

MINERALOGICAL NOTES

AN INFRARED ABSORPTION ANALYSIS OF MAGNETITE

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INTRODUCTION

In recent years, magnetite has been the subject of an increasing number of investigations, especially with respect to the evaluation of environmental factors in igneous and metamorphic petrogenesis. The principal techniques employed in the determination of compositional, structural, and textural characteristics in these studies have included analytical chemistry, emission spectroscopy, X-ray diffractometry, and ore microscopy.

The purpose of this study was to test the utility of infrared absorption spectrophotometry for the examination of magnetite (and certain commonly associated minerals).

EXPERIMENTAL PROCEDURE

Many of the procedural details have already been described (Liese, 1963). The samples were analyzed using a Perkin-Elmer model 621 grating spectrophotometer, with a source intensity of 0.8 ampere. One-half mg of prepared sample was mixed manually with 175 mg of KBr (Hannah, 1963), in order to avoid polystyrene contamination (Lyon, 1963) from vials used in mechanical mixing. Ten discs of the same sample were analyzed in order to estimate precision. Reproducibility was $\pm 1 \text{ cm}^{-1}$ for absorption band frequency and ± 2 percent for band intensity.

According to the infrared study on ferrites by Waldren (1955) and the summary by Rao (1963), anhydrous iron and iron-titanium oxides show absorption bands in the far infrared region. This was confirmed by scanning from 4000 to 300 cm^{-1} on numerous specimens. All samples were scanned from 1200 to 300 cm^{-1} in order to determine common silicate impurities.

RESULTS AND INTERPRETATION

Forty of the magnetites analyzed were separated from granites and gneisses of New England. A dozen "select" specimens of magnetite, ilmenite, and hematite were also analyzed.

Figure 1 shows the spectra of four magnetites, which are representative of 25 of the magnetites that were analyzed. The only substantial absorption band is centered around $570(\pm 5) \text{ cm}^{-1}$. These samples are ilmenite-(and hematite-) poor, as evidenced by the absence of absorption bands at lower frequencies (Fig. 2). Only two magnetites yielded spectra that revealed no absorption at all (Spectrum D, Fig. 1), and these show a marked decrease in Ti, Mn, and Fe(?) content (as revealed by spectrographic analysis).

In order to relate systematic changes in spectra to magnetite:ilmenite variations, a series of sample mixtures was prepared for a range (in weight ratios) from $Mt_{100}:Il_1$ to $Mt_1:Il_{100}$. The ilmenite selected for this artificial series was from Arendal, Norway, and the magnetite (Table 1) was a crystal from an unknown locality. (This magnetite has been used in all other prepared mixtures in this study and is hereafter referred to as the "standard" magnetite.) The spectra for this series are shown in Figure 3.

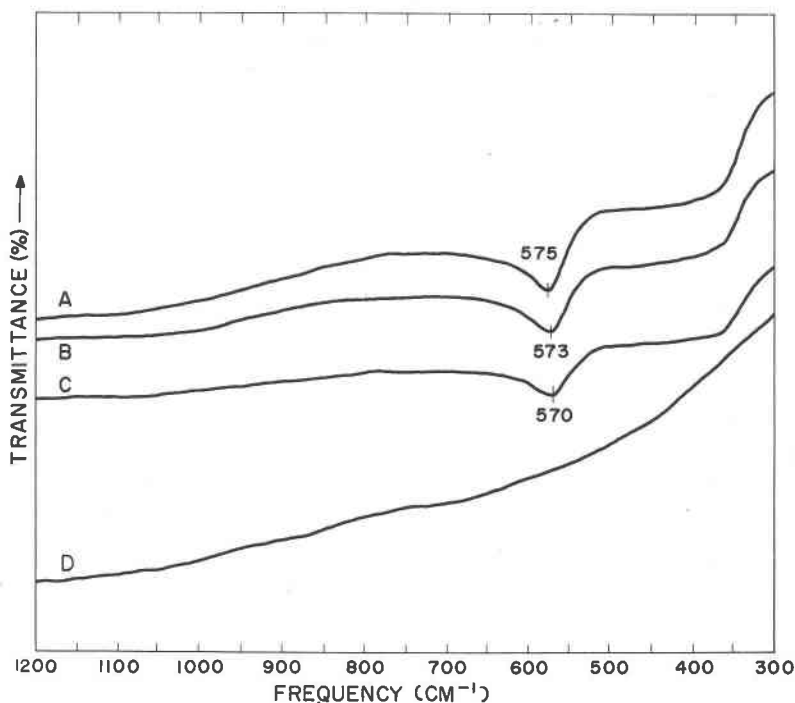


FIG. 1. Representative spectra of some magnetites.

