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INFRARED ABSORPTION FREQUENCY TRENDS FOR ANHYDROUS NORMAL CARBONATES

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ABSTRACT

Empirical studies of infrared absorption spectra of isomorphous anhydrous carbonate minerals indicate that shifts in the frequencies of carbonate-ion vibrations are primarily related to differences in the radius of cations in the external lattice positions. This relationship may be conditioned by the electronic periodicity of the cations. Mass effects are suggested but are not unequivocally demonstrated. Spectral differences among the calcite-group and aragonite-group minerals are interpreted in terms of the coordination change between the two groups and the mineral composition within each group.

INTRODUCTION

A considerable amount of effort has been devoted to the study of calcite, with emphasis on relating infrared absorption bands to various vibrational motions and orientation of the carbonate ion and on acquiring fundamental data on the origin of the fine structure of the spectrum. Relatively little attention, on the other hand, has been given to the relation between the absorption frequency and the chemical and structural environment of the carbonate ion.

Among previous spectral studies outlining general trends, Hunt *et al.* (1950) have observed an approximately linear relationship between the mass of the metallic ion and the wavelength of the 11-micron absorption band when plotted on semi-log paper, indicating a shift of the vibration to lower frequencies with increasing atomic weight of the cation. No reference, however, was made to similar relationships for the other carbonate bands. From independent analyses Adler *et al.* (1950) observed a gradual decrease in vibration frequency of the CO_3^{2-} ion with increasing lattice constant that was attributed primarily to changes in cation radius. A mass effect of the cation was also suggested. More recently, Huang and Kerr (1960) and Weir and Lippincott (1961) reported similar observations. Because correlations of this type are rather limited in scope, further examination of carbonate minerals was undertaken to gain additional insight into the nature and extent of changes in vibration frequency with mineral composition.

The present study is concerned primarily with changes in the infrared spectra of calcite-group and aragonite-group minerals related to radius and mass variations and the periodic grouping of the external cations.

EXPERIMENTAL METHOD

The mineral samples used in this study were obtained from the collections of the U. S. National Museum in Washington, D. C. The identity of each specimen was verified by *x*-ray diffraction analysis.

Infrared spectra were obtained with a Perkin-Elmer recording infrared spectrophotometer, Model 21, using sodium chloride optics. Samples were prepared from approximately 0.85 mg of -300-mesh powder mixed with 300 grams of KBr and pressed under vacuum at 20,000 psi in a tool-steel die having an inner diameter of one-half inch. A blank KBr disc, similarly prepared, was placed in the reference beam to compensate for energy loss resulting from KBr in the sample beam, which, otherwise, precludes full-scale use of the instrument. A scanning rate of about 0.65 microns per minute was employed.

The authors are indebted to Dr. Irving A. Breger and the U. S. Geological Survey for the use of the spectrophotometer.

SPECTRAL FEATURES AND COORDINATION EFFECTS

With few exceptions, the absorption maxima recorded in recent surveys of anhydrous normal carbonate minerals by Adler *et al.* (1950), Hunt *et al.* (1950), Keller *et al.* (1952) and Huang and Kerr (1960) are in fairly good agreement. Only in the case of aragonite have there been any major differences in spectral assignments; these are restricted largely to the 11-micron region and have been resolved in an earlier study (Adler and Kerr, 1962).

Representative infrared curves of the hexagonal calcite-group and orthorhombic aragonite-group carbonates are shown in Figs. 1 and 2, respectively. Vertical reference lines are drawn to accentuate relative band positions. Wavelength data for the v_2, v_3 and v_4 modes, obtained on several specimens of each mineral, are presented in Table 1.

Typical spectra of calcite-group carbonates include three major absorption bands between 2 and 15 microns, each of which may be identified with a particular deformational mode of the CO_3^{2-} ion as depicted by Bhagavantam and Venkatarayudu (1939), and Herzberg (1945, p. 179). These bands have been related to an out-of-plane bending (v_2), an asymmetric stretching (v_3), and a planar bending (v_4) of the carbonate radical. A symmetric stretching mode (v_1) is also characteristic of the carbonate ion but does not ordinarily give rise to absorption in spectra of calcite-group minerals.

