

STUDIES ON THE PYRRHOTITE FROM THE INGALADHAL SULPHIDE LODE, CHITRADURGA DISTRICT, MYSORE STATE

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ABSTRACT

X-ray studies, optical studies and chemical composition of pyrrhotite indicate that in the Ingaladhah copper mine it occurs in both hexagonal and monoclinic modifications as well as in transitional forms. The monoclinic phase might have formed by inversion from the hexagonal phase. The hexagonal form has a composition that appropriates to solvus temperatures of $< 300^{\circ}$ – 360° C. Heated monoclinic and hexagonal monoclinic mixtures of pyrrhotite yielded temperatures ranging from 425° – 460° C. From the questionable validity of the pyrrhotite geothermometer it is concluded that the temperature estimates based on the pyrrhotite solvus cannot be used to know the temperature of formation of pyrite-pyrrhotite assemblage in the Ingaladhah sulphide lode.

INTRODUCTION

THE area around Ingaladhah village (Lat. $14^{\circ} 11' 20''$ N., Long. $76^{\circ} 26' 45''$ E) forms a part of the Chitradurga schist belt in Mysore State where intensive prospecting for copper is in progress. The principal ore minerals occurring in the Ingaladhah copper mine are chalcopyrite, pyrrhotite, pyrite, sphalerite, galena and arsenopyrite, approximately in the order of decreasing abundance. X-ray and optical investigations and chemical composition of pyrrhotite indicate that it occurs in both monoclinic and hexagonal forms. The investigations and their results are presented and discussed in this paper.

OPTICAL PROPERTIES OF PYRRHOTITE

It is brownish-pink in body colour with a fairly high reflectivity. Reflection pleochroism, distinct in air, appreciably increases in oil. Anisotropism is strong in air and is intensified in oil. Its reaction to etching was negative when HCl or FeCl_3 was used and KOH produced an iridescent film. Visual

contrast has developed between the monoclinic and the hexagonal phases of pyrrhotite when a saturated solution of CrO_3 was used as suggested by Arnold (1966).

In some specimens from the adits the hexagonal and the monoclinic phases are mutually intergrown in an aggregate of equant grains. The unetched or slightly etched (hexagonal) grains are at places surrounded by deeply etched (monoclinic) grains. In such cases the former have a few intergrown lamellae of the deeply etched phase. These lamellae are not visible prior to etching. A majority of these lamellae have the appearance of an exsolved phase in that they are apparently crystallographically oriented single crystals with smooth, sharp boundaries. The lamellae terminate or change direction abruptly at grain boundaries of the host (Fig. 1). Most of the drill-core samples of pyrrhotite are slightly or not at all stained (Fig. 2) and are considered to be hexagonal.

X-RAY EXAMINATION

Bystrom (1945), Desborough and Carpenter (1965) and Arnold (1966, 1967) showed that a single, sharp, symmetrical d_{102} (abbreviated from $0\bar{1}2$) reflection at 2.06 to 2.10 Å indicates hexagonal pyrrhotite whereas a split reflection consisting of approximately equal intensity and about $0.3^\circ 2\theta$ apart is indicative of monoclinic pyrrhotite. A split reflection with high angle reflection ($20\bar{2}$) being lower in intensity than the other (102, 202 superimposed) is indicative of a mixture of monoclinic and hexagonal phases of pyrrhotite.

As an aid in identifying the pyrrhotite phases, X-ray diffractometer chart records of the '102' reflection were taken for five pyrrhotite samples from adit-2 of the Ingaladhhal sulphide mine. By rapid scanning procedure of $2^\circ 2\theta$ per minute a single peak at the '102' location was obtained for all the samples. However, when a chart speed of $\frac{1}{2}^\circ$ or $\frac{1}{4}^\circ 2\theta$ per minute was utilised, all specimens exhibited two reflections about 0.29° to $0.3^\circ 2\theta$ apart. The two peaks are of equal intensity for one sample (A/13) indicating its monoclinic nature while for the other samples the high angle reflection is found to be slightly lower in intensity than the other thus suggesting the presence of both monoclinic and hexagonal phases.

Chemical composition of pyrrhotite.—The composition of pyrrhotite was obtained by electronprobe microanalysis and X-ray diffraction.

Electronprobe microanalysis.—Pyrrhotite from six drill core samples was analysed by a 'Cameca' electronprobe microanalyser. The corrected

concentrations of Fe in the pyrrhotite samples and the corresponding atomic percentages are listed in Table I. The results obtained for each sample are the averages of a number of measurements taken at five different points. In the samples analysed no other element except Fe and S was detected by this method.