Based upon these systematic spectral variations it would seem, at first, quite simple to estimate the amount of ilmenite naturally combined with magnetite (from $Mt_{100}:Il_1$ to $Mt_1:Il_1$) under routine operating conditions of infrared absorption spectrophotometry as illustrated in Figure 4. In fact, it would seem that with different instrumental settings (*e.g.*, slower scanning speed, scale expansion) more precise determinations could be made. However, at least three complicating problems exist.

The first involves the variation in Fe and Ti content of ilmenite or magnetite. For example, Figure 2 shows considerable variation in absorp-

tion frequencies and intensities of the Norwegian ilmenites compared to the New England ilmenites, which can be related to the considerable variation in TiO_2 and $\text{Fe}_2\text{O}_3 + \text{FeO}$ contents of the Kragero and Waterford samples (Table 1).¹ Additional mixtures were made of the Waterford ilmenite and the standard magnetite; the spectra are shown in Figure 5. While changes in frequencies and intensities are again very sys-

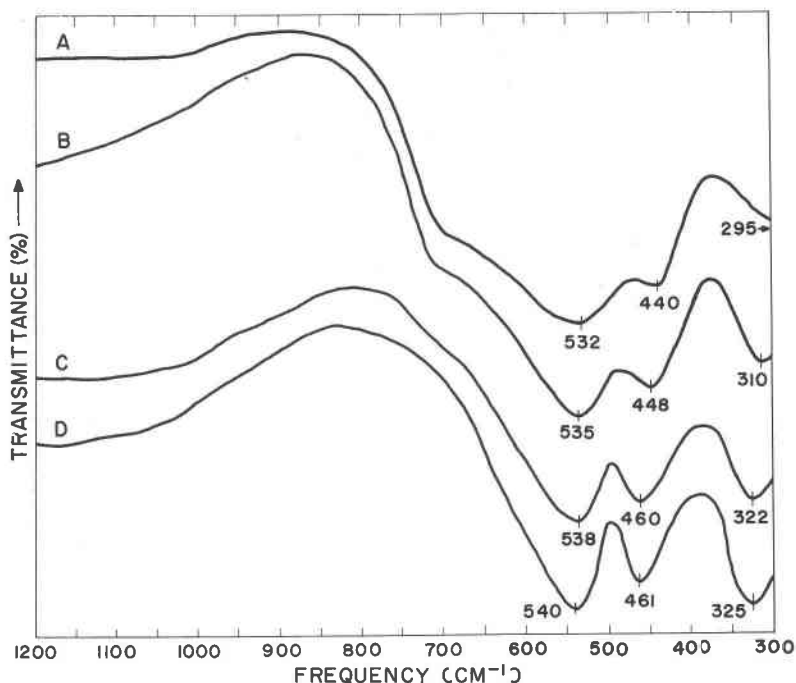


FIG. 2. Spectra of some ilmenites from; A-Arendal, Norway; B-Kragero, Norway; C-Chester, Vermont; and D-Waterford, Rhode Island.

tematic, as expected, differences are very distinct and considerable when compared to equivalent ratios of the mixture with Norwegian ilmenite (Fig. 3).

The presence of almost isostructural hematite intergrown with ilmen-

¹ The shifts to lower frequencies for these two ilmenites correspond to a decrease in Fe and an increase in Ti. This is not expected, since such a compositional change should result in a decrease in mass of the central atoms and a greater force constant (assuming the Ti is quadrivalent). One possible explanation would concern the specific distribution of Ti in the ilmenite structure. Perhaps a more probable explanation would be the actual presence of intergrown hematite. (This emphasizes the need for accurate Fe^{3+} and Fe^{2+} determinations in the chemical analyses).

ite (or with magnetite) is a second formidable problem in the determination of magnetite-ilmenite combinations. Figure 6 illustrates its similar effect on infrared spectra. (The minor band near 395 cm^{-1} was not found in all four hematites analyzed; it may represent contamination from another oxide.)