According to Halford (1946) owing to a symmetry difference in the mineral groups, two maxima should appear in the spectrum of aragonite for both v_3 ($\sim 7\ \mu$) and v_4 ($\sim 14\ \mu$) provided that sufficient resolution is

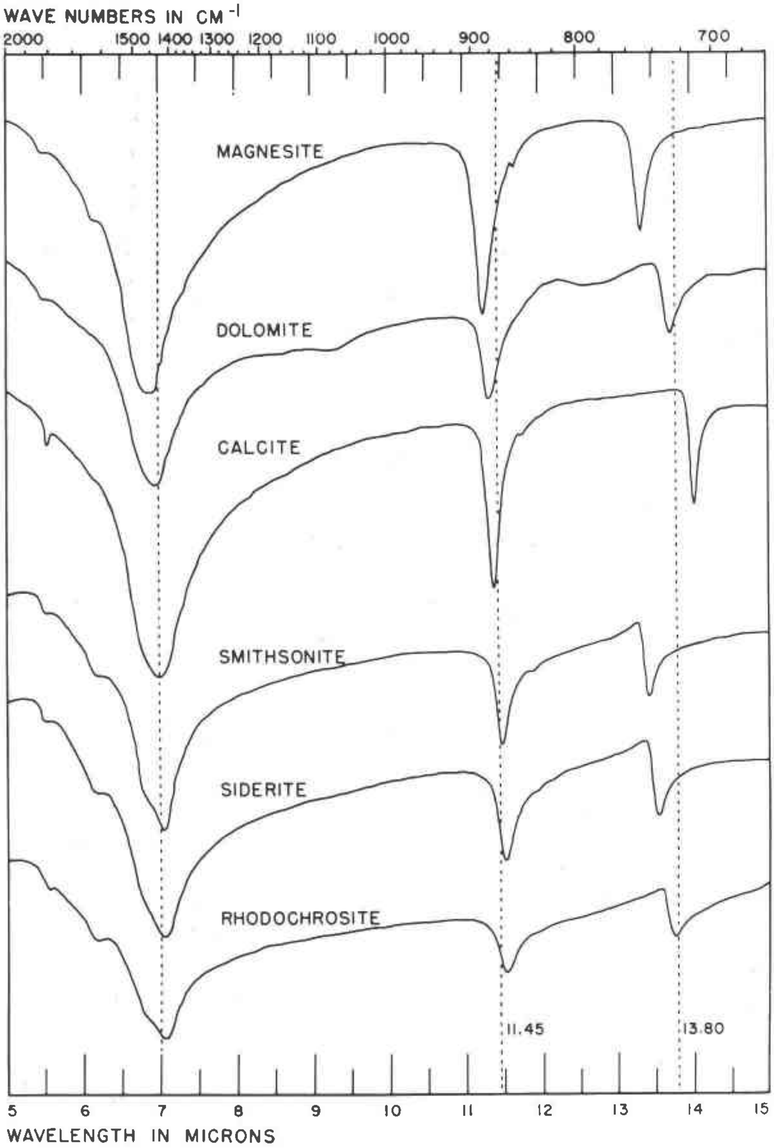


FIG. 1. Infrared spectra of calcite-group minerals. Magnesite (USNM-63842), dolomite (USNM-R2408), calcite (USNM-106158), smithsonite (USNM-R2502), siderite (USNM-82246), rhodochrosite (USNM-113017).

