

Examination of the siderite-magnesite mineral series by Fourier transform infrared spectroscopy

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ABSTRACT

Minerals belonging to the siderite-magnesite series have been studied using Fourier transform infrared spectroscopy. Pronounced shifts were observed in several of the carbonate vibrational bands. Shifts in the 1430-cm^{-1} and 880-cm^{-1} bands and a shift of about 60 cm^{-1} across the series for the 350-cm^{-1} band indicate that FTIR can be used to distinguish members of this solid-solution series. Plots of mole fraction Fe + Mn against band frequency yielded straight lines for the Mg-rich minerals that deviated from linearity as the siderite end of the series was approached. The observed shifts reflect the differing mass and ionic radius of substituting cations and possible compression of the carbonate ion.

INTRODUCTION

Siderite is usually not found as pure FeCO_3 in nature; Both Mn^{2+} and Mg^{2+} can substitute for Fe^{2+} in appreciable amounts. A complete solid-solution series exists between siderite and magnesite, and between siderite and rhodochrosite (Deer et al., 1962). This paper investigates the former series.

Mineral carbonates containing Fe and Mg have been the subject of study by a variety of different techniques, such as X-ray diffraction (Goldsmith et al., 1962; Howie and Broadhurst, 1958), differential thermal analysis (Kulp et al., 1951), and reflectivity measurements (Beran, 1978). Infrared spectroscopy has also been applied to a wide range of carbonates including siderite and magnesite (Huang and Kerr, 1960; Adler and Kerr, 1963a, 1963b; White, 1974; Farmer and Warne, 1978; Wenshi et al., 1985). More recently, Raman microprobe analysis has been used to discriminate among carbonate minerals (Herman et al., 1987).

EXPERIMENTAL DETAILS

Eleven carbonate minerals, spanning the compositional range from siderite to magnesite, were analyzed using standard atomic absorption methods (Table 1). Fourier transform infrared (FTIR) spectra were obtained on a Nicolet MX-1E spectrometer equipped with a Nicolet 1200S data-processing terminal. Samples were prepared by adding a portion of the finely ground material ($<40\ \mu\text{m}$, about 2 mg accurately weighed) to a known amount of cesium iodide (about 450 mg) in the agate capsule of a small vibratory mill. The mixture was milled for 3 min after which a pellet weighing 200 ± 1 mg was pressed in a 13-mm die for 1 min under a load of 9000 kg.

Five hundred forty scans (interferograms) were signal-averaged to produce a primary spectrum in the wave-number range $4800\text{--}225\text{ cm}^{-1}$, from which a reference spectrum of cesium iodide was subtracted to yield the spectrum of the sample. Spectra

were obtained for the pellets and normalized to a concentration of $1\text{ mg}\cdot\text{cm}^{-2}$ in the pellet.

Peak positions of the bands were determined as the point of minimum change in percent transmission with variation in wave number across the peak profile. These were obtained both by manipulation of the screen cursor of the data-processing terminal upon the expanded spectra and by noninteractive computer analysis. The difference between the two methods was typically $\pm 1\text{ cm}^{-1}$ for the broad bands.

RESULTS AND DISCUSSION

Typical spectra of several members of the series are shown in Figure 1 for the range $3200\text{--}200\text{ cm}^{-1}$. Comparison of the spectra reveals that the major bands are affected by substitution. Significant shifts occur in the bands near 1430 cm^{-1} (ν_3), 880 cm^{-1} (ν_2), and particularly in the band near 350 cm^{-1} (ν_6). The largest shifts are observed with the 350-cm^{-1} band (about 60 cm^{-1}), whereas a shift of about 30 cm^{-1} and 20 cm^{-1} occurs for ν_3 and ν_2 , respectively. The band at 740 cm^{-1} (ν_4) shows the least shift (about 10 cm^{-1}).

From Figure 1, it is apparent that the spectra are characterized essentially by two very sharp (ν_2 and ν_4) and two broad bands (ν_3 and ν_6). The asymmetric internal stretching mode ν_3 is characteristically broad for many carbonates. The measured value represents a composite of the transverse and longitudinal components of this vibration and, as seen in Figure 1, shows a shift across the mineral series. Therefore, although the peak position was measured precisely, it is not necessarily an accurate estimate of the asymmetric stretching frequency itself. The broad ν_6 band is a lattice vibration, whereas ν_2 and ν_4 arise from the out-of-plane bending mode and in-plane bending mode of the carbonate ion, respectively.