TABLE 1. CHEMICAL ANALYSES OF THE "STANDARD" MAGNETITE AND TWO ILMENITES^{1,2}

	Magnetite	Ilmenites	
		A	B
SiO ₂	0.1	0.2	0.2
Al ₂ O ₃	0.6	0.2	0.1
Fe ₂ O ₃	78.8	—	—
FeO	19.4	49.9 ³	71.0 ³
MgO	0.5	.02	.01
CaO	.02	.02	.01
Na ₂ O	.01	.01	.02
K ₂ O	.15	.15	.15
H ₂ O ⁺	.05	.03	.03
H ₂ O ⁻	.1	.1	.1
TiO ₂	0.2	47.1	26.5
CO ₂	.0	.0	.0
MnO	.03	.03	.03
Total	100.0	97.8	98.2

¹ Mineral Localities:

- Magnetite —locality unknown
 Ilmenite A —Kragero, Norway
 Ilmenite B —Waterford, Rhode Island

² Analyzed by Earth Sciences, Inc. (Golden, Colorado)

³ Represents total iron. According to D. N. Bloom (Chief Geochemist for Earth Sciences, Inc.): "Under the digestion conditions used for the purpose of FeO determinations, the breakdown of ilmenite is too slow to be certain that no oxidation of the ferrous iron takes place. Therefore, the total iron was determined and reported as FeO."

These two problems demonstrate the difficulty of even semiquantitative determinations. More work is needed on samples that have been chemically analyzed and examined with the ore microscope, in various mineral combinations, before the spectrophotometer can be completely evaluated in this regard.

The third problem concerns silicate impurities. Certain absorption bands of commonly associated silicates occur at frequencies in the immediate vicinity of those representative of magnetite-ilmenite-hematite combinations. Fortunately, the most intense silicate bands occur in the

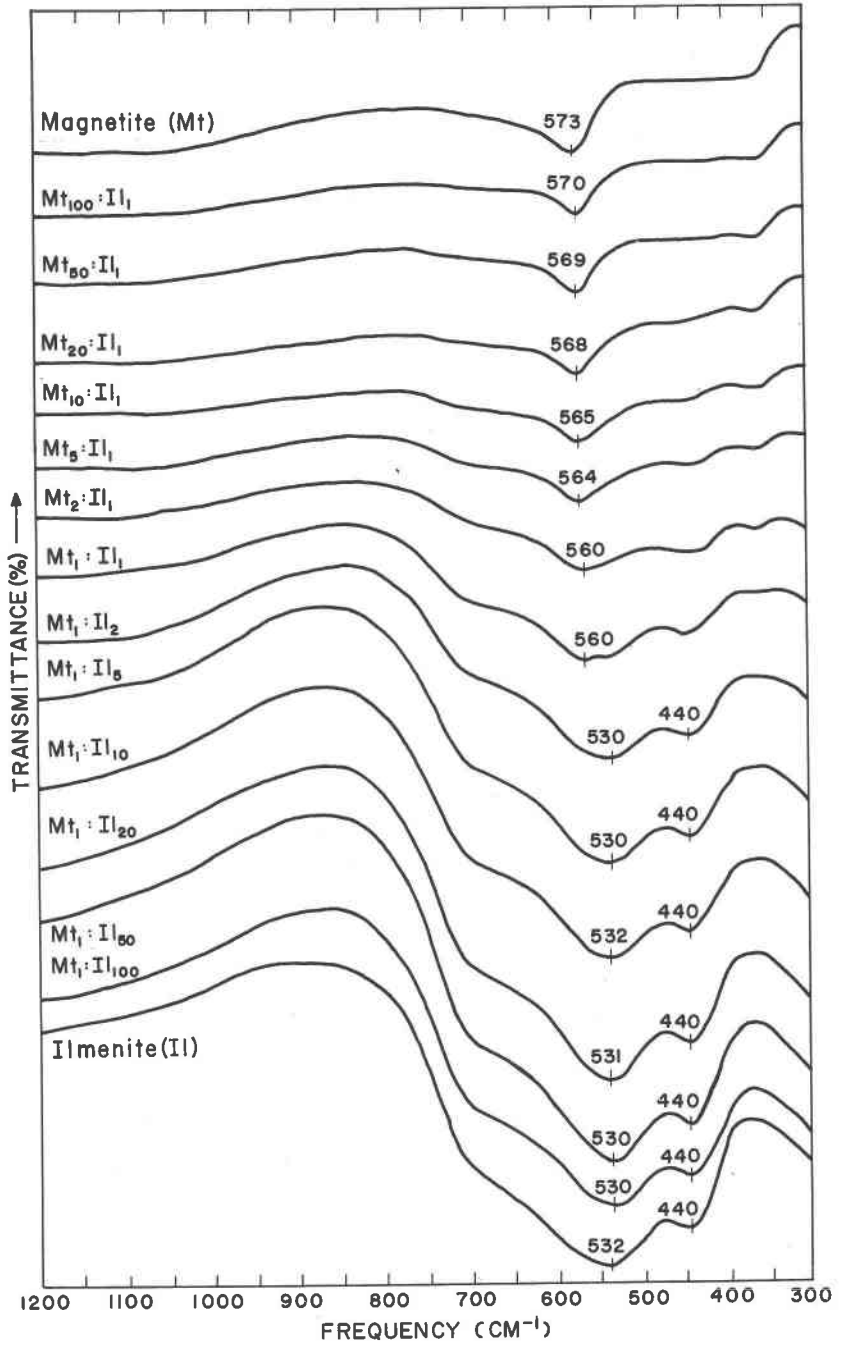


FIG. 3. Spectra of artificial mixtures (weight ratios) of magnetite (standard) and ilmenite (Arendal, Norway).