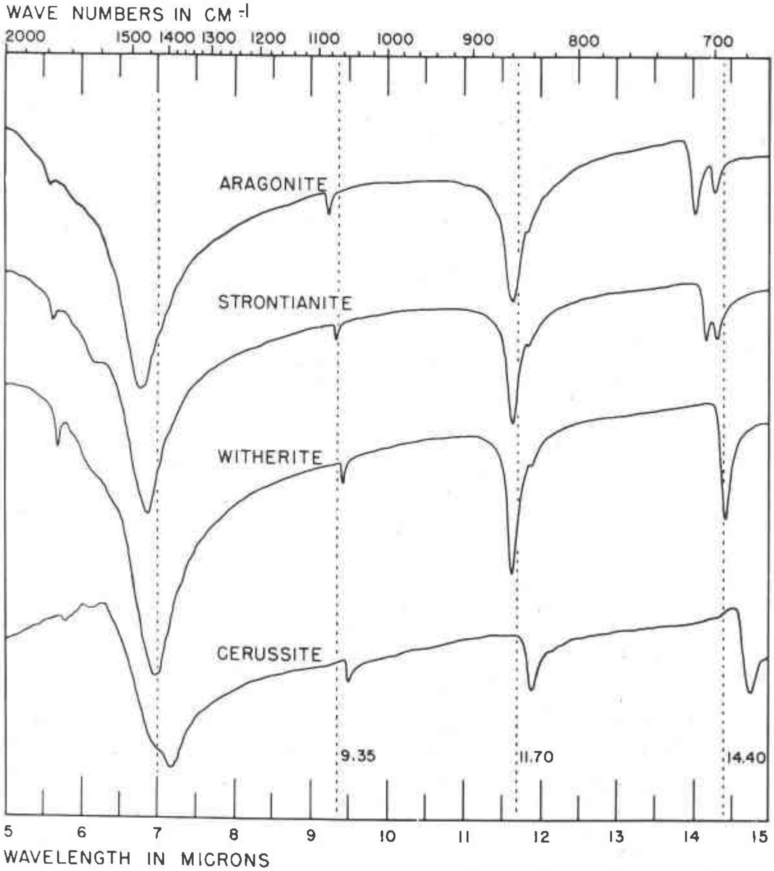


FIG. 2. Infrared spectra of aragonite-group minerals. Aragonite (USNM-R12050), strontianite (USNM-R10065), witherite (USNM-R2560), cerussite (USNM-C2130).

achieved to reveal the splitting. However, resolution of only the v_4 doublet is readily obtained. The split appears in strontianite and aragonite spectra but has not been observed for witherite or cerussite.

Because the vibration frequencies corresponding to the major absorption bands at approximately 7, 11 and 13 microns are primarily related to the vibration energies of the CO_3^{2-} ion, which has a more or less fixed structural configuration, it would seem that only minor differences in spectral absorption frequency might be produced by changes in the environment of that ion. Restricting our consideration to the anhydrous normal carbonates, it is apparent from inspection of Fig. 1 that there are significant differences between the spectra of the dimorphous forms of $CaCO_3$, calcite and aragonite, as well as among the minerals which con-

TABLE 1. INFRARED ABSORPTION BANDS OF CALCITE-GROUP AND ARAGONITE-GROUP MINERALS

Mineral	Locality	Wavelength (microns)			
		v_3	v_2	v_4	
Calcite-group:					
Magnesite	Tulare Co., Calif.[1]	6.86	11.28	13.35	
Magnesite	Oberdorf, Austria	6.94	11.29	13.35	
Dolomite	Guanajuato, Mexico[1]	6.95	11.35	13.72	
Dolomite	Boda, Norway	6.97	11.35	13.71	
Calcite	New Mexico[1]	7.02	11.40	14.02	
Calcite	Eureka, Utah	7.05	11.41	14.03	
Smithsonite	Broken Hill, N. S. Wales[1]	7.04	11.48	13.42	
Smithsonite	Cumberland, England	7.06	11.50	13.45	
Siderite	Braundord, Germany[1]	7.06	11.53	13.54	
Siderite	Eiserfeld, Germany	7.08	11.55	13.58	
Rhodochrosite	Butte, Montana[1]	7.07	11.54	13.75	
Rhodochrosite	Kuratuni, Japan	7.09	11.55	13.77	
Aragonite-group:					
Aragonite	Horschenz, Bohemia[1]	6.80	11.65	14.02	14.31
Aragonite	Guanajuato, Mexico	6.79	11.64	14.04	14.31
Strontianite	Oberdorf, Austria[1]	6.88	11.65	14.16	14.31
Strontianite	Westphalia, Germany	6.86	11.65	14.14	14.29
Witherite	Cumberland, England[1]	6.97	11.63	14.41	
Witherite	Lancashire, England	6.99	11.62	14.41	
Cerussite	Lone Elm, Mo.[1]	7.17	11.90	14.75	
Cerussite	Sardinia, Italy	7.18	11.92	14.75	

