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# MACKINAWITE FROM THE SULFIDE ORES OF THE SINGHBHUM COPPER BELT, INDIA

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ABSTRACT

The mode of occurrence and properties of mackinawite and an associated, optically similar sulfide from the Singhbhum district are described. Electron-probe micronanalysis shows that both minerals are non-stoichiometric iron sulfides containing minor nickel, cobalt, and copper. The mackinawite has a metal:sulfur atomic ratio exceeding unity, whereas the associated phase is slightly metal-deficient.

## INTRODUCTION

Mackinawite, a tetragonal iron sulfide generally containing small amounts of nickel and cobalt, and in some cases copper and even chromium (Clark, 1967, 1969; Clark and Clark, 1968; Springer, 1968), although characterised by Evans *et al.* only in 1964, has been the subject of intensive study since its discovery as a corrosion product of petroleum-carrying pipe more than a decade ago (Meyer *et al.*, 1958). Considerable information on the properties and genesis of the mineral has accumulated, but, no doubt, much remains to be determined. In this communication, observations on mackinawite in the sulfide ores of the Singhbhum Copper Belt, India, are presented.

## MODE OF OCCURRENCE OF MACKINAWITE

In the Singhbhum deposits, mackinawite (in the broad sense—see below) occurs in two distinct assemblages: the copper ores, of the Badia-Mosaboni-Rakha mines, consisting of chalcopyrite, pyrite, pyrrhotite, and minor pentlandite, marcasite, violarite, cubanite, molybdenite, tetradymite, wehrlite, skutterudite, sphalerite, galena, magnetite, and ilmenite; and the nickel ores, consisting of pyrite and millerite, associated with uranium mineralization at Jadugada (Fig. 1).

In the copper ores, mackinawite has developed exclusively within chalcopyrite, often at grain contacts with pyrrhotite, cubanite, and magnetite. In chalcopyrite the mineral occurs as needles oriented in several crystallographic directions, and as poorly-oriented blebs and irregular veinlets (Fig. 2). Some of the needles reveal irregularities in outline at high magnification. Mackinawite clearly repaces millerite at Jaduguda (Fig. 3).

## OPTICAL PROPERTIES

The mackinawite-like phases in these ores comprise two optically-distinct varieties, herein referred to as the pinkish and the grayish. The


FIG. 1. Sketch map showing the location of the Singhbhum Copper Belt, and of the deposits referred to in the text.

pinkish variety, which corresponds to normal mackinawite as described by previous authors, takes a good polish, and is intensely bireflectant in air, from a grayish-pink to pinkish-gray. The reflectance of this mineral varies over a wide range. Photo-cell measurement using a domestic carborundum standard and a Leitz green filter (absorption peak at 530 nm), gave a range of 19–41 $\pm$ 0.5 percent. The dispersion coefficient, $\triangle R$, has been found to attain a maximum at 560–600 nm, by measurement with a photometer ocular of the Valinskii type. The mineral is consistently softer than pyrrhotite but, in most orientations, harder than chalcopyrite. This observation is in apparent conflict with those of Kouvo *et al.*, (1963), as well as of Chamberlain and Delabio (1965). The former workers record a polishing hardness for mackinawite greater than that of pyrrhotite, while the latter consider it to be even softer than galena. In a discussion of the properties of mackinawite from the Ylöjärvi copper-

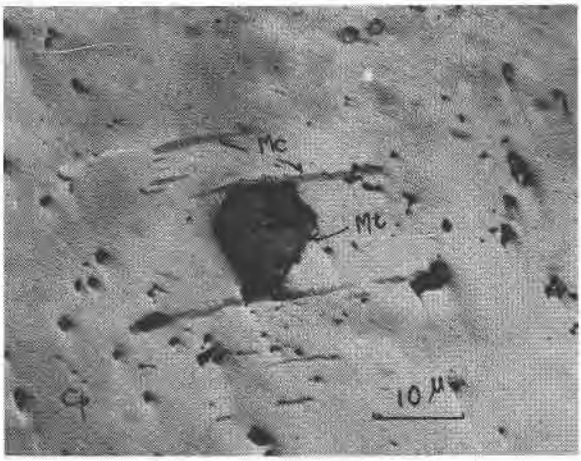


FIG. 2. Lamellae of the gray phase (Mc) concentrated in chalcopyrite in the vicinity of a magnetite grain (Mt) (Oil immersion).

tungsten deposit, Finland, Clark (1966a) suggested that the micro-indentation hardness of the mineral is probably affected by the content of nickel and cobalt in solid solution (see also, Vaughan, 1969; Clark, 1970). Attempts to determine the Vickers micro-indentation hardness


FIG. 3. Mackinawite (Mc) replacing millerite (Mi) Jaduguda mine.

TABLE 1. COMPARATIVE PROPERTIES OF VALLERIITE AND THE SINGHBHUM GRAY SULFIDE

| | Valleriite (after Chamberlain and Delabio, 1965; Genkin and Vyalsov, 1967) | Gray phase, Singhbhum |
|---|---|---|
| Polish | Poor | Poor |
| Color | Dull bronze, similar to graphite | Dull bronze, with a grayish tint, to brownish gray. |
| Bireflectance | Extreme | Moderate to extreme |
| Relief | Lower than that of chalcopyrite | Lower than that of chalcopyrite |
| Reflectance | Very low, 14.2–22% (at 589 nm) | Very low, 12–25% (at 530 nm) |
| Anisotropism | Extreme, white to bronze. | White to grayish, somewhat less extreme than that of valleriite |

of the Singhbhum mackinawite have failed owing to its minute grain size.