TABLE I

X-ray diffraction and electron microprobe data on pyrrhotites

Sample No.	X-ray diffraction			Electron microprobe	
	$d_{102}(\text{\AA})$	Atomic % Fe (Measured)	Atomic% Fe (Calculated)	Atomic% Fe	Inferred Temp. °C.
A/55	2.0612	46.916	46.942	..	425
A/13	2.0592	46.700	46.725	..	460
A/12	2.0601	46.835	46.802	..	445
12C/383	2.0601	46.835	46.802	..	445
S/3	2.0606	46.835	46.848	..	430
7C/112	47.528	<300
7C/208	47.528	<300
7C/247	47.315	<300
7C/319	47.190	360
7C/582	47.635	<300
5C/289	47.252	325

A/55, A/13, A/12 and S/3: Pyrrhotite samples from adit-2.

12C/383: Pyrrhotite from drill hole No. 12 C at 383 feet depth.

7C/112, 7C/208, 7C/247, 7C/319, 7C/582: Pyrrhotite samples from drill hole No. 7C at 112, 208, 247, 319 and 582 feet depths respectively.

5C/289: Pyrrhotite from drill hole No. 5C at 289 feet depth.

X-ray diffraction.—Arnold and Reichen (1962) indicated that d_{102} versus composition relationship, established on the basis of synthetic hexagonal pyrrhotite, can be used to estimate the metal content of natural hexagonal pyrrhotites provided the combined concentration of impurities like Ni, Co, Cu, etc., in solid solution is less than 0.6% by weight. The results of spectrographic analysis of pyrrhotite from the Ingaladhhal mine indicate that the combined concentration of such impurities in any sample does not exceed the above limit thus permitting the use of Arnold and Reichen's d_{102} spacing versus composition curve.

It is known that on heating both monoclinic pyrrhotite and monoclinic-hexagonal mixture formed in the two phase field between the two pyrrhotites invert to a metastable high temperature hexagonal form. From X-ray and optical studies pyrrhotite from the adits of the Ingaladhhal mine is seen to be either wholly monoclinic or a mixture of monoclinic and hexagonal phases. In order to employ the hexagonal spacing curve to determine their compositions, following Yund and Hall (1969), the samples were heated at 325° C for 5 minutes in evacuated pyrex glass tubes and then quenched. The quenched pyrrhotite samples showed a single 102 X-ray reflection and their compositions were determined using the X-ray determinative curve of Arnold and Reichen (1962). The measured spacings and the corresponding iron contents are listed in Table I. The iron contents of the pyrrhotites X-rayed were also calculated using the equation given by Yund and Hall (1969) and are included in the same table for comparison.

PYRRHOTITE GEOTHERMOMETRY

Arnold (1962) considered that the pyrrhotite solvus may be used to estimate the temperatures of formation of naturally occurring pyrite-pyrrhotite assemblages. If the two minerals were deposited at different times and were in a position to react with each other, it is assumed that equilibrium was attained at the conditions of deposition of the later phase and the temperature measured will be that at which the later phase crystallised. The values obtained for pyrrhotite from the Ingaladhhal mine, uncorrected for confining pressures, range between 460° C and 425° C for samples from the adit and between 360° C and < 300° C for the core samples obtained from deeper levels. Since pyrrhotite was the first ore mineral to form in the Ingaladhhal lode closely followed by pyrite (Acharyulu and Borreswara Rao, 1972) the estimated temperatures may represent the formation temperatures of pyrite coexisting with pyrrhotite.

DISCUSSION

Arnold (1966) showed that there is a clear-cut relationship between the structural type and the composition of pyrrhotite. Hexagonal pyrrhotite is found to have a compositional range of 48.1 to 47.45 atomic per cent metals (Arnold, 1967; Yund and Hall, 1969; Haynes and Hill, 1970) while the monoclinic phase ranges in composition between 46.75 and 46.7 (Gronvold and Haraldsen, 1952; Desborough and Carpenter, 1965 and Arnold, 1969). Clark (1966), however, considers that the composition field of synthetic monoclinic pyrrhotite widens from 46.8 atomic per cent Fe at $308^\circ \pm 5^\circ$ C. to 46.4 atomic per cent Fe at 45° C, the boundaries of the field sloping to more sulphur-rich compositions with decreasing compositions. Yund and Hall (1969) also have obtained similar results. Pyrrhotite having intermediate compositions is considered to be a mixture of hexagonal and monoclinic phases.

