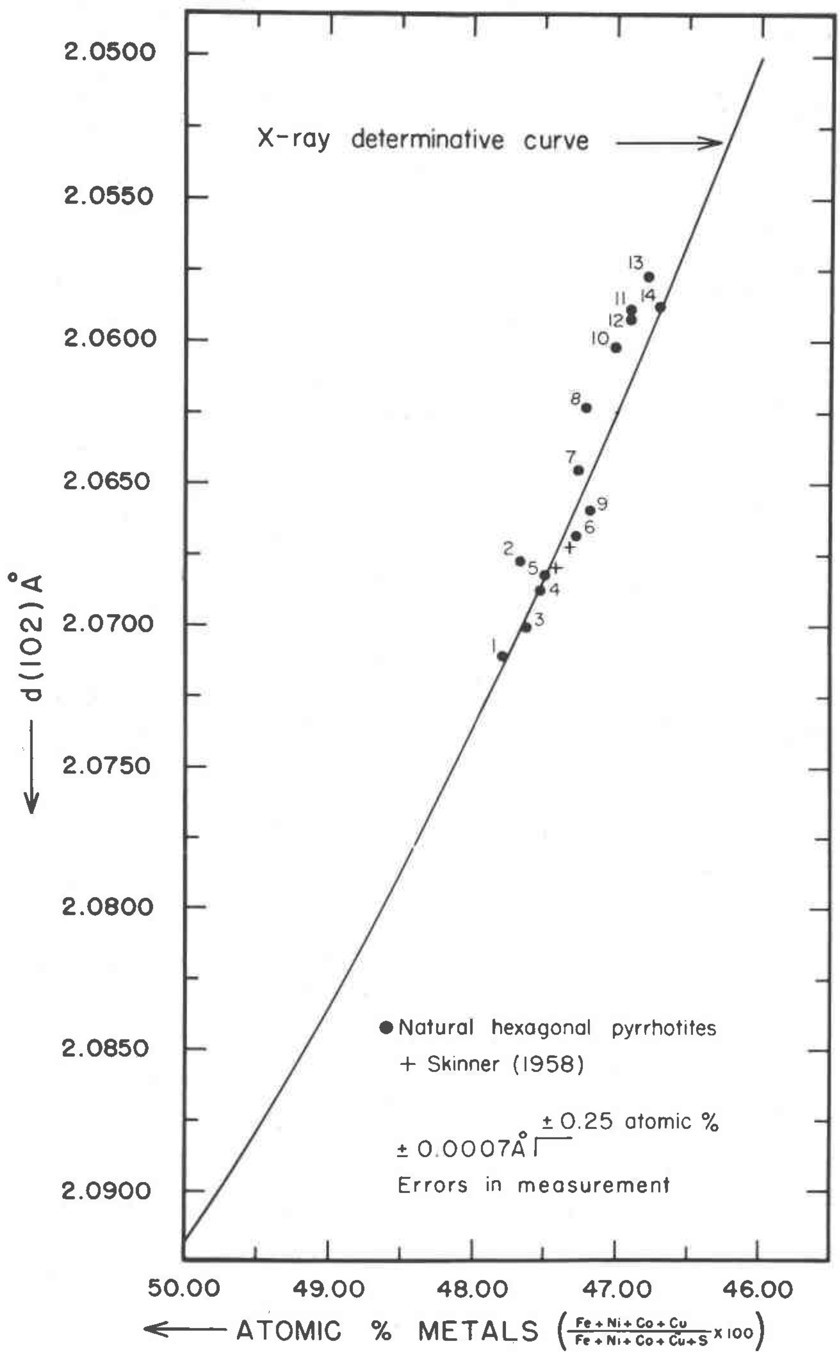

FIG. 1. Comparison of composition versus *d*(102) relationship for natural and synthetic pyrrhotite solid solutions.

tite, but the total metal content—that is, iron plus metal impurities replacing iron in the structure.

METHODS AND RESULTS

Fourteen natural terrestrial pyrrhotites from a variety of geological environments were selected for analysis on the basis of their relatively wide range in metal-to-sulfur ratio and the absence of intimately admixed sulfides. Each sample was crushed under inert liquid, and the 150- to 200-mesh fractions were purified by both magnetic and heavy-liquid separations. The samples are listed in Table 1. All but sample No. 8 (comprising a few crystals) contained small quantities of quartz and calcite in amounts that may be estimated from the deficit in the total of metals and sulfur (Table 1).

