

## FAR INFRARED (500–30 $\text{CM}^{-1}$ ) SPECTRA OF SOME CARBONATE MINERALS<sup>1</sup>

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### ABSTRACT

Several well resolved major and minor bands are present in the far infrared spectra (500–30  $\text{cm}^{-1}$ ) of the isomorphous members of the calcite and aragonite groups. The major absorption bands are probably diagnostic of the minerals. Shifts in frequency of certain lattice mode vibrations may be related to mass and radius differences of the cationic component of the carbonate, although effects attributable to cation substitution are not unambiguously demonstrated.

### INTRODUCTION

While the infrared spectra of the different anhydrous carbonates have been studied in detail in the conventional infrared range (4000–400  $\text{cm}^{-1}$ ) by Schaefer and Schubert (1916), Schaefer *et al.* (1926), Halford (1946), Hunt *et al.* (1950), Miller and Wilkens (1952), Adler and Kerr (1962, 1963a, 1963b), Huang and Kerr (1960), Weir and Lippincott (1961) and others, relatively little information is available on the far infrared spectra (400–30  $\text{cm}^{-1}$ ) of these carbonates. Scattered through the literature are references to predicted (and occasionally measured) absorption bands in the region below 400  $\text{cm}^{-1}$  (Schaefer *et al.*, 1926; Schaefer and Matossi, 1930; Kohlrausch, 1943; Herzberg, 1945; Brugel, 1962). Miller *et al.* (1960) present some data for the region 700–300  $\text{cm}^{-1}$ . The purpose of this paper is to present spectra for the far infrared (500–30  $\text{cm}^{-1}$ ) region for some of the more common carbonate minerals.

The quality of the spectra range from good to poor. While a detailed interpretation is impossible owing to incomplete knowledge of the far infrared spectra of inorganic materials, certain empirical relations are suggested between members of the two carbonate isomorphous groups.

Carbonate absorption bands in the far infrared region 500–30  $\text{cm}^{-1}$  can be of four origins: (1) internal vibrations of a polyatomic ion, essentially a molecular effect, (2) torsional vibrations of water molecules in the sample, (3) lattice vibration modes, and (4) sum and difference modes. The third possibility is the most likely origin for some of the major absorption bands measured in this study. It has long been known that carbonates have lattice vibrational modes in this region (Schaefer *et al.*, 1926; Schaefer and Matossi, 1930). The effect of water was minimal in this study inasmuch as anhydrous carbonates were examined (excepting analytical reagent grade  $\text{MgCO}_3$ , which was a mixture of hydrated

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forms). Miller *et al.* (1960) in their study state that "most of the carbonates give evidence of strong absorption beyond 300  $\text{cm}^{-1}$ ." Since the lowest fundamental ( $\nu_4$ ) of  $\text{CO}_3^{2-}$  is 680  $\text{cm}^{-1}$  (Kohlrausche, 1943), the evidence again points to lattice vibration modes as the most likely cause of a number of the strong far infrared absorption bands measured in this investigation. Some of the bands also probably represent changes in the internal vibrations of the carbonate ion caused by changes in cationic mass.

Because of structural differences, the absorption spectra of the arago-

TABLE 1. FAR INFRARED ABSORPTION BANDS OF CARBONATE MINERALS

Minerals	Composition	Absorption Bands ( $\text{cm}^{-1}$ ) <sup>1</sup>
<i>Calcite group</i>		
Calcite	$\text{CaCO}_3$	315S, 228S, 190S(Sh), 106S
Magnesite	$\text{MgCO}_3$	440S(Sh), 387bS, 306S, 256S, 230S, 187W(Sh), 164W
Rhodochrosite	$\text{MnCO}_2$	465S, 395M(Sh), 312S, 264W(Sh), 205S 180S, 162S
Siderite	$\text{FeCO}_3$	330S, 300M-W(Sh), 215W, 208S, 184S, 165W(Sh)
<i>Aragonite group</i>		
Strontianite	$\text{SrCO}_3$	270b(Sh), 220W, 180W(Sh), 145W
Witherite	$\text{BaCO}_3$	319W, 240W(Sh), 200S, 185W(Sh), 157M, 138M, 90WM
Cerussite	$\text{PbCO}_3$	470S, 396W, 380W, 315M, 276M, 210M(Sh) 175S, 130W(Sh), 120b(Sh)

