

FOURIER TRANSFORM INFRARED STUDIES OF ALUMINOUS GOETHITES AND HEMATITES

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Abstract—Synthetic aluminous hematites and goethites have been examined by Fourier-transform infrared spectroscopy. For aluminous hematites prepared at 950°C a linear relationship exists between Al content and the location of the band near 470 cm⁻¹, up to 10 mole % Al substitution which is shown to be the solubility limit. The spectra of aluminous goethites prepared in two different ways are qualitatively similar to each other, but differ as to the relationship between the position of the band near 900 cm⁻¹ and the Al content. The spectra of the two series of hematites produced by calcining the goethites at 590°C also show a strong dependence of band position and intensity on the goethite preparative method.

Key Words—Aluminum, Fourier transform, Goethite, Hematite, Infrared.

INTRODUCTION

Hematite (α -Fe₂O₃) and goethite (α -FeOOH) are the most abundant of the iron-containing species found in soils and clays. The ionic replacement of Fe by Al in each has been widely reported (e.g., Norrish and Taylor, 1961; Janot and Gibert, 1970; Davey *et al.*, 1975; Schwertmann *et al.*, 1977; Bigham *et al.*, 1978; Mendelovici *et al.*, 1979), and a variety of techniques have been employed to characterize such substituted minerals (Fysh and Clark, 1982a, 1982b, and references therein). Dispersive infrared (IR) spectroscopy has been used by several workers for the characterization of aluminous goethites (e.g., Jónás and Solymár, 1970; Fey and Dixon, 1981), but we know of no published infrared data relevant to aluminous hematites. Infrared analysis of specimens containing these minerals is an attractive alternative to other means of characterization, as it offers the possibility of quantitatively examining with a single measurement *all* of the species present.

The new generation of infrared spectrometers, based on the Michelson interferometer and known as Fourier transform infrared (FTIR) spectrometers, have significant advantages over dispersive instruments in terms of sensitivity, energy throughput, resolution, and wavenumber accuracy (Koenig, 1975). These advantages make FTIR particularly suitable for the study of minerals which are generally highly absorbing and prone to radiation scattering. High-quality spectra of sufficient resolution to enable a meaningful assessment of ionic replacement are readily obtained by FTIR. This high resolution also ensures that accurate corrections for band overlap due to the presence of a variety of mineral species can easily be made. Thus, the FTIR method has potential for characterizing naturally occurring specimens and should provide more accurate quantitative information than conventional IR techniques. The present study of the FTIR spectra of alu-

minous goethites and hematites has been undertaken to provide standard data with which to compare such analyses.

EXPERIMENTAL

Specimen preparation

The specimens examined here were extensively characterized by Mössbauer spectroscopy (see Fysh and Clark, 1982a, 1982b), and a more complete account of their preparation is found therein.

Aluminous goethites. Two series of aluminous goethites were prepared by ageing co-precipitated hydroxides in alkaline solution under different conditions. Following the ageing of the co-precipitate (12–24 hr at about 135°C for the hydrothermal series, 13 days at 60°C for the low-temperature series), the goethites were decanted and boiled in 3 M KOH for 30 min to dissolve any aluminum hydroxide phases which may have formed during ageing. The caustic solution was decanted and the goethites were washed several times in hot distilled water with successive decantations. The final suspension was then dialyzed against running distilled water for 21 days and dried overnight in an air oven at 70°C. The goethites were crushed in an agate mortar and stored in air-tight vials prior to chemical and FTIR analysis.

Aluminous hematites. Aluminous hematites prepared in two different ways were examined. A high-temperature series was prepared by firing co-precipitated hydroxides at 950°C, while a second low-temperature series was made by calcining at 590°C aluminous goethites prepared in the manner described above.