The use of these vibrational frequencies to determine mineral composition was investigated. From Figure 2—

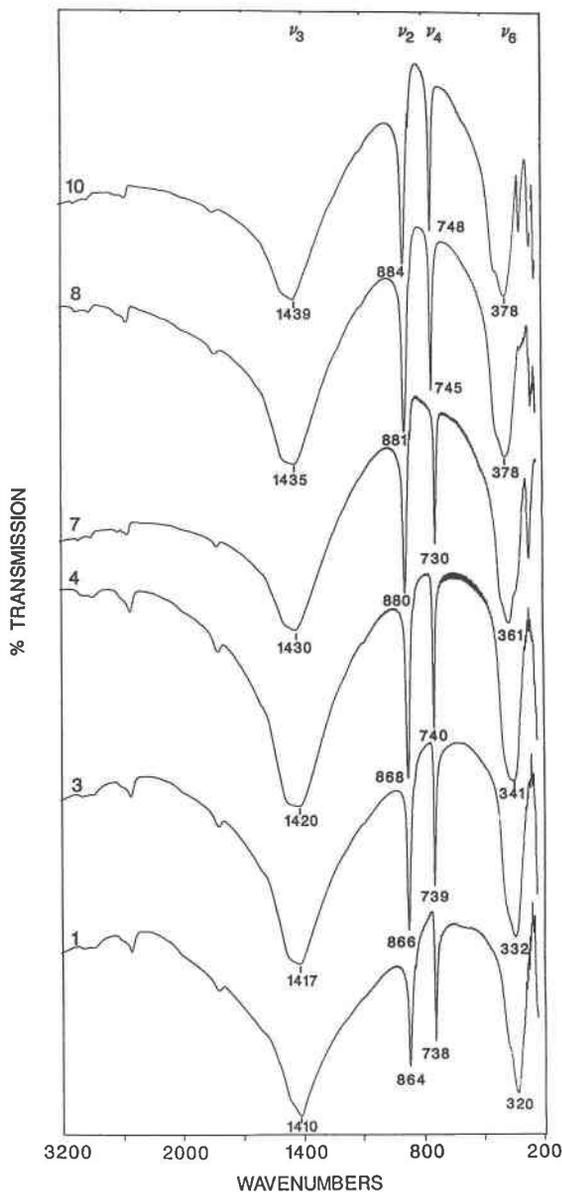


Fig. 1. FTIR spectra of members of the siderite-magnesite series. The numbered spectra follow the sequence shown in Table 1.

the plot of ν_2 against mole fraction Fe in the mineral samples—it is apparent that the trend toward lower frequencies follows the increase in substitution by Fe. However, two points fall noticeably below the line. They correspond to samples 5 and 6 (Table 1) that contain 8.6 and 10.3% Mn, respectively. These amounts are significantly higher than the levels encountered in the remaining carbonates, which otherwise contain about 0.5 to 2.9% Mn. It is more useful, therefore, to consider the combined mole fraction Fe + Mn, since Mn, because of its closeness in mass and radius to Fe, is expected to exert a similar influence upon the observed frequency. Such a result is

TABLE 1. Composition of members of the siderite-magnesite mineral series

| Sample* | Fe (%) | Mn (%) | Mg (%) | Ratio 1† | Ratio 2† |
|--|--------|--------|--------|----------|----------|
| 1. (Fe _{0.95} Mn _{0.042} Mg _{0.007})CO ₃ | 45.95 | 2.00 | 0.15 | 0.955 | 0.997 |
| 2. (Fe _{0.87} Mn _{0.058} Mg _{0.075})CO ₃ | 42.68 | 2.79 | 1.60 | 0.907 | 0.966 |
| 3. (Fe _{0.83} Mn _{0.044} Mg _{0.13})CO ₃ | 41.45 | 2.15 | 2.74 | 0.894 | 0.941 |
| 4. (Fe _{0.77} Mn _{0.010} Mg _{0.22})CO ₃ | 39.53 | 0.50 | 4.89 | 0.880 | 0.890 |
| 5. (Fe _{0.74} Mn _{0.086} Mg _{0.16})CO ₃ | 36.40 | 8.61 | 1.85 | 0.777 | 0.961 |
| 6. (Fe _{0.66} Mn _{0.21} Mg _{0.13})CO ₃ | 33.01 | 10.30 | 2.88 | 0.715 | 0.938 |
| 7. (Fe _{0.48} Mn _{0.027} Mg _{0.50})CO ₃ | 26.69 | 1.46 | 12.03 | 0.664 | 0.701 |
| 8. (Fe _{0.19} Mn _{0.049} Mg _{0.76})CO ₃ | 11.44 | 2.93 | 20.22 | 0.331 | 0.415 |
| 9. (Fe _{0.15} Mn _{0.008} Mg _{0.85})CO ₃ | 9.20 | 0.49 | 23.03 | 0.281 | 0.296 |
| 10. (Fe _{0.042} Mn _{0.006} Mg _{0.95})CO ₃ | 2.75 | 0.59 | 26.91 | 0.091 | 0.110 |
| 11. MgCO ₃ | 0.00 | 0.00 | 28.83 | 0.00 | 0.00 |

* 1, Denmark; 2, Broken Hill, NSW; 3, location unknown; 4, Kalgoorlie, Western Australia; 5, location unknown; 6, Exmoor, UK; 7, Traversella, Italy; 8, Mount Bischoff, Tasmania; 9, Kambalda, Western Australia; 10, Sheldand Lindsey, UK; 11, Rockhampton, Queensland.