<sup>1</sup> S=Strong, M=Medium, W=Weak, Sh=Shoulder b=broad.

nite and calcite group minerals showed distinct spectral relations between members of the same isomorphous group. Regardless of similarities or differences between members, the major and minor far infrared absorption bands of the carbonates appear to be diagnostic for each mineral.

#### PROCEDURE

The carbonate specimens examined (Table 1) were obtained from the mineral collection of the Department of Geology, The University of Kansas, through the courtesy of Dr. Elliot Gillerman, and were supplemented by equivalent reagent grade material. The far infrared spectra were obtained through the courtesy of Allan Budd and the Lincolnwood Laboratory, Beckman Instruments, Inc. All samples were examined by

X-ray diffraction in order to monitor their purity and to verify their identification. On the basis of the X-ray diffraction studies, the major absorption bands recorded in the far infrared region are most likely characteristic of the particular carbonate examined and not of any impurities present.

The samples were ground in a nitrogen atmosphere (to prevent water pickup) to a size of  $5 \mu$  or less. These samples were then run as nujol mulls between 0.40 mm-thick high density polyethylene plates over the range 33 to  $500 \text{ cm}^{-1}$ . Measurements were made on a Beckman IR-11 spectrophotometer. Sample size varied depending on the amount required to obtain satisfactory spectra but generally was about 0.5 mg. The spectra were done essentially in two parts. The first part from 33 to around  $150 \text{ cm}^{-1}$  was run with intentionally heavy mulls to enhance any absorptions in this region. For the second part, above  $150 \text{ cm}^{-1}$ , the mulls were thinned to give as well-defined a spectra as possible. In several cases, owing to the intensity of absorption, the trimmer comb, which in the Beckman IR-11 is used to set 100 percent transmission, was removed from the beam to give maximum spectral intensity. Four separate scales for the four gratings were employed in obtaining a full spectrum. Grating and filter changes were made via external switches, and it was not necessary to break the purge or otherwise open the instrument during the course of the full range scan.

The resolution of the IR-11 over the range covered was better than  $5 \text{ cm}^{-1}$  and in most cases was between 2 and  $3 \text{ cm}^{-1}$ . The scanning time for each full spectrum was of the order of 35–45 minutes.

#### RESULTS AND DISCUSSION

The present investigation is concerned both with the presentation of the far infrared spectra of the seven carbonate minerals studied (Fig. 1–2), and with a discussion of the absorption spectra of these carbonates. As a control, the spectra of four carbonates of reagent grade were also measured. Spectral data for the four sample pairs (natural and artificial) are compared in Table 2.

*Calcite group.* Study of the  $\text{MgCO}_3$  data indicated that fewer absorption peaks were present in magnesite than in its reagent grade counterpart (see Table 2). This is caused by the fact that the reagent grade material is actually  $\text{MgCO}_3 \cdot n\text{H}_2\text{O}$  (*i.e.*, a mixture of hydrated forms of  $\text{MgCO}_3$ , as clearly indicated by the X-ray diffraction pattern), whereas magnesite is strictly  $\text{MgCO}_3$ . The strong absorption peak at  $387 \text{ cm}^{-1}$  is present only in the magnesite sample. Four bands, three of them strong, are present in spectra of both magnesite and reagent grade  $\text{MgCO}_3$ . These