Chemical analysis

The aluminous goethites were analyzed for iron and aluminum at the laboratories of the Comalco Research Company, Melbourne. Samples were dissolved in acid,

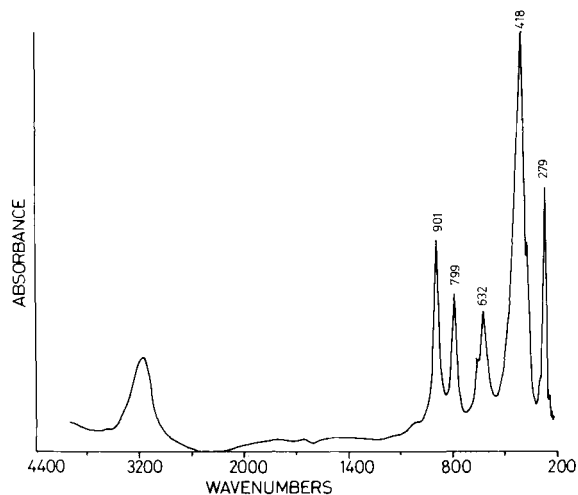


Figure 1. Full range spectrum of a typical aluminous goethite (Al content = 9.4 mole %).

and total Fe was determined spectrophotometrically. Total R_2O_3 ($R = Al + Fe$) was determined by precipitation with ammonia; Al_2O_3 was estimated by subtraction of Fe_2O_3 from R_2O_3 . The aluminum contents assumed for the low-temperature hematite preparations are those of the original goethites.

The high-temperature hematite preparations resisted acid dissolution, and the aluminum contents assumed for these materials are simply those of the initial co-precipitated hydroxides. This assumption appears to be reasonable not only because of the small losses incurred during firing, but because the various Mössbauer spectroscopic parameters all showed a linear dependence on the Al contents determined in this way (Fysh and Clark, 1982b).

Fourier transform infrared analysis

FTIR spectra were obtained on a Nicolet MX-1E FTIR spectrometer equipped with a Nicolet 1200S data-processing terminal. The alkali-halide pellet technique was employed. A sample of the finely ground mineral (~2 mg, accurately weighed) was added to a known amount (~450 mg) of high purity CsI (Merck, 99.5%) in the agate capsule of a small vibratory mill. The mixture was milled for 2 min after which two pellets each weighing 200 ± 1 mg were pressed in a 13-mm die under a load of 9 tonne for 1 min. The pellet judged by appearance to be the more homogeneous was used to obtain the spectrum. Five hundred and forty scans (interferograms) of nominal resolution 2 cm^{-1} were signal-averaged to obtain a primary spectrum in the range $4000\text{--}225 \text{ cm}^{-1}$, from which a reference spectrum of pure CsI was subtracted to yield the sample spectrum. The instrument was continually purged with dry nitrogen and was internally referenced to a helium-neon laser, thus requiring no external calibration. The

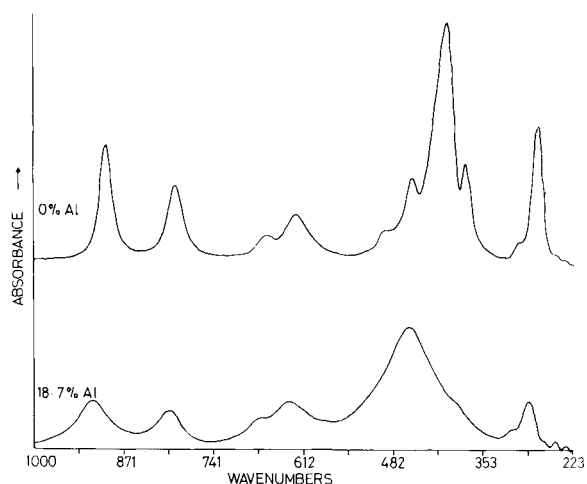


Figure 2. Expansion of part of goethite spectra showing shift in line positions and line broadening accompanying incorporation of aluminum into the structure.

spectra were normalized to a pellet concentration of 1 mg/cm^2 .