TABLE 1. CHEMICAL AND *X*-RAY DATA FOR NATURAL PYRRHOTITE

No.	Sample	Analyses (weight per cent)						Weight per cent metals*	Atomic per cent metals*	$d(102)$ ± 0.0007 Å
		Chemical		*X*-ray spectrometer						
		Fe	S	Ni	Co	Cu	Total			
1	McAfee, N. J.	60.40	37.91	0.02	0.05	0.02	98.40	61.47	47.80	2.0711
2	Bergbau, Austria	60.32	38.08	0.02	<0.01	0.12	98.54	61.36	47.67	2.0677
3	Moise River, Quebec	60.82	38.45	0.02	0.03	0.05	99.37	61.31	47.63	2.0701
4	Toncray, Virginia	60.50	38.50	0.02	0.16	0.10	99.28	61.22	47.53	2.0687
5	Hybla, Ontario	60.82	38.67	<0.01	<0.01	0.15	99.64	61.19	47.50	2.0682
6	Bluebell, B. C.	60.78	38.96	<0.01	0.02	0.07	99.83	60.97	47.28	2.0668
7	Highland Surprise, Idaho	60.49 60.15	38.82 38.60	0.03 0.03	0.02 0.02	0.07 0.07	99.43 98.87	60.96 60.96	47.26	2.0645
8	Tretca, Yugoslavia	60.80	39.05	<0.01	0.02	0.05	99.92	60.88	47.21	2.0623†
9	Funter Bay, Alaska	59.56	38.34	0.06	0.07	0.01	98.04	60.89	47.19	2.0659
10	Highland Surprise, Idaho	60.15 59.79	39.04 38.63	0.01 0.01	0.01 0.01	0.02 0.02	99.23 98.46	60.66 60.77	47.01	2.0602
11	Riondell, B. C.	59.68	39.14	0.47	0.09	0.02	99.40	60.62	46.90	2.0588
12	Clearwater Brook, N. B.	60.27	39.20	0.03	0.02	0.01	99.53	60.61	46.90	2.0592
13	Highland Surprise, Idaho	59.32	38.79	0.04	<0.01	0.07	98.22	60.51	46.79	2.0577
14	Kisbanya, Romania	60.01	39.32	<0.01	<0.01	<0.01	99.33	60.41	46.70	2.0587

* $\frac{\mathrm{Fe} + \mathrm{Ni} + \mathrm{Co} + \mathrm{Cu}}{\mathrm{Fe} + \mathrm{Ni} + \mathrm{Co} + \mathrm{Cu} + \mathrm{S}} \times 100.$

† $d(102)$ obtained on material heated at 600° C. for 18 hours.

Source of Samples:

1, 9. Edward Sampson, Princeton University.
2. Smithsonian Institution, Washington, D. C., No. 80788.
3. L. A. Clark, Geophysical Laboratory, Washington, D. C.
4. C. S. Ross, U. S. Geological Survey.
6. R. D. Westervelt, Queens University.
7, 10, 13. V. C. Fryklund and R. G. Coleman, U. S. Geological Survey.
8. Smithsonian Institution, Washington, D. C., No. R9252.
12. W. Petruk, McGill University.
14. H. D. Holland, Princeton University.

Table 1 summarizes the results of iron and sulfur analyses performed on 200-mg samples of the concentrates. The samples were dissolved in a solution of bromine in carbon tetrachloride and nitric acid according to the method described by Hillebrand *et al.* (1953). The solutions were adjusted to 0.1 N hydrochloric acid and passed through a cation-exchange resin column (Amberlite IR-120) to separate metals from sulfate. Iron and sulfur were then determined by standard wet chemical methods (Hillebrand *et al.*, 1953).