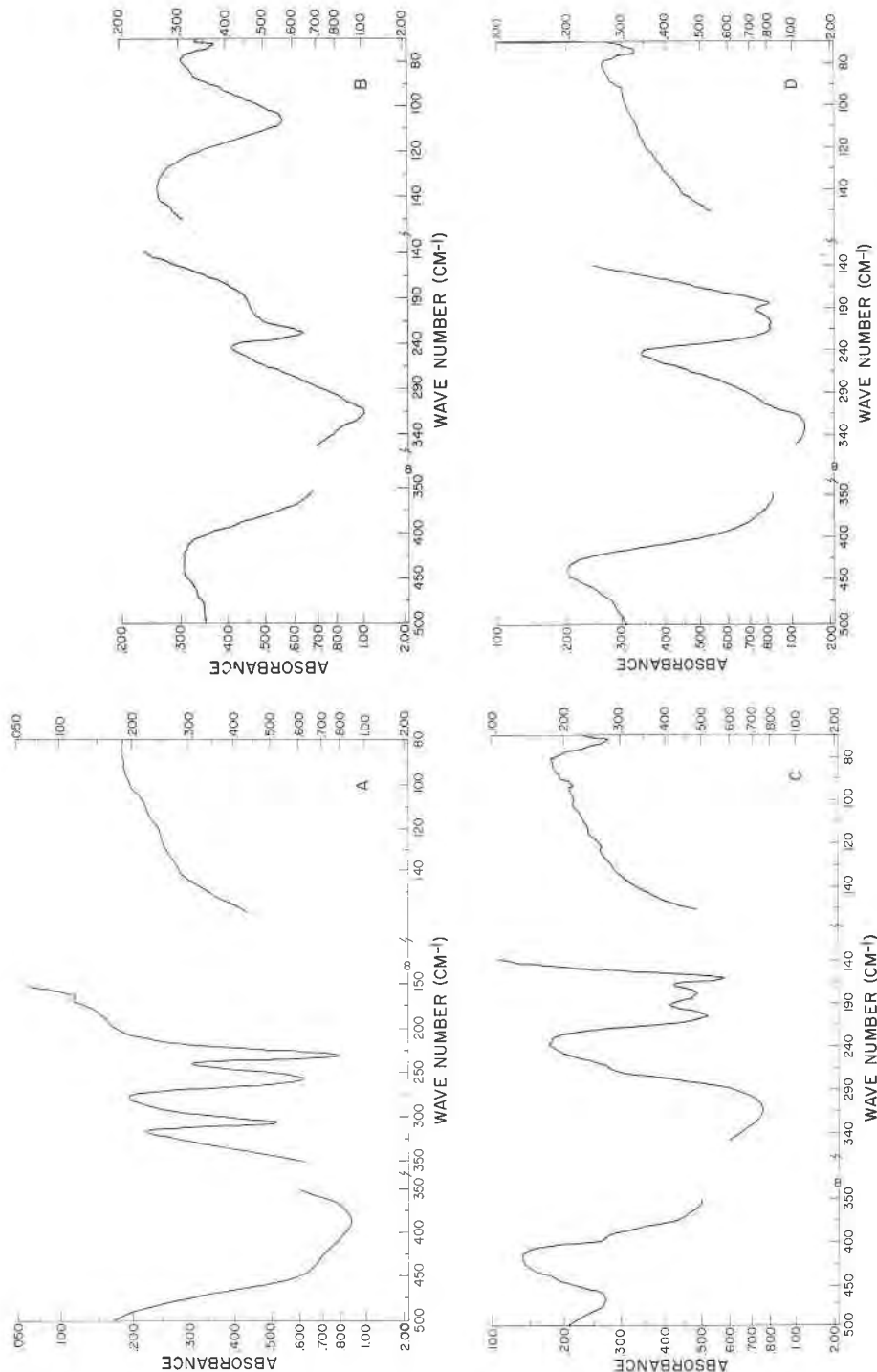


Fig. 1. Far infrared absorption spectra of calcite group minerals A, magnesite; B, calcite; C, rhodochrosite; D, siderite.