† Ratio 1: Fe/(Fe + Mn + Mg). Ratio 2: (Fe + Mn)/(Fe + Mn + Mg).

shown in Figure 3 in which all points fall on a smooth curve.

The plots of mole fraction Fe + Mn against ν_3 and ν_6 are shown in Figures 4 and 5, respectively. Overall, the plots obtained for ν_2 and ν_3 are quite similar. An initial linear dependence at the magnesite end of the series gradually deviates at the siderite end. In both Figures 3 and 4, this deviation appears at about 0.7 mole fraction Fe + Mn. The effect is most pronounced for the lattice mode ν_6 , however, where a significant decrease in frequency is evident beyond 0.5 mole fraction.

Both magnesite and siderite possess the calcite structure, and sites occupied by Mg²⁺ are replaced by Fe²⁺ or Mn²⁺ during substitution. This replacement possibly occurs in a fashion analogous to dolomite (CaMg(CO₃)₂), which is known to be derived from the calcite structure (White, 1974). Similarity in the structures of dolomite-group and calcite-group minerals is reflected in their infrared spectra (Huang and Kerr, 1960).

In dolomite the cation sites of the calcite structure are occupied by two different cations. One cation layer is occupied by Ca²⁺ ions, and the alternate layer by smaller cations such as Mg²⁺ or Fe²⁺. This 1:1 ordering could apply to the magnesite-siderite series and involve layers of Mg²⁺ alternating with those of Fe²⁺ and Mn²⁺.

It appears that the carbonate internal modes of vibration are not greatly perturbed by the presence of Fe²⁺ or Mn²⁺ until a level of about 0.7 mole fraction is reached. However, ν_6 is more readily influenced at lower levels of substitution. A possible explanation may lie in the changes that occur to the compression of the carbonate ion as it is packed among the different cations. This would especially influence ν_6 , which is a lattice mode and is therefore sensitive to the behavior of cation neighbors around the carbonate ion. Moreover, as suggested by White (1974), the compression would be larger for small cations and would decrease as cation size increases, resulting in a decrease in frequency.

Finally, these plots serve to distinguish between mem-

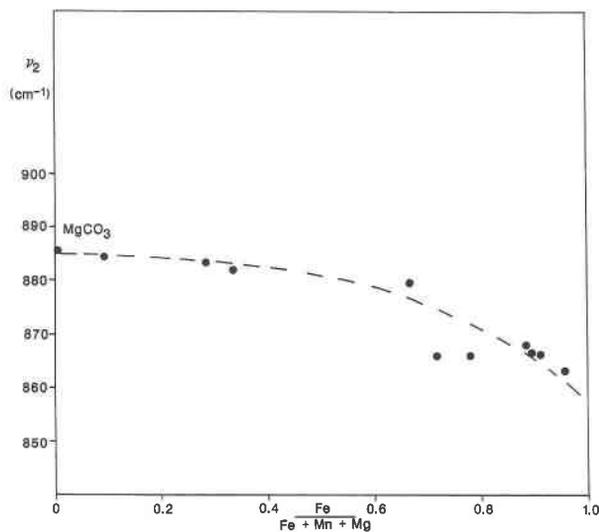


Fig. 2. Plot of 880-cm⁻¹ band (ν_2) against mole fraction Fe.

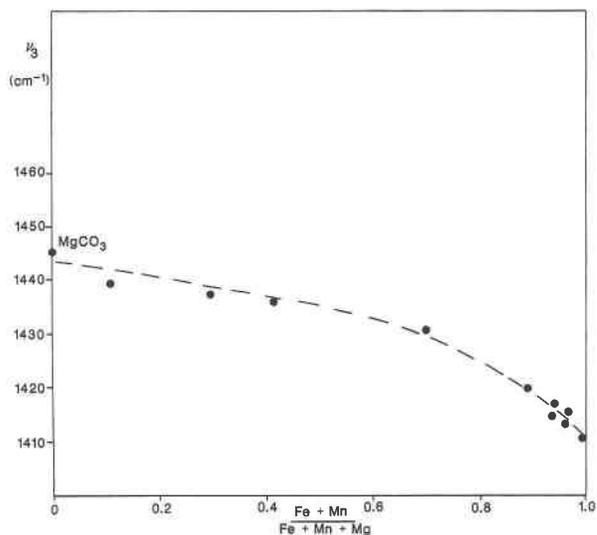


Fig. 4. Plot of 1430-cm⁻¹ band (ν_3) against mole fraction Fe + Mn.

