

## AN X-RAY DIFFRACTION AND REFLECTANCE SPECTROSCOPY STUDY OF IRON SULPHIDES

Edward A. Cloutis, ER Georesearch Ltd., 4 Huntstrom Road N.E., Calgary, Alberta, Canada T2K 5W3, and Michael J. Gaffey, Department of Earth and Environmental Sciences, Rensselaer Polytechnic Institute, Troy, New York 12180-3590

The reflectance spectra of some iron sulphides exhibit a range of spectral slopes and occasional  $\text{Fe}^{2+}$  absorption bands. The spectral and X-ray diffraction data suggest that the spectral differences are attributable to one or more of the following: iron content variations, crystal structure, and degree of crystallinity.

**Introduction:** The diffuse spectral reflectance properties (0.3-2.6  $\mu\text{m}$ ) of some powdered iron sulphides have been examined to determine how variations in composition, degree of crystallinity and crystal structure can affect iron sulphide spectra. Spectroscopy may be applicable to characterizing iron sulphides in various types of geological samples (e.g., thin sections, mineral separates) and has implications for geological remote sensing of iron sulphide occurrences and for pyrite-pyrrhotite geothermometry [1].

**Experimental Procedure:** 0-45  $\mu\text{m}$  sized samples of natural pyrite (PRT101), marcasite (MAR101), pyrrhotite (PRH101), meteoritic troilite (TRO201) from the Canyon Diablo iron meteorite, and synthetic troilite ( $\text{FeS}$ ; TRO202) have been spectrally characterized. The 0.3- to 2.6- $\mu\text{m}$  reflectance spectra were measured at the RELAB facility at Brown University [2] at  $i=0^\circ$ ,  $e=15^\circ$  and 5 nm resolution relative to halon. The compositions of the natural samples have been determined by electron microprobe (Table 1). The composition of the synthetic troilite sample is stoichiometric  $\text{FeS}$  (99.9% purity). The samples were also characterized by X-ray diffraction (XRD).

**Results:** XRD data indicate that the pyrrhotite (monoclinic) and synthetic troilite contain no measurable impurities. The meteoritic troilite sample contains a small amount (<5%) of graphite. The pyrite sample is contaminated with a small amount of quartz and the marcasite sample is composed of subequal amounts of pyrite and marcasite. The amount of small angle XRD scattering was used to assess relative degrees of crystallinity.

The sample reflectance spectra are shown in Figure 1. The pyrite (PRT101) spectrum exhibits 2 distinct absorption bands near 0.89  $\mu\text{m}$  and 1.98  $\mu\text{m}$ , similar to other pyrite spectra [3,4]. These bands are attributable to crystal field transitions in octahedrally coordinated  $\text{Fe}^{2+}$  [4,5].

The marcasite spectrum (MAR101) exhibits an absorption band near 0.9  $\mu\text{m}$ , but no band near 2.0  $\mu\text{m}$ . Because of the presence of appreciable pyrite in this sample, the marcasite spectral properties cannot be uniquely ascertained.

The pyrrhotite (PRH101) spectrum is relatively featureless. The overall spectral slope differs from other pyrrhotite spectra [4], suggesting that compositional and/or structural differences in pyrrhotite may be amenable to spectral analysis. The gradual reflectance increase suggests that this sample is somewhat disordered, consistent with the presence of low angle scattering in the XRD trace.

The meteoritic troilite spectrum (TRO201) is similar in shape to the pyrrhotite spectrum and to a previously measured troilite spectrum [6]. The synthetic troilite spectrum (TRO202) differs significantly from the TRO201 spectrum, with a distinct absorption band near 0.93  $\mu\text{m}$ , a weaker band near 2.49  $\mu\text{m}$ , a much flatter slope in the near-infrared and a more abrupt reflectance increase near 0.6  $\mu\text{m}$ .

**Discussion:** The appearance of  $\text{Fe}^{2+}$  crystal field absorption bands is limited to the pyrite and synthetic troilite spectra. The absorption bands in the 0.3- to 0.6- $\mu\text{m}$  region of the synthetic troilite spectrum are attributable to  $\text{Fe}^{2+}$  crystal field transitions [5].

The two troilite samples are compositionally similar. The XRD traces exhibit only small differences in low angle scattering and minor differences in relative peak heights. This suggests that spectral shape variations are largely attributable to differences in the degree of crystallinity. The presence of an  $\text{Fe}^{2+}$  band in the synthetic troilite sample near 0.9  $\mu\text{m}$  suggests that small changes in composition can affect the appearance of this band.

