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Application of Ro and Ar Measurements to the Study of Pyrrhotite and Troilite

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Abstract

Naturally occurring troilite (FeS) and pyrrhotite ($Fe_{1-x}S$) can be distinguished by reflectivity (R*o*), tarnishing characteristics, and angle of apparent rotation (Ar). R*o* values at 546 nm relative to a metallic silicon standard with an assumed reflectivity of 38.8 percent are as follows: troilite (FeS) = 39.05 percent; intermediate pyrrhotite ($\sim Fe_{11}S_{12}$) = 36.4 percent; intermediate pyrrhotite ($\sim Fe_9S_{10}$) = 36.9 percent; and monoclinic pyrrhotite ($\sim Fe_7S_8$) = 37.8 percent. Within a two hour period after buffing, R*o* values for troilite decrease 0.8 percent while values for hexagonal pyrrhotite and monoclinic pyrrhotite are constant. Ar measurements at 520 nm are as follows: troilite (tarnished) = 2.5°; troilite (within 15 minutes after buffing) = 2.15°; intermediate pyrrhotite ($\sim Fe_9S_{10}$) = 2.0°; and monoclinic pyrrhotite ($\sim Fe_7S_8$) = 1.85°.

The non-systematic relationship between the Fe/S ratio and R*o* values for pyrrhotite and troilite suggests that minor modifications of the NiAs structure represented by certain superstructure-types have a pronounced effect on the optical properties.

Introduction

This paper describes reflectance measurements and rotation properties of a suite of naturally occurring pyrrhotites. The results indicate a very interesting non-systematic behavior between certain optical properties and the Fe/S ratio. Differences in optical properties of naturally occurring phases provide a useful means of identification.

Many published values of the reflectivities of pyrrhotite are for unspecified compositions. Von Gehlen and Piller (1965) measured the dispersion of the reflectivities R*o* and R*e* for a hexagonal pyrrhotite ($\sim Fe_9S_{10}$). Desborough and Carpenter (1965) report measurements of R*o* at 546 nm for monoclinic pyrrhotite and two hexagonal pyrrhotites. This is the first attempt to evaluate optical techniques as determinative methods for pyrrhotite identification.

Composition and Structure of Pyrrhotite

Naturally occurring pyrrhotite can be subdivided into three types—troilite, intermediate pyrrhotite, and monoclinic pyrrhotite. All possess a NiAs-type substructure but differ in composition and superlattice dimensions. Variation in composition is due to omission of iron atoms in the structure (Hagg and Sucksdorf, 1933). Troilite, the iron-rich member, is stoichiometric FeS and has a superlattice of the $\sqrt{3}A$, $2C$ type (Hägg and Sucksdorf, 1933). Monoclinic pyrrhotite is the most iron-deficient type with a composition of approximately Fe_7S_8 (46.67 atomic percent iron) and a $2A$, $4C$ cell (Bertaut, 1953; Wuensch, 1963; Carpenter and Desborough, 1964). Intermediate in composition between troilite and monoclinic pyrrhotite is "hexagonal" or intermediate pyrrhotite. According to recent studies by Morimoto *et al* (1970), the composition ranges between $Fe_9S_{10} - Fe_{11}S_{12}$ (47.37 − 47.83 atomic percent iron). Superlattice types thus far recognized for intermediate pyrrhotite include three hexagonal phases; $5C$ (Carpenter and Desborough, 1964), $4C$ (Fleet and MaCrae, 1969), and $6C$ (Morimoto *et al*, 1970); and $11C$ which is orthorhombic. Intergrowths between troilite and intermediate pyrrhotite and between intermediate and monoclinic pyrrhotite have been recognized in nature and produced experimentally by several investigators. A reliable technique for determining composition from *d*-spacing measurements has been described by Arnold (1962) and subsequently refined by Toulmin and Barton (1964).

Minor elements known to substitute in pyrrhotite include nickel, copper, cobalt, and manganese. Arnold (1967) reports that the maximum combined concentration of these elements determined from a suite of 78 pyrrhotite samples is 0.942 percent. Batt (1972) has investigated nickel in solid solution in monoclinic and hexagonal pyrrhotite by microprobe measurements of a suite of samples of unspecified location or occurrence. He reports that monoclinic pyrrhotite contains between 0.4–0.5 percent Ni and intermediate pyrrhotite contains 0.8–0.9 percent Ni.