RESULTS AND DISCUSSION

Aluminous goethites

All of the spectra of the two series of goethites studied are qualitatively similar in appearance (e.g., Figure 1) and closely resemble those which have already been reported (e.g., Jónás and Solymár, 1970) except for the improved resolution of the minor contributing bands. Each of the bands exhibits a shift in wavenumber with increasing Al content, together with a broadening of the spectral lines due to the increasing range of atomic environments present (e.g., Figure 2). Previous work has shown that the position of the band located near 900 cm^{-1} (attributed to O-H bending) exhibits the greatest Al dependence (Jónás and Solymár, 1970); this relationship is confirmed by the present results. The

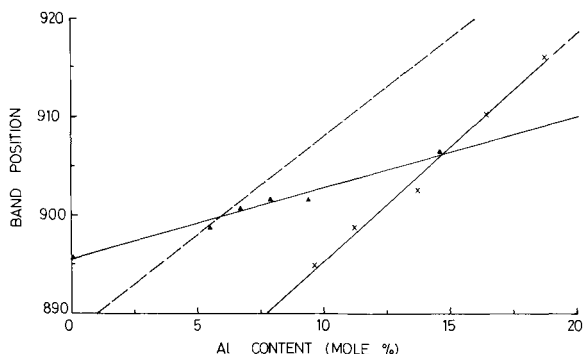


Figure 3. Variation with Al content of 900-cm^{-1} band position of the hydrothermal (Δ) and low-temperature (\times) series of goethites, with respective lines of best-fit. Dashed line gives results of Jónás and Solymár (1970).

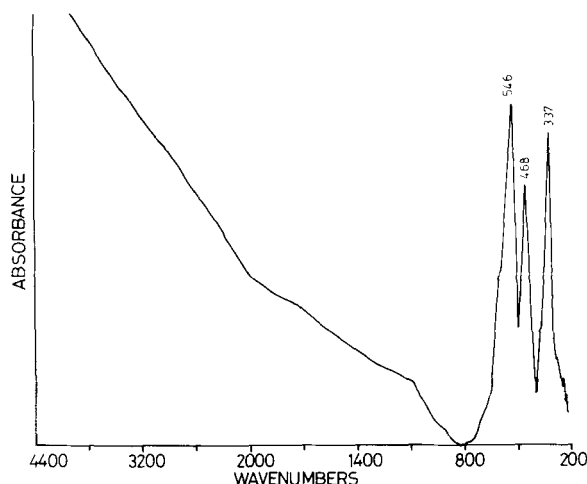


Figure 4. Full range spectrum of high-temperature hematite.

variation with Al content of the position of this band is shown in Figure 3, together with the results of Jónás and Solymár (1970).

Clearly, the three series of results, although each presents a reasonably linear dependence of band position on Al content, are in considerable disagreement. Several authors (e.g., Yariv and Mendelovici, 1979) have noted that IR band positions, intensities, etc. reported for supposedly identical minerals often show minor differences due to such effects as specimen crystallinity and non-stoichiometry. Rendon and Serna (1981) and Serna *et al.* (1982) showed that morphological variations may also be a major cause of spectral differences in the case of microcrystalline materials. Fey and Dixon (1981), in fact, noted that differing degrees of structural hydration may lead to shifts in the 900-cm^{-1} band of goethite. Jónás and Solymár (1970) used a third preparative method so that it seems likely that the three different sets of results shown in Figure 3 may be due to variations in the degree of structural hydration and/or morphology resulting from the mode of preparation.

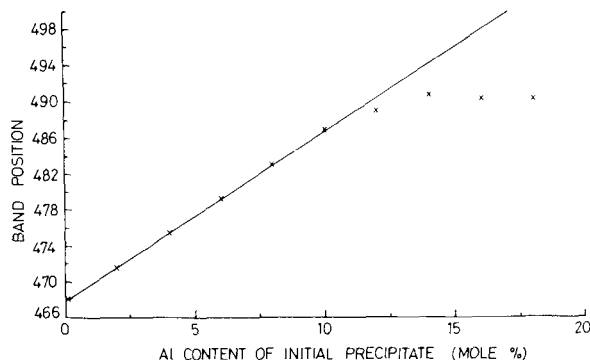


Figure 5. Variation with Al content of 470-cm^{-1} band position for the high-temperature series of hematites.