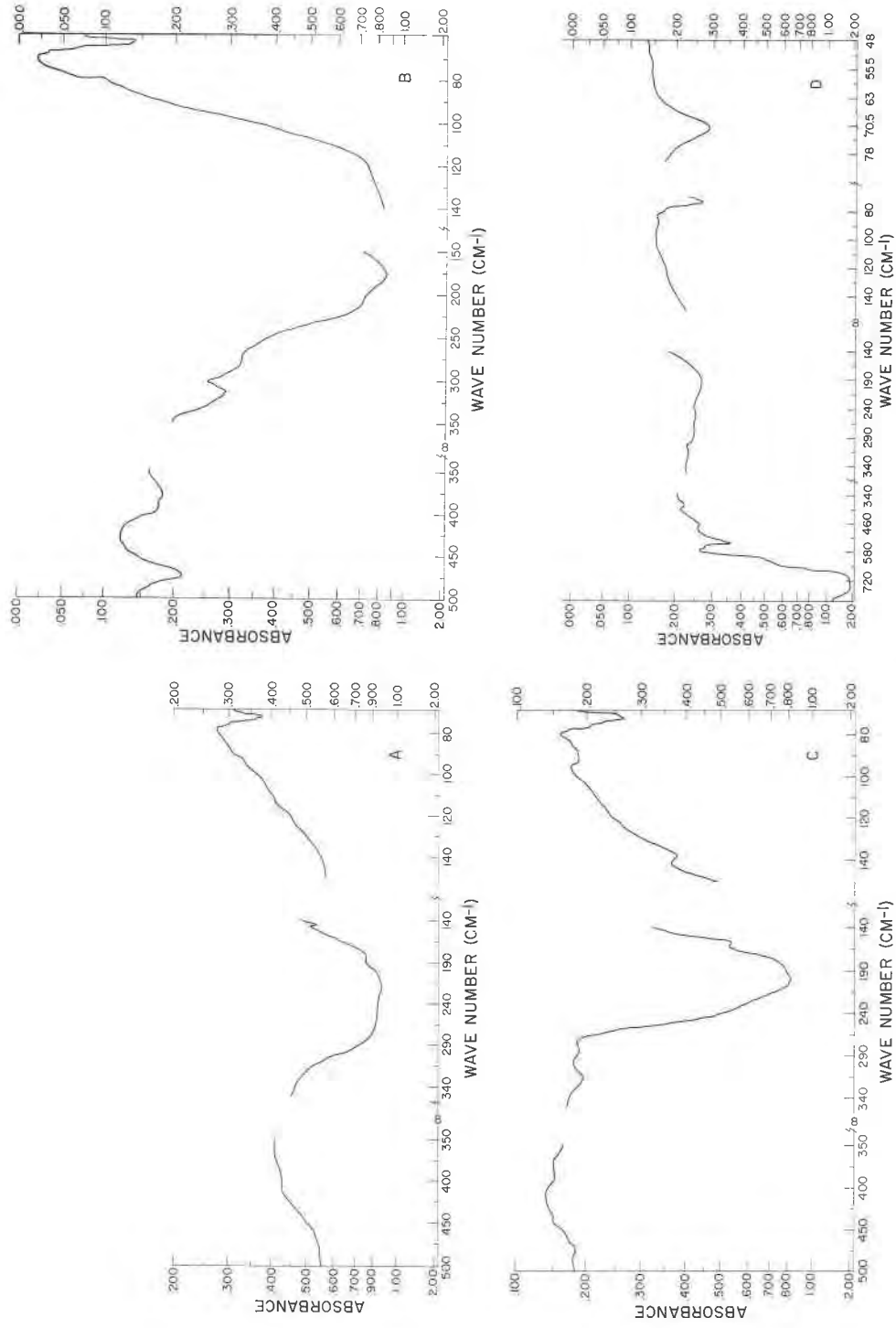


FIG. 2. Far infrared absorption spectra of aragonite group minerals. A, strontianite; B, cerussite; C, witherite; D, nujol (mull blank).