[1] Infrared spectra are shown in Figs. 1 and 2.

stitute the calcite and aragonite groups. These differences may be partially attributed to a modification in lattice structure, which involves primarily a change in the coordination of the metal ion from 6-fold (in calcite) to 9-fold (in aragonite) as well as a concomitant change in lattice symmetry. The transition is accompanied by the appearance of an additional band (v_1) and splitting of the v_4 mode in the spectrum of aragonite as well as by a shift in the wavelength position of absorption bands common to both minerals. However, spectral variations within each group cannot be explained on this basis since the intra-group coordination remains constant.

Comparison of the data in Table 1 for aragonite and calcite shows that the transition from calcite to aragonite apparently shifts the wavelength of v_2 and v_3 whereas, except for the splitting, v_4 remains essentially unchanged. The observed changes involve displacement of the out-of-plane bending mode, v_2, to a lower frequency (longer wavelength) while the stretching mode, v_3, is shifted to a higher frequency (shorter wavelength). The high-frequency band of the v_4 pair shows no deviation from the v_4 absorption position for calcite.

From structural evidence it would appear that alteration of the electrostatic valency of the Ca—O bond as a result of the coordination change is instrumental in producing a displacement of the CO_3^{2-} vibrations by virtue of a change in the environment of the oxygen atom. The electrostatic valency of the C—O bonds is constant for aragonite and calcite, but the manner of binding of oxygen atoms to the rest of the structure differs, and, thereby, provides a basis for spectral change.

Density determinations on aragonite and calcite may be construed as reflecting a closer approach between adjacent oxygen atoms of neighboring carbonate groups in the more dense aragonite lattice, thus presaging a shortening of the C—O distance and a concomitant increase in the frequency of all vibrations of the carbonate ion. The spectral data, however, do not completely support this hypothesis, as only v_3 increases in frequency. Therefore, it must be supposed that a change in the orientation of the calcium ions about oxygen causes modification of these vibrations through a change in Ca—O bond directions and strength.

From information provided by this study it is apparent that a variation in the physical parameters of the external lattice ions can modify the internal vibrations, and it is not surprising, therefore, that the change in coordination about oxygen from 2-fold in calcite to 3-fold in aragonite would also produce considerable changes.

In addition to the aforementioned frequency changes, the v_1 fundamental, which is infrared inactive for calcite, appears to be activated by the structural transition to aragonite. The absorption in the 9-micron region observed for minerals of the aragonite group coincides approximately with frequency values for the v_1 mode given by Herzberg (1945) and Bhagavantam and Venkatarayudu (1939). If the interpretation of the assignment is correct, the appearance of this mode is of considerable interest because it suggests a distortion in the symmetry of the internal oscillation which may reflect asymmetry in the carbonate ion.

INTRA-GROUP SPECTRAL VARIATIONS

Because the vibration frequency of a given molecular structure, such as the CO_3^{2-} ion, is dependent on the reduced mass (u) of the participating atoms and the restoring forces (k) between these atoms, the relationship invoked by Barnes *et al.* (1944), namely,