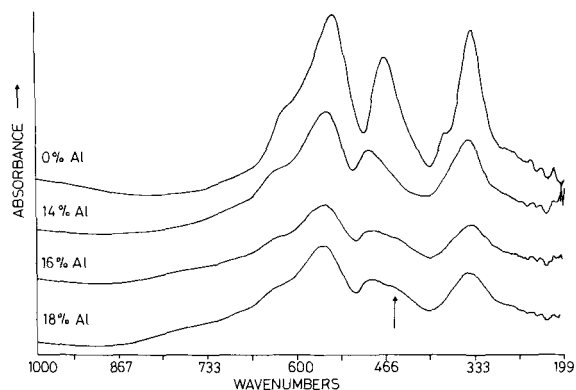


Figure 6. Expansion of part of high-temperature hematite spectra showing new band (arrowed) observed at high Al contents and assigned to α -alumina.

Interestingly, Mössbauer spectroscopic analysis of the two series of goethites studied here did not distinguish between them, with the 4.2°K magnetic hyperfine splittings of specimens within each exhibiting the same aluminum dependence (Fysh and Clark, 1982a). This observation reflects the fact that the Mössbauer technique is sensitive only to comparatively gross changes in the iron local environment, so that specimens having differences in the 900-cm^{-1} O–H bending band, but the same Al content, appear identical.

Aluminous hematites

High-temperature series. The spectra of all of the high-temperature hematites are similar, exhibiting 3 major well-resolved bands (e.g., Figure 4). The strongly sloping baseline is due to light scattering by the hematite crystallites. Two of the bands (located near 550-cm^{-1} and 470-cm^{-1}) show some change in position with increasing Al content. This change is more marked for the 470-cm^{-1} band, and for this reason it was chosen to indicate the effects of aluminum on the hematite spectrum. The variation with Al content of the position of the 470-cm^{-1} band is shown in Figure 5. The relationship is remarkably linear to about 10 mole % Al content of the initial precipitate.

Very similar behavior was observed for the Mössbauer-spectroscopically determined decrease of room-temperature, magnetic hyperfine splitting with increasing Al content for these same specimens (Fysh and Clark, 1982b); for Al contents greater than about 12 mole % the magnetic hyperfine splitting remains fairly constant. Fysh and Clark suggested that this degree of substitution probably represents the solid solubility limit of Al in Fe_2O_3 for the particular preparative method employed, with any further Al presumably being exsolved as a minor surface phase. This conclusion is supported by the present results—a band at 460-cm^{-1} was noted only for the three highest Al concentrations

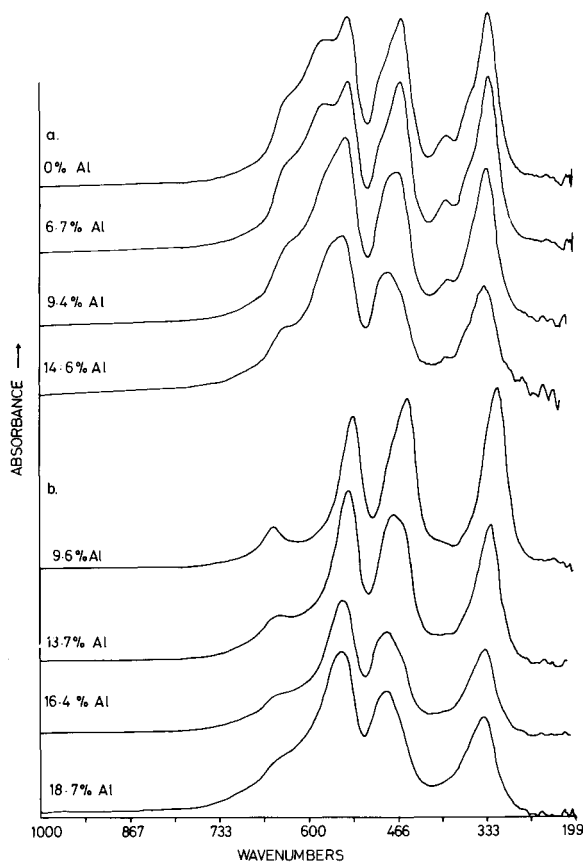


Figure 7. Selected expanded spectra of low-temperature hematites showing two series of minerals from (a) hydrothermal and (b) 60°C aged goethites.