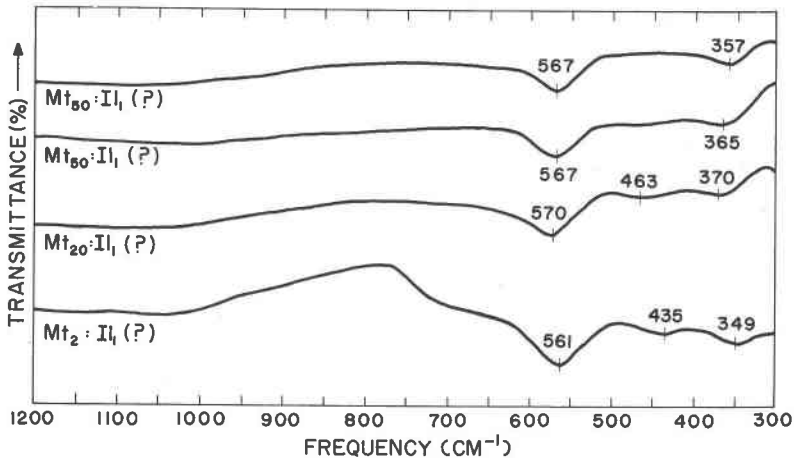


FIG. 4. Spectra of some natural impure magnetites and their interpreted Mt:Il(?) ratios.

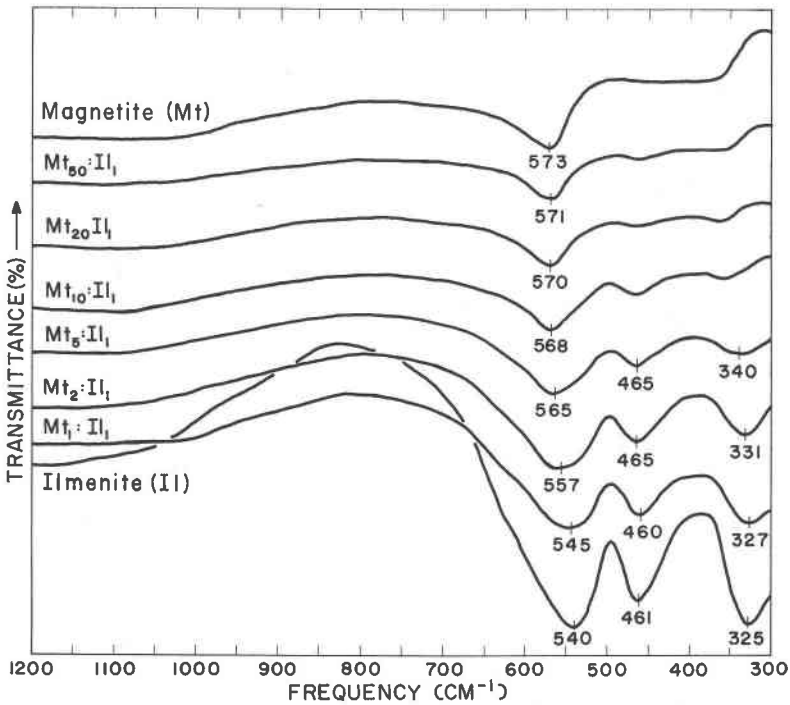


FIG. 5. Spectra of artificial mixtures (weight ratios) of magnetite (standard) and ilmenite (Waterford, Rhode Island).