Pyrrhotites selected for study represent the three principal structural types and have compositions which include most of the range established for natural pyrrhotites. Most of the samples have large, optically continuous grains which display sharp extinction and are free from intergrowths or inclusions of other minerals.

Methods

Sample preparation

Trimmed rock slabs are mounted in cold-setting plastic (Castoglas) in circular or rectangular molds. Surfaces are hand-ground under running water on successively finer grades of Carborundum paper (grit numbers 60, 120, 180, 320, and 600) prior to polishing. For initial polish, successively finer grades of diamond paste (9, 6, 3, and 1 micron) impregnated in a synthetic, short-napped polishing cloth (AB Texmet, Buehler, Ltd.) are utilized.

Final polish is achieved by hand buffing according to the procedure of Cameron and Van Rensburg (1965). The buffing compound consists of a slurry of hematite rouge, chromic acid, and water. This mixture provides both mechanical abrasion and chemical etch and yields an excellent polish for pyrrhotites, and the reflectivity standard, metallic silicon. Satisfactory reflectance measurements are not likely to be obtained if the hand buffing stage is omitted.

Reflectivity apparatus

A Zeiss Universal Pol microscope equipped with a vertical illuminator, prism reflector, inclined binocular, and vertical photo-tube was adapted for reflectivity measurements. The back of a polaroid camera housing mounted above a camera focusing eyepiece on the vertical photo-tube is replaced by a light-proof plyboard box standing 6 inches above the camera housing. The window of a photomultiplier tube (Photovolt, Model 21-C) is seated in a hole at the top of the plyboard box. The sides of the box are firmly attached to the camera stand, but the top is adjustable so that an image viewed directly under the crosshairs through the binocular can be aligned with the center of the photomultiplier tube. A black plastic cylinder extends 1 in. below the window of the photomultiplier tube. A circular opening 0.25 in. in diameter at the base of the cylinder restricts the diameter of the light beam striking the photomultiplier tube. Mounted over the end of the cylinder is a Zeiss precision line 546 ± 2 nm filter. The photomultiplier tube is connected to a photovolt photometer (Model 520-M).

Intensity stabilization of a 60W tungsten bulb is achieved with a current-voltage regulated DC power supply unit (Hewlett Packard, Model 6282A).

A Zeiss 40x Epiplan objective is used in measurement of reflectivity. The field diaphragm is closed so that the field of view is restricted to 50 microns. The illumination aperture is placed near the minimum setting (1 on scale).

Reflectance measurements

Reflectance measurements are made relative to ultra-pure (99.9999%) single crystal silicon mounted on the (100) face. Jansen *et al.* (1969) have calculated the reflectance of metallic silicon at 546 nm from ellipsometric determinations of ψ, the azimuth angle of the reflected ellipse and Δ, the relative phase retardation of the two reflected components. They report a value of 38.83 percent. In this paper, measurements are relative to a value of 38.8 percent. Silicon is a useful standard for determining *o* ray reflectivity (R*o*) of pyrrhotite because R*o* values for pyrrhotite are within 1.5 percent of the value for silicon. Hence, potential errors arising from non-linear response of the photometer or from light-scattering in the optical system are considerably reduced. Although silicon does not tarnish over extended periods, the standards are buffed prior to use each day and pyrrhotite samples are buffed immediately before reflectance measurements are taken.

Prior to measurement of pyrrhotite reflectivity, the silicon standard is placed under the microscope and by sensitivity adjustment the scale is set at 38.8 or some arbitrary value on the 10x scale. An optically continuous grain of pyrrhotite is located, and the lowest scale reading obtained by rotating the stage is recorded. Finally, the silicon standard is remeasured. If the initial value for silicon is unchanged, the recorded value for pyrrohtite is assumed to be valid. If the scale is initially set at a value other than 38.8 percent, the readings for pyrrhotite must be proportionally corrected to this value.

Precautions which minimize errors during measurement include: (1) checking the objective centering; (2) careful focusing prior to each measurement; and (3) careful levelling of polished sections on clay over a glass slide with a Leitz level press. The degree of levelling can be determined by observing the upper focal plane of the objective with a Bertrand lens. The image of the condenser aperture diaphragm should not move upon rotation of the stage if the surface being measured is level. Sources of error in reflectance measurements have been summarized by Piller and Von Gehlen (1964).