TABLE 2. COMPARISON OF FAR INFRARED ABSORPTION PEAKS FOR NATURAL AND REAGENT-GRADE MATERIAL\*

Sample	Absorption Bands ( $\text{cm}^{-1}$ )
MgCO <sub>3</sub> -N	440S (Sh), 387S, 306S, 256S, 230S, 187W (Sh), 164W
MgCO <sub>3</sub> -AR	440M, 303W, 296W, 277W, 255S, 230S, 210S, 138S
CaCO <sub>3</sub> -N	315S, 228S, 190S (Sh), 106S
CaCO <sub>3</sub> -AR	318S, 230S, 185M, 108S
SrCO <sub>3</sub> -N	270b (Sh), 220W, 180W (Sh), 145W
SrCO <sub>3</sub> -AR	240S, 200S, 180S, 144S
BaCO <sub>3</sub> -N	319W, 240Sh, 200S, 185W (Sh), 157M, 138M, 90W
BaCO <sub>3</sub> -AR	240W (Sh), 215S, 177S, 137M

\* S = strong, M = Medium, M-weak, Sh = Shoulder, b = broad, N = natural, AR = analytical reagent grade.

bands (440, 306, 256, and 230  $\text{cm}^{-1}$ ) can be considered to be the primary lattice vibration modes of MgCO<sub>3</sub> in the range 100–450  $\text{cm}^{-1}$ . Some of the additional absorption bands in the reagent grade material are probably due to water. Since some structural effects would be present in the hydrated forms but not in magnesite, the appearance of additional bands in the hydrated forms is not surprising.

For calcite, the correspondence in absorption peaks between the reagent grade and natural material is excellent (Table 2). The position of the 315–318  $\text{cm}^{-1}$  absorption band also agrees well with that at 320  $\text{cm}^{-1}$  reported by Miller *et al.* (1960). Similarly the peaks at 190 and 106  $\text{cm}^{-1}$  also corroborate very well those listed at 182 and 106  $\text{cm}^{-1}$  by Schaefer *et al.* (1926). No 228  $\text{cm}^{-1}$  peak has been reported in the literature. Peaks for calcite listed by Kohlrausch at 142, 156, and 282  $\text{cm}^{-1}$  (1943) were not observed in these spectra; nor was the lattice mode at 257  $\text{cm}^{-1}$  noted by Hexter (1958).

Little information on the predicted lattice modes of iron and manganese carbonates is available. However, the strong FeCO<sub>3</sub> absorption bands at 330 and 208  $\text{cm}^{-1}$  are again in good agreement with the values of 333 and 196  $\text{cm}^{-1}$  given by Schaefer *et al.* (1926). No corresponding data for MnCO<sub>3</sub> have been published. There is, however, no chance of missing the strong bands in the MnCO<sub>3</sub> spectrum. One might predict similar absorption bands for Mn and Fe carbonate, owing to their similarity of mass, cationic radius, and electronic structure. Of the absorption bands present, four are similarly positioned: these are the 162, 180, 205 and 321  $\text{cm}^{-1}$  bands in MnCO<sub>3</sub> and the 165, 184, 208, and 300  $\text{cm}^{-1}$  bands of FeCO<sub>3</sub>. The remaining bands do not correspond even closely.

*Aragonite group.* Reasonably close agreement of absorption peaks between the mineral and reagent-grade samples is evident (Table 2) for  $\text{BaCO}_3$  and  $\text{SrCO}_3$ . The  $270\text{ cm}^{-1}$  peak in strontianite is broad; nevertheless, it can be correlated with the sharp  $240\text{ cm}^{-1}$  peak of the reagent material. For witherite no indication of the  $319$  and  $157\text{ cm}^{-1}$  lattice modes are seen in the reagent sample. However, the  $\text{BaCO}_3$  bands at  $200$  and  $177\text{--}185\text{ cm}^{-1}$  agree well with the listed lattice modes of  $215$  and  $182\text{ cm}^{-1}$  given by Schaefer *et al.* (1926). The weak absorption at  $90\text{ cm}^{-1}$  was the only band observed below  $100\text{ cm}^{-1}$  for any of the samples studied.