The over-all accuracy of the chemical analyses is difficult to assess owing to the errors inherent in analyzing for iron and in particular sulfur. If an error of 0.28 per cent by weight is assumed for the results of iron plus sulfur, however, all analyses agree with those obtained by the x-ray method. Duplicate analyses were performed on samples Nos. 7 and 10, and the totals differ by 0.56 per cent and 0.77 per cent, respectively (Table 1). After calculating the metals and sulfur to 100 per cent pyrrhotite, however, the percentages of iron are identical for the duplicates on No. 7 and differ by 0.11 per cent on No. 10. The precision of measurement is thus within 0.1 per cent by weight of Fe. The iron-to-sulfur ratios (1.558, 1.558; 1.541, 1.547) agree very closely in spite of the differences in the totals on the duplicates. Small amounts of calcite and quartz impurities are present in the sample.

Nickel, cobalt, copper, and manganese, which are generally the most important impurities in solid solution in natural pyrrhotite, were measured by x-ray fluorescence spectroscopy. Synthetically prepared pyrrhotites containing approximately the same percentage of iron, sulfur, and impurities as contained in the natural samples were used as standards. Manganese in every case is less than 0.01 per cent by weight, hence is omitted from the table.

The lower limit of detection of the metals was 0.01 per cent by weight, and the accuracy of the determination is about 15 per cent of the amount present, except at the lower limit of detection where it is lower.

The uncertainty expected in the combined content of iron, nickel, cobalt, and copper is equal to the sum of errors incurred in measuring the concentration of these elements. The analysis of sample No. 11 carries the largest calculated error of ± 0.36 per cent by weight metals (equivalent to about ± 0.28 atomic per cent); whereas, the errors attached to the remaining analyses range between ± 0.29 and ± 0.32 per cent by weight metals, which are approximately equivalent to ± 0.23 and 0.25 atomic per cent, respectively. Thirteen of the analyses coincide with the x-ray determinative curve (Fig. 1) well within these uncertainties. The analysis of the remaining sample (No. 8) deviates from this curve by 0.23 atomic per cent metals, which is equal to the uncertainty calculated for this analysis.

The *d*(102) value for each sample is listed in Table 1. The measurements were made with a Norelco wide-angle focussing diffractometer equipped with an automatic chart recorder. Each $(102)_\alpha$ reflection was measured relative to the $(200)_\alpha$ reflection of Lake Toxaway quartz located at 54.17° 2θ Fe $K\alpha$.[4] The final 2θ $(102)_\alpha$ values are the average of eight measurements, four of which were obtained from pairs of reflections scanned from low angles to high and four by scanning from high angles to low. Scanning and chart speeds were 1° per minute and $\frac{1}{2}$ inch per degree. Peak positions were measured to ±0.01° 2θ using a vernier scale. Standard deviations of the mean 2θ $(102)_\alpha$ values and the corresponding *d*(102) values are respectively ±0.02° and ±0.0007 Å.

All (102) reflections were single and moderately sharp with the exception of that obtained from sample No. 8. Two reflections, about 0.35° 2θ apart and of about equal intensity, were obtained from this sample instead of a single reflection, indicating monoclinic symmetry according to Byström (1945). In order to invert this sample to hexagonal symmetry it was heated at 600° C. for 18 hours in an evacuated, sealed, silica glass tube. The *d*(102) for this sample given in Table 1 is that of the inverted material. Heating of this specimen could be performed without changing the composition of pyrrhotite, because of the high purity of the sample (99.92 per cent pyrrhotite).

The effect that relatively small concentrations of nickel, cobalt, and copper in solid solution in pyrrhotite might have on *d*(102) was investigated experimentally. This was done by substituting these elements for iron and comparing the resulting *d*(102) with that of impurity-free pyrrhotite having an equal atomic ratio of metal to sulfur (see pairs in Table 2). The pyrrhotites were prepared synthetically in 1-gram lots by reacting mixtures of the metals and sulfur in sealed, evacuated, silica glass capsules at 675° C. for about 18 hours, then completely melting them at 1225° C. They were ground under inert liquid to avoid oxidation and remelted several times to ensure uniformity of composition. Examination of the preparations in polished sections revealed only pyrrhotite, indicating that the metals were in solid solution.

The results of this work, summarized in Table 2, show that no significant change in *d*(102) was caused by a substitution of 2.00 per cent by weight of Ni, 1.27 per cent by weight of Co, or 0.6 per cent by weight of Cu individually for iron; or by a combined substitution of 0.98 per cent by weight of Ni, 0.99 per cent by weight of Co, and 0.6 per cent by weight of Cu for iron. This is evident from the fact that the *d*(102) of pure and impure pyrrhotite having equal atomic ratios of metal to sulfur is the same, within the errors in the measurements.