In contrast to the pinkish variety, the gray phase exhibits a strong bireflectance from gray to dull-bronze with a tint of gray, and is distinctly softer than chalcopyrite. Its reflectance is markedly lower than that of the normal variety (12–25 $\pm$ 0.5 percent under identical instrument conditions), and the anisotropism is rather less intense. This phase is, therefore, somewhat similar to valleriite in its optical properties (Table 1).

## ANALYTICAL DATA

Quantitative analyses of both types of mackinawite described above were performed on an electron microprobe. The results of this work are shown in Table 2. Synthetic pyrite and chemically pure copper, nickel, and cobalt were used as standards for sulfur and those metals, and interelement corrections were calculated following the procedure of Springer (1967, 1968).

Berner (1964) and Clark (1966b) have suggested that the cation: anion atomic ratio of at least the iron end-member of the mackinawite series is greater than one. Springer (1968) considered that, within the limits of error of existing microprobe techniques, mackinawite appears to have the stoichiometric composition. Clark and Clark (1968), however, have demonstrated that the Ylöjärvi iron-mackinawite is significantly iron-rich, or sulfur-poor, relative to troilite. Both analyses of the normal,

Table 2. Chemical Composition of Mackinawite and the Associated Gray Phase, Singhbhum, India

| Type | Elements | Fe | S | Ni | Co | Cu | Total | Metal: Sulphur atomic ratio |
|---|---|---|---|---|---|---|---|---|
| Pink (normal) | 1. | 54.74 | 35.63 | 7.99 | 0.30 | 0.57 | 99.23 | 1.02 |
| | 2. | 54.35 | 35.76 | 8.07 | 0.41 | 0.69 | 99.28 | 1.01 |
| Gray | 3. | 53.23 | 38.20 | 7.62 | 0.31 | 0.58 | 99.94 | 0.92 |
| | 4. | 53.06 | 37.87 | 7.59 | 0.33 | 0.51 | 99.36 | 0.93 |

pink mackinawite from Singhbhum (Table 2) yield metal: sulfur ratios exceeding unity, in agreement with this observation.

It is noteworthy that copper was detected in the Singhbhum mackinawites. Clark and Clark (1968) and Springer (1968), among other recent workers, have also reported the presence of minor copper in this mineral.

From Table 2, it is evident that the grayish mackinawite-like phase, although containing similar minor constituents to the normal variety, possesses a distinctly lower metal:sulfur ratio, and is apparently sulfur-rich with respect to the stoichiometric composition.

## Thermal Properties

*In vacuo* heating studies carried out on the pinkish mackinawite variety from these ores showed that the characteristic optical properties of the mineral change to those of pyrrhotite at 220–225°C. In essentially identical experiments, Kouvo *et al.*, (1963) reported a phase transformation for mackinawite at 210°C, and Takeno (1965), who found similar, but varying, apparent breakdown temperatures, suggested that the upper thermal stability limit of this mineral is dependent on its metal: sulfur ratio. Clark (1966a, b), on the other hand, proposed that the stability relations of mackinawite are a function of the degree of substitution of iron by other metals, which have the general effect of increasing the upper stability limit from a minimum temperature of *ca.* 135°C shown by the natural iron end-member. This conclusion is supported by earlier work by the present author (1967).

## Discussion

From the analyses presented in this paper, it is clear that the grayish, poorly-reflectant phase which occurs in the Singhbhum ores is not valleriite, but is chemically allied to normal mackinawite. In several polished sections, normal mackinawite is observed to grade outwards into the gray phase, suggesting that the latter is an alteration product of the normal variety. This alteration involved a significant depletion in total metal content, but had little effect on the minor element content of the mackinawite. It may be tentatively suggested that this phase, whose relationship to mackinawite *sensu stricto* remains unclear, may have been observed by some previous workers who have found metal:sulfur ratios for mackinawite of less than unity by microprobe analysis.

Clark and Clark (1968) suggest that the formation of mackinawite in some ores is a reflection of a late-stage depression in sulfur fugacity, below that represented by pyrrhotite and troilite-bearing assemblages, generally under hypogene conditions, and such an origin appears likely in the case of the Singhbhum deposits. In these ores, mackinawite occurs only when pyrrhotite is present, and is absent where pyrite and/or marcasite are the only iron sulfides, as in the Nandup-Turamdih section of the Belt. It is considered that the mackinawite in the Singhbhum deposits probably formed during the retrograde alteration of previously metamorphosed assemblages.

The sulfur-rich gray phase, on the other hand, may have developed as a result of local supergene alteration. A. H. Clark (written communication, 1970) has observed an optically-similar mineral, with a metal: sulfur ratio of less than one, which has clearly formed as a supergene oxidation product of normal, metal-rich mackinawite in the Carrizal Alto copper deposit in northern Chile. Textural evidence suggests strongly that some of the mackinawite in the Singhbhum deposits formed through replacement of other sulfides, but exsolution from chalcopyrite may have occurred locally. Such a mode of formation is suggested by the presence of appreciable nickel in chalcopyrite immediately surrounding some mackinawite lamellae.

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