(see Figure 6), and can in fact be attributed to α - Al_2O_3 (Farmer, 1974). De Grave *et al.* (1982) recently detected corundum in the X-ray powder diffraction pattern of 15 mole % Al-substituted hematite after the sample was heated to 900°C. Thus, FTIR analysis may indicate the extent of solid solubility in some mineral systems, despite previous assertions to the contrary (Tarte, 1968; Fey and Dixon, 1981).

Low-temperature series. Within the low-temperature hematites examined, two different 'sub-series' of specimens are immediately apparent, based upon the appearance of the spectra obtained (see Figures 7a and 7b). Both series of spectra exhibit the usual three sharp hematite bands, but differ with respect to minor bands at around 600 cm^{-1} , 670 cm^{-1} , and 380 cm^{-1} , the last band not being apparent for one series. The sub-series differ also in the dependence of band position on Al content of the specimens (Figure 8). Unlike the high-temperature hematites (Figure 5), *all* of the major bands shift in position with increasing Al content. These shifts, however, do not begin until about 7 mole % Al substitution; it appears that the structural changes resulting

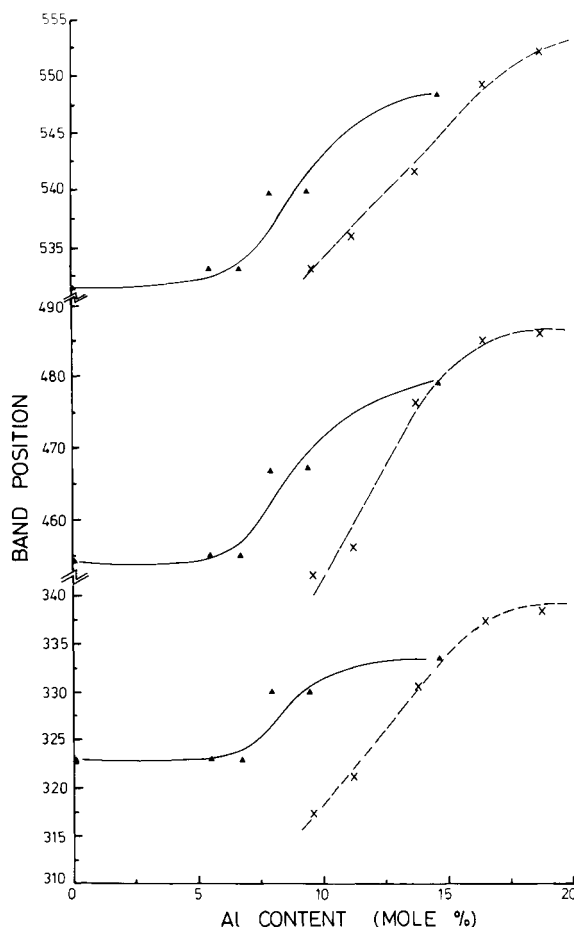


Figure 8. Variation with Al content of the position of the three major bands of low-temperature hematite. Points marked with a Δ denote specimens derived from hydrothermal goethites, while those marked with \times represent specimens from low-temperature goethites. The curves drawn are intended only to represent the data.

from low levels of Al incorporation are not reflected in the FTIR spectra of hematites prepared in this way.

As was discussed by Fysh and Clark (1982b), hematite prepared by calcining goethite at temperatures below ~ 700 – 800°C can hold >10 mole % Al as may be seen from Figure 8. As indicated in Figure 8, the differences in behavior of the two sets of low-temperature hematites correlate with their having been derived from the two series of goethites studied. It is well known that a disordered or proto-hematite forms from goethite upon dehydration at $\sim 400^\circ\text{C}$, and that complete structural order is not achieved until temperatures in excess of ~ 600 – 700°C (Fysh and Clark, 1982b). These authors noted that ordered and disordered aluminous hematites have very different 4.2°K magnetic hyperfine splittings and suggested that this difference was due to a superstructural ordering in the c direction. Yariv and Mendelovici (1979) previously noted dif-

ferences in the IR spectra of hematite and proto-hematite (their spectra being very similar to those obtained here for the pure end members of the high- and low-temperature series of hematites). Rendon and Serna (1981) and Serna *et al.* (1982) explained significant differences in the IR spectra of goethites heated to less than $\sim 600^\circ\text{C}$ and to $\sim 950^\circ\text{C}$ in terms of morphological changes. From the present results it is clear that the factors responsible for the differences in the spectra of the initial goethites are not removed by firing at 590°C , and in fact such differences become more noticeable for aluminous hematites.