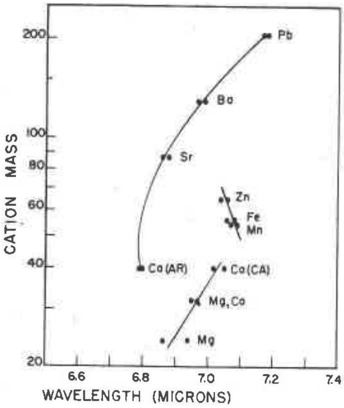
$$v = \frac{1}{2\pi c}\sqrt{\frac{k}{u}} \tag{1}$$

should have a bearing on the differences observed in carbonate spectra involving fundamental modes of this ion. If, in addition, the equation by Badger (1934), namely,

$$k_0 = 1.86 \times 10^5/(R - d_{ij})^3, \qquad (2)$$

expressing the relationship between force constant (k_0) and interatomic distance (R), is applied a correlation between interatomic distance and vibration frequency is obtained in which all other terms are constant for a given atomic group. It apparently follows, therefore, that the vibration frequency is inversely dependent on the interatomic distance between vibrating atoms in the carbonate radical.

These relationships cannot be applied directly in the analysis of cationic substitution effects on the CO_3^{2-} vibration inasmuch as only parameters of the carbon and oxygen atoms are involved. Nevertheless, any change in mineral structure that involves a change in R should modify the molecular vibration frequencies. Empirical evidence that internal vibrations are not completely independent of influence of the rest of the mineral structure exists in the spectra obtained by Adler *et al.* (1950) and Huang and Kerr (1960), which show considerable variations in the absorption patterns of anhydrous and hydrous carbonates that are undoubtedly related to structural and compositional differences. Because these differences are manifest only in the extra-molecular lattice components, and in some cases produce no apparent coordination or symmetry change, it may be inferred that the vibration modes of the carbonate ion are indeed sensitive to various types of ex-



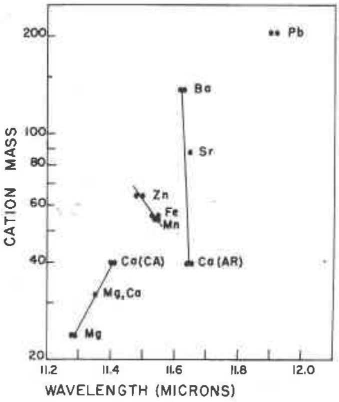


FIG. 3 (left). Variation of the v_3 carbonate vibration with change in cation mass.
FIG. 4 (right). Variation of the v_2 carbonate vibration with change in cation mass.

ternal influence. It is also evident that R would be modified in the adjustment of the carbonate ion to its external environment.

The relationship between the mass of the extra-molecular ions and the vibration of the molecule is an unknown entity for which there exists little empirical evidence. That which has been presented (Hunt *et al.*, 1950, and Weir and Lippincott, 1961) is essentially conflicting. It has been mentioned that Hunt *et al.* (1950) interpreted their data on the 11-micron absorption of carbonates as indicative of an apparent shift of the v_2 fundamental toward longer wavelengths with increasing cationic mass. However, it is apparent from inspection of Fig. 4 that this wavelength-cation-mass trend exists only for the dolomite series, as the observed shift with increasing mass for rhodochrosite, siderite and smithsonite is to shorter wavelengths. Similar trends for the calcite-group carbonates are also observed for v_3 and v_4 (Figs. 3 and 5).