Measurement of rotation properties

The angle of apparent rotation (Ar) was measured for specimens of troilite, intermediate pyrrhotite ($\sim Fe_9S_{10}$), and monoclinic pyrrhotite (Fe_7S_8). This property is the angular deviation between the major axis of the ellipse of vibration of the reflected ray and the polarizer direction when a mineral grain showing maximum anisotropism is in the 45° position. It is a measure of the degree of anisotropism. For the theory of rotation properties and the techniques involved in their measurement, the reader is referred to the discussion by Cameron (1961). Compositions were determined by the $d(102)$ method of Arnold (1962).

Results

Reflectivity

Both troilite and intermediate pyrrhotite are sensibly uniaxial positive. Hence the reflectivity of R*o* is the lowest value and is constant for all orientations. Within our error of measurement, monoclinic pyrrhotite also shows uniaxial characteristics so that R*o* = $R\beta$. This is consistent with the pseudohexagonal nature of the monoclinic structure and the low β angle (Wuensch, 1963; Carpenter and Desborough, 1965).

Composition determinations by the X-ray method of Arnold (1962) and R*o* values for pyrrhotite are summarized in Table 1 and presented graphically in Figure 1. Troilite has the highest reflectivity (39.05%). R*o* values for intermediate pyrrhotites range from 36.4 percent for high-iron intermediate pyrrhotite ($\sim Fe_{11}S_{11}$) to 36.9 percent for low-iron intermediate pyrrhotite ($\sim Fe_9S_{10}$). The value for monoclinic pyrrhotite is 37.8 percent. The precision of R*o* values based on the mean deviation from 4 independent sets of measurements made over a three month period is better than ±0.15 percent (Table 1).

The reflectivity-composition curve for intermediate pyrrhotite projects across the intermediate-monoclinic immiscibility region to the value for monoclinic pyrrhotite (Figure 1). For these phases, variations in R*o* appear to correlate with the Fe/S ratio. The reflectivity of troilite lies considerably above the projected trend of this curve.

TABLE 1. Measured Values, Compositions, and Localities of Sample Studied

Sample	Locality	d_{102}	Atomic % Fe (e.s.d.=0.12)	Ro (%)*
		Troilite		
DNM	Del Norte Co., Calif. (NMNH 94472)	2.0928	50.00	39.05(10)**
		Intermediate Pyrrhotite		
Fon-3	Fontana mine, Swain Co., N.C.	2.0696	47.62	36.43(10)
Sav-1	Savannah mine, Jackson Co., N.C.	2.0684	47.53	36.64(10)
Ch-S	Cherokee mine, Polk Co., Tenn.	2.0692	47.58	36.82(06)
EK-2	Elk Knob mine, Watauga Co., N.C.	2.0669	47.39	36.85(09)
Ch-1	Cherokee mine, Polk Co., Tenn.	2.0669	47.39	36.92(05)
		Monoclinic Pyrrhotite		
CPNY	Crown Point, Essex Co., N.Y.	2.0582***	46.66†	37.80(08)
W-89	Essex Co., N.Y.	2.0582***	46.66†	37.77(15)

* *Estimated standard deviations e.s.d. are given in parentheses and are expressed relative to the last decimal cited. Thus 39.05(10) and 36.92(05) respectively represent e.s.d. values of 0.10 and 0.05.*

** *This value extrapolated from tarnish curve data (see Figure 2).*

****Spacing from mid-point of monoclinic peaks.*

† *Composition from Desborough and Carpenter (1965).*

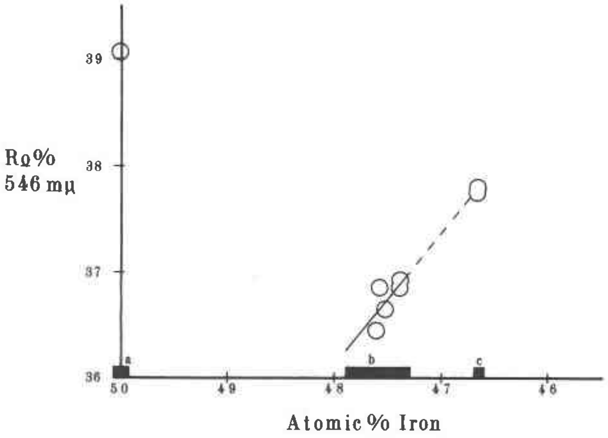

FIG. 1. Reflectivity (R*o*) of natural pyrrhotites and troilite. Composition range for natural phases shown at base of diagram (a = troilite, b = "hexagonal" or intermediate pyrrhotite, c = monoclinic pyrrhotite).