For cerussite, the absorption bands at  $120$  and  $175\text{ cm}^{-1}$  agree well with the values of  $118$  and  $177\text{ cm}^{-1}$  given by Kohlrausch (1943). The weak

TABLE 3. FAR INFRARED SUM AND DIFFERENCE MODES

Mineral	Sum Peaks	Difference Peaks
<i>Calcite group</i>		
Calcite	None	None
Magnesite	None	$440 - 256 = 184$
Rhodochrosite	$264 + 205 = 469$	$465 - 205 = 260$
Siderite	None	None
<i>Aragonite group</i>		
Strontianite	None	None
Witherite	$185 + 138 = 323$	$319 - 138 = 181$
	$157 + 90 = 247$	$319 - 185 = 134$
Cerussite	$120 + 276 = 396$	$470 - 175 = 395$
	$175 + 210 = 385$	$396 - 376 = 120$

band at  $396\text{ cm}^{-1}$  is in accord with that listed at  $400\text{ cm}^{-1}$  by Miller *et al.* (1960). A peak at  $156\text{ cm}^{-1}$  listed by Schaefer *et al.* (1926) was absent in our spectra. No absorption bands were noted in the  $30\text{--}90\text{ cm}^{-1}$  range in any of the samples studied. The absorption peak at  $72\text{ cm}^{-1}$ , seen in all the spectra, is due to polyethylene. Figure 2 shows the nujol spectrum to which all other spectra were compared.

Considering both the absorption bands for each carbonate mineral as reported herein and the respective fundamental modes in the  $4000\text{--}400\text{ cm}^{-1}$  region, a list of possible subtractive or additive combinations was compiled and is given in Table 3.

*Mass and radius effects.* These studies indicate that the position of lattice vibrational mode frequencies for the different carbonates may be related to differences in the atomic mass and/or radii of the positive ion. Previous infrared studies have outlined general trends of this type in relation to the fundamental vibration modes of the carbonate ion. For

example, Hunt *et al.* (1950) observed a rough linear relation between the cation mass and wavelength of the 850–900  $\text{cm}^{-1}$  absorption band when plotted on semi-log paper. The curve indicated a shift of vibration to lower frequencies with increasing atomic weight of the cation. A mass effect of the cation was also suggested by Adler *et al.* (1950) and similar observations were also reported by Huang and Kerr (1960) and Weir and Lippincott (1961). For the far infrared region, however, little if any information of this type is available. Shifts in this region are likely to be more obvious than changes occurring in the 4000–600  $\text{cm}^{-1}$  range.

The vibrational frequency involving fundamental modes for any given molecular structure (e.g.,  $\text{CO}_3^{2-}$ ) is (Barnes, *et al.* 1944)

$$V = \frac{1}{2\pi c} \sqrt{\left(\frac{k_o}{\mu}\right)},$$

where

$\mu$  = reduced mass of participating atoms

$k_o$  = force constant

$V$  = vibrational frequency in wave numbers

and

$c$  = velocity of light.

Badger (1934) expresses the relationship between the force constant ( $k_o$  in dynes/cm) and interatomic distance ( $R$  in Angstrom units) as:

$$k_o = 1.86 \times 10^5 / (R - d_{ij})^3.$$

The term  $d_{ij}$  is a constant characteristic of all diatomic molecules made up of one element in the  $i$ th row and one in the  $j$ th row of the periodic table.

Although the latter equation was developed for diatomic molecules, Badger also suggested its possible use in the construction of potential functions for polyatomic molecules, and in the interpretation of their spectra. These relationships cannot, of course, be applied directly to the analysis of the effects of cationic mass or radius on the lattice vibration modes of the carbonate minerals. Nonetheless these equations do indicate that any change in  $R$  should modify or influence the lattice vibration frequencies of the different carbonate minerals. Evidently  $R$  would be changed by any adjustment of the  $\text{CO}_3^{2-}$  ion in relation to its external environment.