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[4] $\lambda \text{Fe } K\alpha = 1.9373$ Å.

TABLE 2. $d(102)$ VALUES OF PURE AND IMPURE SYNTHETIC PYRRHOTITE HAVING IDENTICAL ATOMIC PER CENT METAL CONTENTS

Pair No.	Weight per cent					Weight per cent metals	Atomic per cent metals	$d(102)$ ±0.0007 Å
	Fe	S	Ni	Co	Cu			
1	61.47	38.53	—	—	—	61.47	47.80	2.0717
	59.50	38.50	2.00	—	—	61.50	47.80	2.0711
2	63.50	36.50	—	—	—	63.50	49.97	2.0917
	62.26	36.47	—	1.27	—	63.53	49.97	2.0913
3	60.09	39.91	—	—	—	60.09	46.36	2.0540
	59.52	39.88	—	—	0.60	60.12	46.36	2.0545
4	62.04	37.96	—	—	—	62.04	48.41	2.0776
	59.55	37.89	0.98	0.99	0.60	62.12	48.41	2.0764

DISCUSSION AND CONCLUSIONS

Figure 1 summarizes the data presented in Table 1. Composition versus $d(102)$ of each pyrrhotite sample is represented by a numbered point where the number corresponds to that in the table. The two crosses located to the right of the experimental x-ray determinative curve represent two pyrrhotites from the Nairne pyritic formation reported by Skinner (1958). Nickel and cobalt in these were not detected by the x-ray spectrograph (B. J. Skinner, oral comm. 1959). The agreement between the sixteen points and the determinative curve is generally good, since the departures of the points from the curve are less than the maximum estimated error in the chemical analyses and the measurement of $d(102)$.

The distribution of points about the determinative curve, however, is not random, especially in the more metal-deficient region. Points 8 and 10–14, for instance, fall to the left of the curve. This distribution can be accounted for by small systematic analytical errors, or perhaps the $d(102)$ versus composition relation for natural and synthetic pyrrhotites differs somewhat at more metal-deficient compositions.

Because the non-random distribution of points is probably due to experimental error, no new curve based on these analytical data is presented. Instead, since all points deviate from the experimental determinative curve by less than ±0.23 atomic per cent metals, it is suggested that this experimentally derived curve be used for estimating the metal content of natural pyrrhotite to about ±0.23 atomic per cent, with certain reservations discussed below.

It has been shown that substituting as much as 2.57 per cent by weight of Ni, Co, and Cu for Fe in synthetic pyrrhotite does not measurably affect the structure (pair No. 4 in Table 2). Such data are unfortunately not available for natural pyrrhotite, which might conceivably behave differently. It is, therefore, recommended that the determinative curve be applied to natural pyrrhotite containing less than a total of about 0.6 per cent by weight of Ni, Co, and Cu in solid solution. This is equal to the maximum concentration of these elements in the natural pyrrhotites studied here.

This restriction does not seriously limit the usefulness of the determinative curve. Fleischer's (1955) summary of minor elements in pyrrhotite, for instance, shows that 93 per cent of analyzed pyrrhotites contain less than 0.5 per cent by weight Ni, 99 per cent contain less than 0.5 per cent by weight Co, and 96 per cent contain less than 0.5 per cent by weight Cu.

It is evident from Fig. 1 that the compositions of the analyzed pyrrhotites are restricted to the metal-deficient portion of the *x*-ray determinative curve. A preliminary survey of pyrrhotite compositions (Arnold, 1958) has shown that about 90 per cent of naturally occurring terrestrial pyrrhotites are very metal deficient. Therefore, the metal-deficient portion of the determinative curve is the most useful portion.

ACKNOWLEDGMENTS

The authors are grateful to Drs. G. Kullerud, J. R. Smith, B. J. Skinner, and P. Toulmin, III, for reviewing the manuscript and for suggestions that contributed to its improvement. Thanks are due also to Dr. Isidore Adler for advice on preparing the pyrrhotite *x*-ray spectrographic standards, and to Dr. Skinner for the suggestion of heating monoclinic pyrrhotite to the hexagonal form thus permitting use of the *x*-ray determinative curve to estimate the composition also of this pyrrhotite.

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Manuscript received April 22, 1961.