Tarnish rates for the various types of pyrrhotite are illustrated in Figure 2. In a period of about two hours subsequent to buffing, R*o* values for troilite decrease 0.8 percent while values for hexagonal and monoclinic pyrrhotite are constant.

Angle of Apparent Rotation (Ar)

Dispersion curves for Ar values for the three types of pyrrhotite are presented in Figure 3. The curves show $v > r$ for all wavelengths. Troilite which has tarnished shows significantly higher Ar values for the lower wavelengths than troilite measured within 15 minutes from hand buffing.

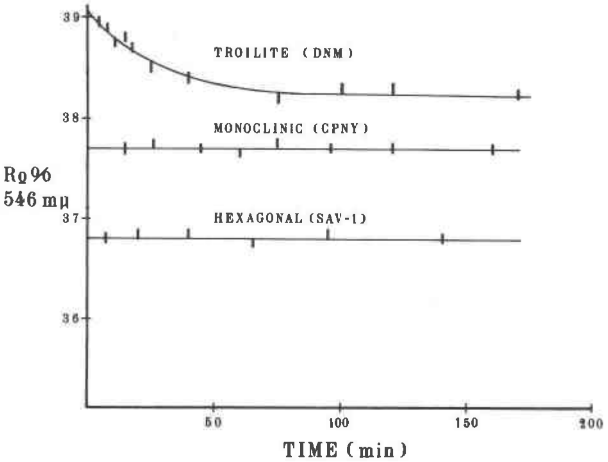

FIG. 2. Tarnish curves for natural pyrrhotite and troilite showing decrease in R*o* for troilite with time.

Conclusions

The optical data presented in this paper indicate that the minor modifications of the NiAs structure represented by the various superstructure types have a pronounced effect on the optical properties. If the Fe/S ratio alone controlled variations in R*o*, a decrease in R*o* would most likely correspond to a drop in the Fe/S ratio. Instead, a reverse trend is indicated by measurements of intermediate and monoclinic pyrrhotite. Thus structure plays a more determinative role.

The structure-composition types of pyrrhotite can be readily distinguished. Troilite can be distinguished by higher R*o* and Ar values as well as its tarnishing characteristics. For hexagonal and monoclinic pyrrhotite, R*o* variations show an inversely proportional relationship with the iron content. These variations are sufficiently large that a deviation in R*o* of ±0.1 percent enables accuracy in determining pyrrhotite composition comparable to that available from the X-ray spacing method of Arnold (1962), that is, within ± 0.1–0.2 atomic percent Fe. Recent advances in reflectance equipment and ancillary apparatus afford precision much greater than that obtained with the equipment used in this study. If pyrrhotites of known composition and structure are used as standards, extremely accurate determinations are possible. It may even be possible to distinguish between various superlattice types of the intermediate pyrrhotites referred to previously.

A principal advantage of reflectance measurements as a means of identifying the structure and composition of natural pyrrhotites is the short period of time (about two minutes) required per determination. In rocks or ores containing only trace quantitites of pyrrhotite, the technique is quite useful as crushing, grinding, and mineral separation are not required.

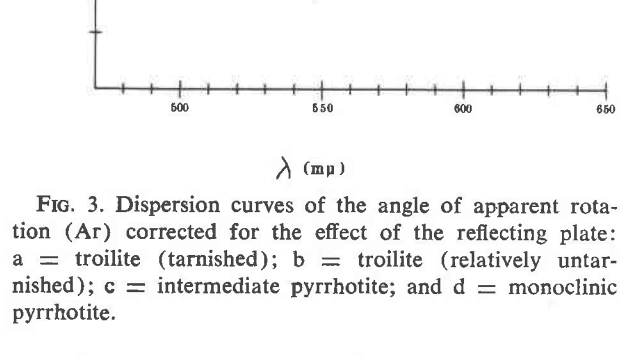

FIG. 3. Dispersion curves of the angle of apparent rotation (Ar) corrected for the effect of the reflecting plate: a = troilite (tarnished); b = troilite (relatively untarnished); c = intermediate pyrrhotite; and d = monoclinic pyrrhotite.

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