In order to detect any relation between cationic mass, radii, and wave number, appropriate plots were made in Figures 3 and 4. Although first perusal suggests no relationships, careful examination shows possible



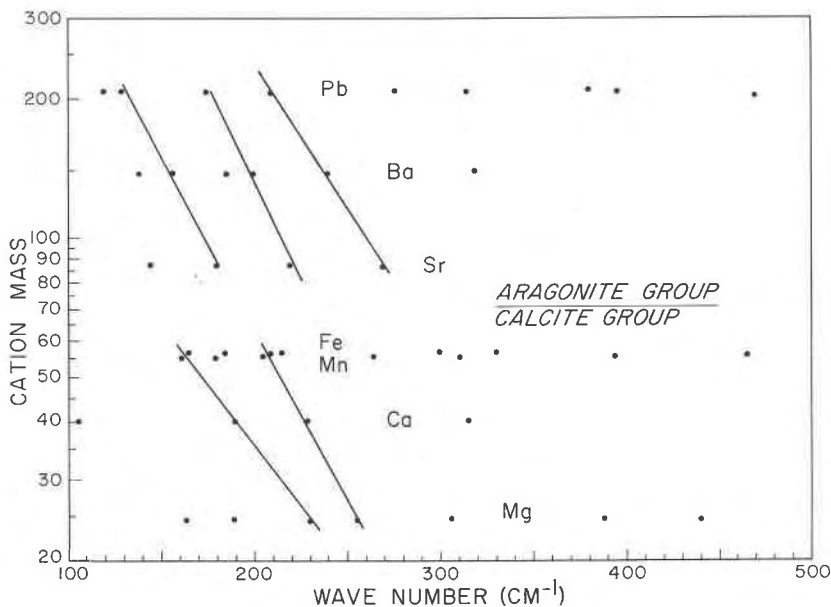


FIG. 3. Variation of some lattice vibration modes with change in cation mass. All peaks are shown, including sum and difference modes.

trends indicated by solid lines. The meaning of such trends is moot. However, if one excludes all points that are possibly the result of subtractive or additive combinations, the trend lines for both the cationic mass and radius plots are unaffected. Assuming that the trend lines do have some significance, then it is obvious that within each group (*i.e.*, calcite and aragonite) certain lattice vibration frequencies shift as either the cationic mass or radius increases.

In the calcite group the lattice vibration mode (Fig. 3) shifts with increasing mass from  $256\text{ cm}^{-1}$  in magnesite to 205 and  $208\text{ cm}^{-1}$  in  $\text{MnCO}_3$  and  $\text{FeCO}_3$  respectively. These are all strong bands. Similarly the  $230\text{ cm}^{-1}$  band in magnesite shifts to 162 and  $165\text{ cm}^{-1}$  respectively for  $\text{MnCO}_3$  and  $\text{FeCO}_3$ . The  $256\text{ cm}^{-1}$  band of  $\text{MgCO}_3$  may possibly be a subtractive combination ( $440 - 187 = 253$ ), but the weakness of the  $187\text{ cm}^{-1}$  band would seem to preclude this; none of the other bands can be accounted for on the basis of either additive or subtractive combinations.

For the aragonite group three possible trend lines are shown in Figure 3. All indicate a shift in lattice frequency with increasing mass of the metal ion. The subparallelism of the three lines strongly suggests that the bands involved are acting as a triplet and shifting in concert, inasmuch as the shift for each trend is essentially the same (*i.e.*,  $52 \pm 8\text{ cm}^{-1}$ ).