All 5 spectra exhibit overall spectral shapes characteristic of powdered semiconductors [4]. The synthetic troilite sample exhibits the most abrupt reflectance rise near 0.6  $\mu\text{m}$ , the flattest near-infrared slope and the least low angle X-ray scattering. This suggests that the degree of crystallinity affects spectral shape in the wavelength region associated with valence to conduction transition and that measures of spectral slope in the transition region may be most effective for assessing relative degrees of crystallinity.

Pyrite can be discriminated from the other natural sulphides on the basis of its well defined  $\text{Fe}^{2+}$  absorption bands. Comparisons of the compositionally similar PRT101 and MAR101

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samples suggests that differences in the crystal structure [7] will control the appearance of  $Fe^{2+}$  bands while comparison of the two troilite samples indicates that composition may also be a factor.

The wavelength positions of minimum reflectance of the  $Fe^{2+}$  absorption bands in the pyrite and synthetic troilite samples differ (0.89 and 1.98  $\mu m$  versus 0.93 and 2.49  $\mu m$ , respectively) and may be due to differences in iron content and/or crystal structure; differences in degree of crystallinity are not likely to significantly affect band positions.

**Conclusions:** The data strongly suggest that the spectral properties of iron sulphides are a function of iron content, crystal structure and degree of crystallinity. Differences in degree of crystallinity may affect the shape of the reflectance rise. Differences in iron content can affect the appearance of  $Fe^{2+}$  absorption bands near 0.9  $\mu m$  and 2.0  $\mu m$ . Differences in crystal structure may also affect the appearance of  $Fe^{2+}$  absorption bands and overall spectral shape. The relative importance of each of these factors cannot however be deduced from the current sample set.

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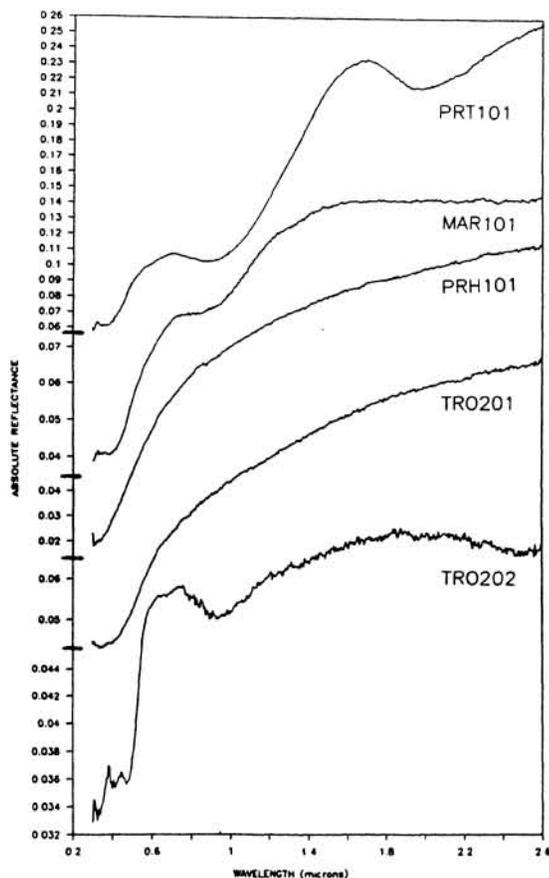


Table 1. Composition of the iron sulphides used in this study.

Wt%	Pyrite PRT101	Marcasite MAR101	Pyrrhotite PRH101	Troilite TRO201
Fe	45.97	45.45	58.53	61.50
Ni	0.00	0.00	0.70	0.03
Na	0.06	0.02	0.03	0.01
S	54.10	54.98	40.36	37.71
V	0.00	0.00	0.00	0.00
Co	0.01	0.04	0.07	0.02
P	0.00	0.00	0.00	0.00
Cr	0.00	0.00	0.08	0.32
Mg	0.08	0.00	0.04	0.00
Mn	0.00	0.00	0.00	0.00
Cu	0.00	0.00	0.00	0.00
Al	0.08	0.04	0.05	0.02
Pb	0.00	0.00	0.00	0.00
Zn	0.00	0.00	0.18	0.08
Ti	0.00	0.00	0.00	0.00
Total	100.30	100.53	100.04	99.69
Fe	7.84	7.71	10.80	11.56
S	16.07	16.26	12.97	12.35

Fig. 1. Absolute reflectance spectra (0.3-2.6  $\mu m$ ) of natural pyrite (PRT101), marcasite (MAR101), pyrrhotite (PRH101), meteoritic troilite (TRO201) and synthetic troilite (TRO202). Vertical scale varies for each sample.