bers of the magnesite-siderite series. Wenshi et al. (1985) examined the spectra of a large group of magnesite-siderite minerals using a grating instrument and, from a plot of mole fraction Fe against ν_2 , derived a straight line ($R^2 = 0.969$). They concluded that a correlation exists between frequencies and chemical composition. However, their data also suggest some deviation from linearity at the high-Fe end.

Our results indicate that the plot in Figure 5 is particularly useful in distinguishing members of the series because of the resolution it affords along the sideritic or high-Fe portion of the curve. The ν_6 frequency value decreases by about 3 cm⁻¹ per 1% increase in total cation content across the series. However, this curve is not par-

ticularly sensitive to the high-Mg end of the series. The shift in the 880-cm⁻¹ band is more suitable in distinguishing members of the magnesite series. The first five points (samples 7-11 in Table 1) yield an acceptable line that can be used for this purpose [$\nu_2 = 885.3 - 7.8(\text{Fe} + \text{Mn}) / (\text{Fe} + \text{Mn} + \text{Mg})$, $R^2 = 0.986$]. Less useful is the plot in Figure 4 that yields a poorer linear fit [$\nu_3 = 1443 - 18.8(\text{Fe} + \text{Mn}) / (\text{Fe} + \text{Mn} + \text{Mg})$, $R^2 = 0.904$]. As mentioned earlier, although the measured value for each ν_3 frequency is precise, each does not necessarily define the true frequency value, which may account for the increased scatter. Indeed, this may be true of earlier-reported values of the asymmetric stretching frequency (White, 1974).

It is clear that the inherent precision of FTIR allows the

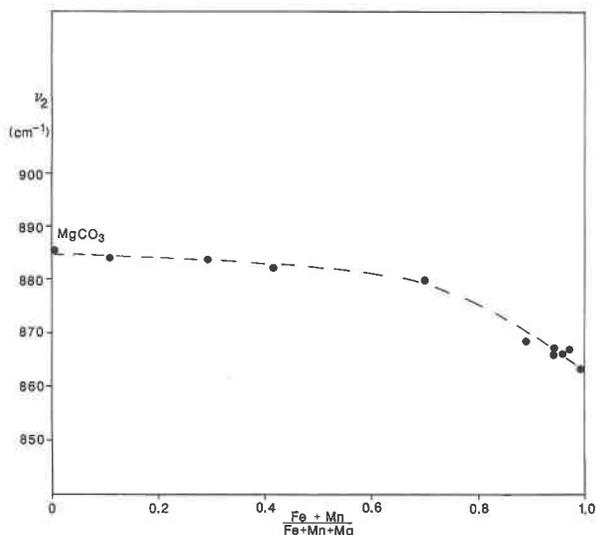


Fig. 3. Plot of 880-cm⁻¹ band (ν_2) against mole fraction Fe + Mn.

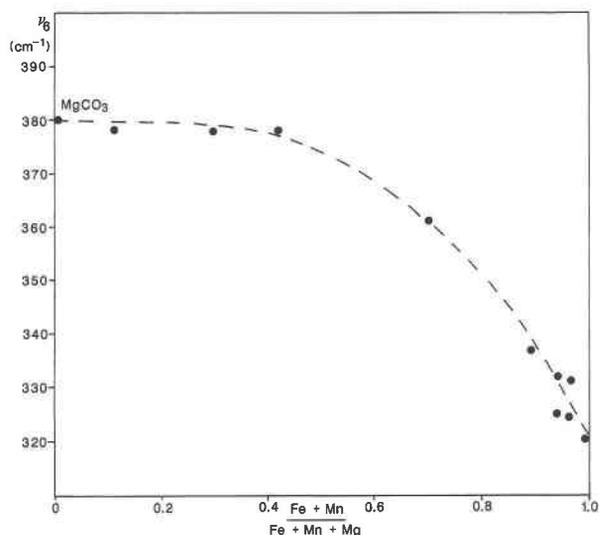


Fig. 5. Plot of 350-cm⁻¹ band (ν_6) against mole fraction Fe + Mn.

substitution effects to be clearly visible for infrared-active carbonate vibrations. The technique could be applied to distinguishing even relatively small changes in the chemical composition of this series due to cationic substitution.

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