CONCLUSIONS

The present results amply demonstrate the ability of Fourier transform infrared analysis to detect spectral changes accompanying ionic replacement of Fe by Al in hematite and goethite. It is also quite clear that for aluminous goethite and 'disordered' aluminous hematite the spectra depend strongly on morphology, structural hydration, and degree of crystallinity, which are in turn dependent on the preparative method employed. For high-temperature hematites, however, a linear relationship exists between Al content and the location of the band near 470 cm^{-1} , up until the solubility limit. This relationship indicates the ability of FTIR to distinguish the solubility limit of aluminous hematite. It is apparent from the above results that it will not generally be possible to establish reference standards for the FTIR analysis of natural hematite/goethite-containing specimens solely on the basis of synthetically prepared minerals. It may, however, be reasonable to characterize a series of naturally occurring calibration specimens (after pre-extraction of accompanying aluminum- or iron-containing species), thus forming the basis for FTIR analysis of a particular orebody.

ACKNOWLEDGMENTS

The authors express their appreciation to Mr. R. Van Den Heuvel for obtaining the FTIR spectra and to the Broken Hill Proprietary Co. Ltd. for permission to publish this work.

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(Received 7 December 1982; accepted 10 March 1983)

Резюме—Синтетические глиноземистые гематиты и гетиты исследовались при помощи фурье преобразованной инфракрасной спектроскопии. В случае глиноземистых гематитов, подготовленных в температуре 950°C , существует линейная зависимость между содержанием Al и положением полосы около 470 cm^{-1} , до 10 мольных % подстановки Al, что является пределом растворимости. Спектры глиноземистых гетитов, подготовленные двумя способами являются качественно похожими на себя, но различаются положением полосы около 900 cm^{-1} в результате разных содержаний Al. Спектры двух серии гематитов, образованных путем кальцинации гетитов при температуре 590°C , также указывают на сильную зависимость положения полосы и ее интенсивности от метода приготовления гетита. [E.G.]

Résumé—Synthetische Al-hältige Haematite und Goethite wurden mittels Fouriertransform Infrarotspektroskopie untersucht. Bei Al-hältigen Haematiten, die bei 950°C synthetisiert wurden, existiert eine lineare Beziehung zwischen dem Al-Gehalt und der Lage der Bande bei ca. 470 cm⁻¹. Dies gilt bei einer Substituierung durch Al bis zu 10 Mol.-%. Dies ist auch die Grenze der Löslichkeit. Die Spektren von Al-hältigen Goethiten, die auf zwei verschiedene Arten hergestellt wurden, sind qualitativ einander ähnlich aber unterscheiden sich bezüglich der Position der Bande bei ca. 900 cm⁻¹ aufgrund unterschiedlicher Al-Gehalte. Die Spektren von zwei Haematitserien, die durch Kalzinierung der Goethite bei 950°C hergestellt wurden, zeigten ebenfalls eine starke Abhängigkeit der Bandenlage und -intensität von der Präparationsmethode des Goethits. [U.W.]

Résumé—Des hématites et des goethites aluminées synthétiques ont été examinées par spectroscopie infrarouge transforme-Fourier. Il existe pour des hématites aluminées préparées à 950°C une relation linéaire entre le contenu en Al et la situation de la bande près de 470 cm⁻¹, jusqu'à 10 mole % de substitution d'Al qu'on peut montrer être la limite de solubilité. Les spectres de goethites aluminées préparées de deux manières différentes sont qualitativement semblables, mais différent quant à la position de la bande près de 900 cm⁻¹ à cause de différents contenus en Al. Les spectres des deux séries d'hématites produites en calcinant les goethites à 950°C montrent aussi une forte dépendance de la position et de l'intensité de la bande sur la méthode de préparation de la goethite. [D.J.]