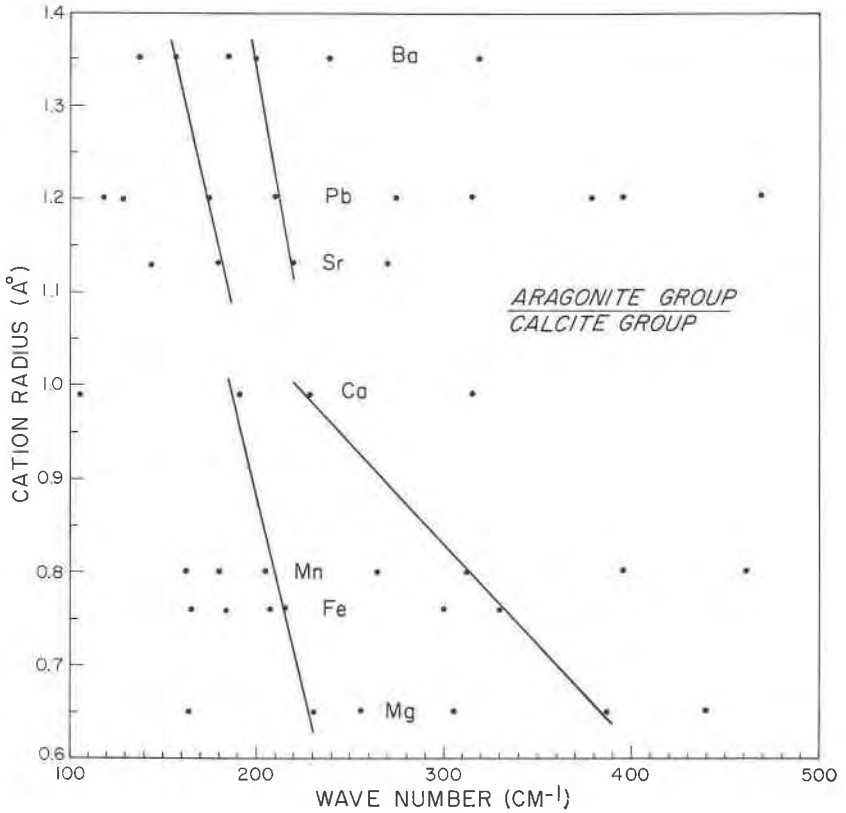


FIG. 4. Variation of some lattice vibration modes with change in cation radius. All peaks shown, including sum and difference modes.

Selected linear relations are also indicated by the plot of cationic radius *vs* wave number (Fig. 4). The strongest shift is in the calcite group where the 387  $\text{cm}^{-1}$  lattice mode in magnesite shifts to the 228  $\text{cm}^{-1}$  position in calcite. Again, none of the absorption bands involved are the result of subtractive or additive combinations. Clearly, frequency of selected lattice vibration modes decreases with increasing cation mass and radius for the minerals of both the aragonitic and calcitic groups.

Aragonite ( $\text{CaCO}_3$ ) and smithsonite ( $\text{ZnCO}_3$ ) were not available at the time this study was made. Nevertheless, if the cationic mass and radius trends observed are real, one can speculate on the possible positions of selected absorption bands in the far infrared spectra of these two minerals. For the cationic radius trend, absorption peaks should be observed at approximately 295 and 230  $\text{cm}^{-1}$  for aragonite and at about 340 and 220

$\text{cm}^{-1}$  for smithsonite. On the basis of a mass relation, then aragonite peaks should occur at 325 and 230  $\text{cm}^{-1}$  (near calcite) and at 260  $\text{cm}^{-1}$ . Smithsonite peaks at 200 and 150  $\text{cm}^{-1}$  are indicated.

#### CONCLUSIONS

(1) Several well-resolved major and minor absorption bands are present in the far infrared spectra of carbonate minerals of the aragonitic and calcitic groups.

(2) The major absorption bands are probably diagnostic for the respective carbonates.

(3) There is a linear relation between band shifts and the atomic radius or mass of the cations contained in the isomorphous groups.

(4) The effects attributable to cation substitution are not unambiguously demonstrated.

These suggestions are offered as plausible speculations, to indicate areas for future research. Most assuredly they are not final answers.

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