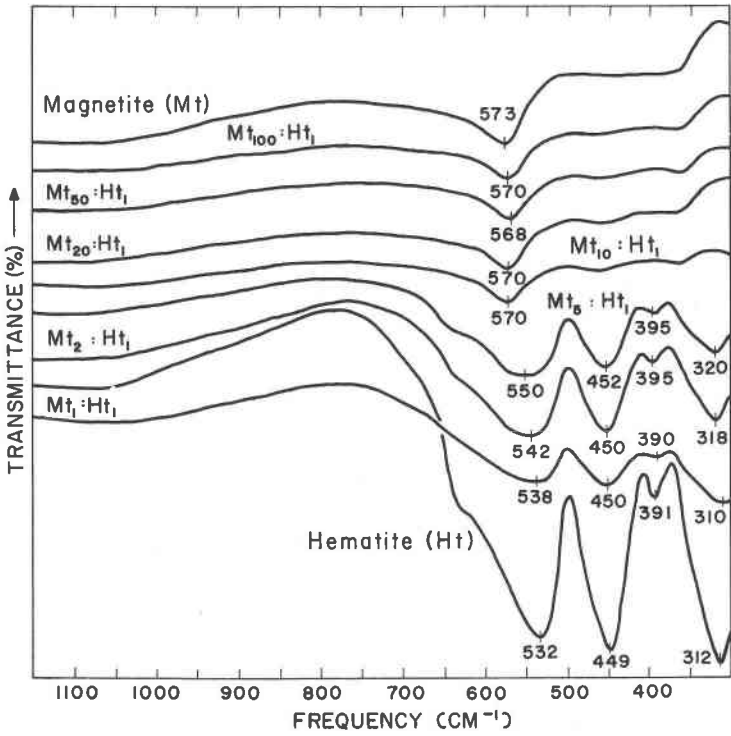


FIG. 6. Spectra of artificial mixtures (weight ratios) of magnetite (standard) and hematite (Cumberland, England).

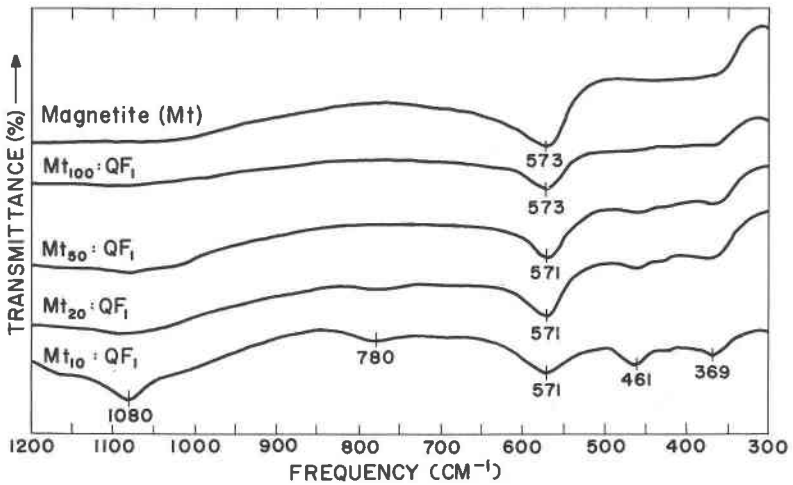


FIG. 7. Spectra of artificial mixtures (weight ratios) of magnetite (standard) and quartzofeldspathic (QF) material.

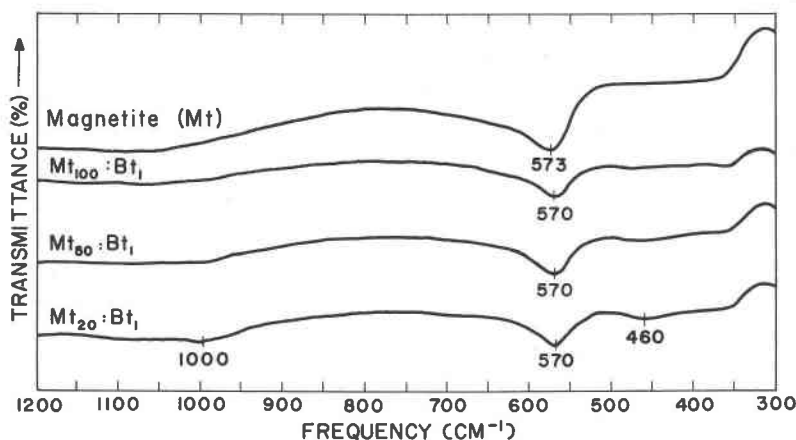


FIG. 8. Spectra of artificial mixtures (weight ratios) of magnetite (standard) and biotite (Bt).

range 800 to 1200 cm^{-1} , which is free of these heavy metal oxide absorptions. Thus, even their presence in minor amounts can be determined. The spectra in Figures 7 and 8 illustrate this, and the spectra in all the preceding figures confirm the high purity (relative to silicates) of the samples.

CONCLUSIONS

Based on this preliminary infrared absorption examination, it is concluded that: (1) magnetite relatively free (98 percent by weight) of ilmenite or hematite can be distinguished routinely from magnetite of lesser purity; and (2) silicate impurities in magnetite (hematite, ilmenite) can be detected when present in small amounts (2 percent by weight).

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