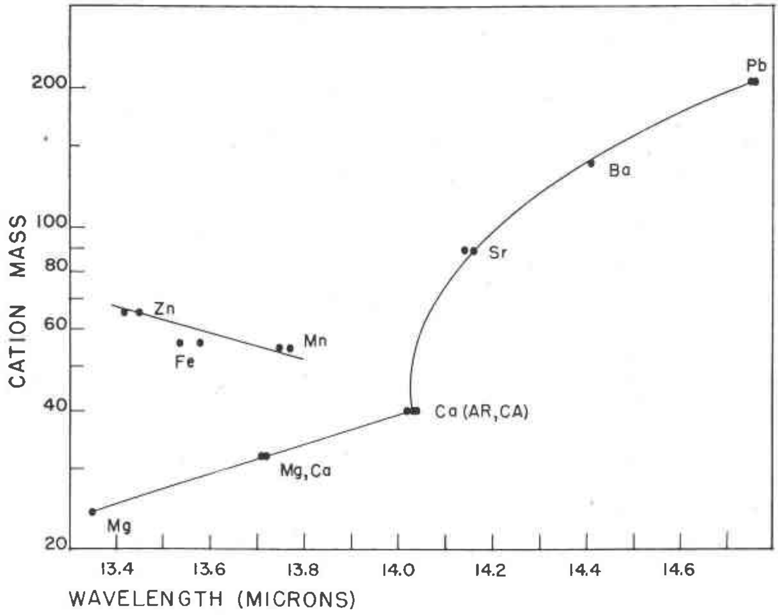


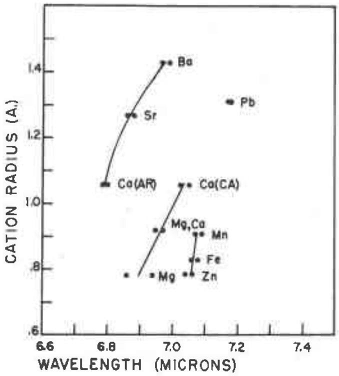
FIG. 5. Variation of the v_4 carbonate vibration with change in cation mass.

With respect to the aragonite group, the effect on v_2 of increasing mass is seemingly negligible except ostensibly in the case of cerussite which shows marked displacement of v_2 to a longer wavelength. The curves for v_3 and v_4, on the other hand, show a curvilinear relationship.

From comparison of Figs. 3, 4 and 5 it is apparent that, with the exception of the 11-micron aragonite-group absorption, the wavelength-cation mass plots are similar for the three fundamental bands of the calcite-group and aragonite-group minerals; however, the trends are by no means unidirectional. The anomalous position of the Mn, Fe and Zn carbonates is of particular interest and will be discussed subsequently.

Figures 6 to 8 show the wavelength-ionic radius dependence of calcite and aragonite minerals. For all three absorption bands, excepting again the 11-micron band of the aragonite group, there is a decrease in wavelength with decreasing ionic radius. Data based on comparison of lattice constants with absorption wavelengths yield similar trends.

It should be noted that, to conform to observed lattice constant differences between their carbonates, the ionic radius of zinc is taken as slightly less than that of iron although published data (Evans, 1948, p. 171) indicate them to be identical. This selection is not arbitrary inasmuch as it is desirable for spectroscopic considerations to utilize empirical radii which approximately reflect the lattice constants.



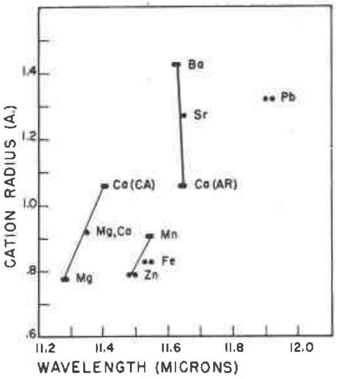


FIG. 6 (left). Variation of the v_3 carbonate vibration with change in cation radius.
FIG. 7 (right). Variation of the v_2 carbonate vibration with change in cation radius.

With the exception of cerussite, the aragonite-group minerals yield linear wavelength-radius trends. The irregular displacement of cerussite bands to longer wavelengths will be discussed subsequently.

The consistent straight-line relationship observed for the dolomite series is of particular interest with respect to predicting the effects on absorption frequency of ionic substitution in a solid-solution series. In the dolomite structure, substitution of Ca for Mg is ordered in such a manner that each cation is situated in alternate layers between carbonate ions, and each radical is bonded to an equal number of Ca and Mg ions. This structure provides for a uniform, though asymmetrical, field of influence about all the carbonate ions. The apparent effect on the CO_3^{2-} vibrations is such that all three bands are found at wavelengths that are approximately the average of the corresponding values for calcite and magnesite.