Pyrrhotite from core samples of the Ingaladhhal sulphide lode ranges in composition from 47.252 to 47.635 atomic per cent Fe while those from adit-2 have compositions ranging between 46.72 and 46.94 (Table I). Pyrrhotites having 47.5 or more atomic per cent Fe are considered to be hexagonal, those with compositions not exceeding 46.7 atomic per cent Fe are monoclinic and those having intermediate compositions are mixtures of monoclinic and hexagonal phases. From Table I it is clear that pyrrhotite occurring at deeper levels is either hexagonal or a mixture of hexagonal and monoclinic phases in which the hexagonal phase predominates. Pyrrhotite from the upper levels is either monoclinic or a mixture of monoclinic and hexagonal forms in which the monoclinic phase predominates. This inference finds support from optical and X-ray data. From the sphalerite geothermometry detailed elsewhere (Acharyulu and Borreswara Rao, 1972) it is considered that ore deposition took place at higher temperatures at lower levels while the same was at comparatively lower temperatures near the surface. This indicates that the hexagonal pyrrhotite has crystallised direct from ore solutions and upon cooling the same phase might have inverted to monoclinic symmetry. Complete inversion of the hexagonal phase might have been responsible for the occurrence of pure monoclinic phase and partial inversion to a mixture with predominance of monoclinic phase at the surface levels.

The estimated temperatures of crystallisation of pyrrhotite-pyrite assemblages in the Ingaladhhal sulphide lode were not corrected for confining pressures as the pyrite hexagonal pyrrhotite solvus, according to Arnold (1962),

is not affected by confining pressures upto 2,000 bars and the influence of higher pressures is unknown. Barton *et al.* (1963) have drawn attention to the discrepancy between short equilibration times in the synthetic sulphide systems compared with the immense periods presumably available for such equilibration in the natural environment. Clark (1964) has asserted that equilibration at low temperatures in natural iron sulphide assemblages is so widespread as to make estimates of crystallisation temperature from pyrrhotite compositions a dubious procedure. Temperature estimates from monoclinic pyrrhotite are regarded still less reliable. Kullerud *et al.* (1963) found that monoclinic pyrrhotites from a variety of source rocks gave solvus figures in the 500° C range. Wright (1966) also found a similar range for monoclinic pyrrhotites from virtually pyrite-free samples. Buseck (1964), Desborough and Carpenter (1965) warn especially against the use of monoclinic pyrrhotite as a geothermometer but Clark (1965) has established apparently consistent geotemperature gradients using exclusively monoclinic pyrrhotite. More recently Yund and Hall (1969) concluded that monoclinic pyrrhotite can form directly at low temperatures as well as from inversion of hexagonal pyrrhotite on cooling. Hence it is not valid to use the composition of natural monoclinic pyrrhotites co-existing with pyrite in conjunction with Arnold's (1962) hexagonal pyrrhotite solvus unless it can be demonstrated that the pyrrhotite was originally hexagonal and the only change has been partial or complete inversion to the monoclinic form. Desborough and Carpenter (1965) showed that numerous processes may lead to the development of pyrrhotite and pyrrhotite-pyrite assemblages in ore deposits and considered that the composition of pyrrhotite associated with pyrite may be completely meaningless in terms of geothermometry. Arnold (1957) demonstrated that the low temperature reaction rates are sufficiently rapid to ensure that slowly cooled natural pyrrhotites would assume the low temperature phase relations regardless of the original temperature of crystallisation. Thus the application of the pyrrhotite-pyrite geothermometer is somewhat problematical and the conclusion of Arnold (1967) that natural pyrrhotites are low temperature phases would appear to compound the difficulties.

The values obtained from pyrrhotite geothermometer range between 460° and 425° C. for the samples from the adits and between 360° C. and > 300° C. for the core samples obtained from deeper levels of the Ingaladhhal sulphide lode. In the core samples the co-existing sphalerites gave a temperature range of 340° to 460°C. and show a temperature gradient that increases with depth (Acharyulu and Borreswara Rao, 1972) while

the reverse is found when the pyrrhotite compositions are considered. From this observation and from the questionable validity of the pyrrhotite-geothermometer discussed above, the estimates based on the pyrrhotite-pyrite geothermometer are considered invalid to give the formation temperature of pyrrhotite-pyrite assemblage in the Ingaladhah lode.

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