The near parallelism of wavelength-ionic radius trends observed for v_2, v_3 and v_4 for both the dolomite-series minerals and the Mn, Fe and Zn carbonates suggests a similarity in response among these calcite-group carbonates to changes in ionic radius. A mass effect may be inferred from the plotted data. In the sequence Mn-Fe-Zn, mass increases whereas radius decreases. The radius effect is one of increasing the vibration frequency from Mn→Fe→Zn, whereas the mass increase may ordinarily be considered to produce the opposite effect. For the dolomite series and aragonite group any mass effect would presumably reinforce the vibration-frequency shift caused by a change in ionic radius and would, therefore, be masked by the radius effect. However, for the series Mn-Fe-Zn the two effects would produce opposing trends (Fig. 11). In Figs. 3 to 8 unidirectional trends for the three intercepts are obtained from the ionic radius-vibration frequency plots, whereas mass-frequency trends are not unidirectional. Although the radius effect is predominant as illustrated in Fig. 11, one may interpret as a mass effect the displacement of the Mn-Fe-Zn-carbonate intercept to longer wavelengths, as noted in Figs. 6 to 8, so that it parallels rather than coincides with the calcite-dolomite-magnesite intercept.

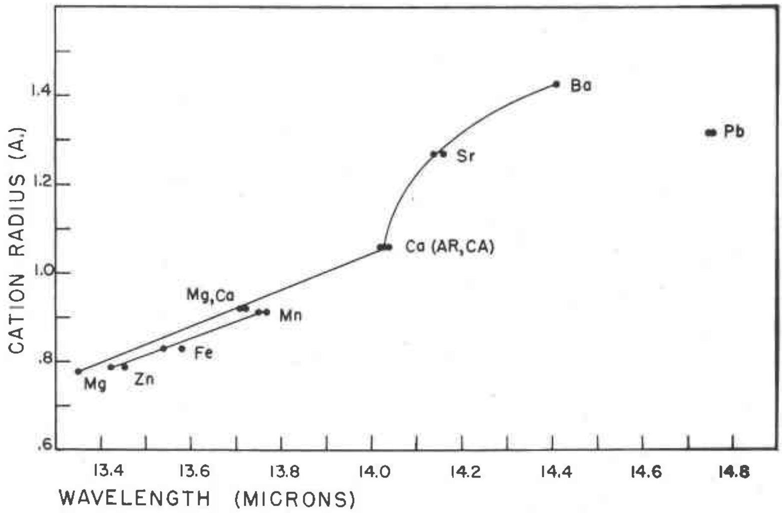
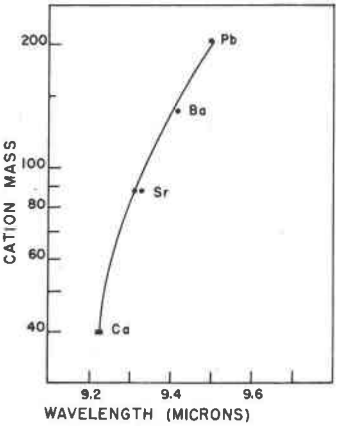


FIG. 8. Variation of the v_4 carbonate vibration with change in cation radius.

With regard to the 9-micron band, which obviously corresponds to the v_1 mode, it is evident from Figs. 9 and 10 and from the data in Table



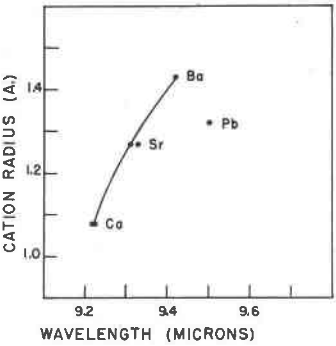


FIG. 9 (left). Variation of the v_1 carbonate vibration with change in cation mass.
FIG. 10 (right). Variation of the v_1 carbonate vibration with change in cation radius.

2 that changes in the wavelength of this band are in agreement with the trends observed for the v_3 and v_4 modes.

The foregoing relations are more or less consistent with the interpretation advanced by Weir and Lippincott (1961), namely, that increased repulsion between neighboring oxygen atoms caused by a constriction of the lattice with introduction of smaller metallic ions should be reflected in a corresponding shortening of the C—O bond and an increase in the frequencies of vibration of the carbonate ion. Although

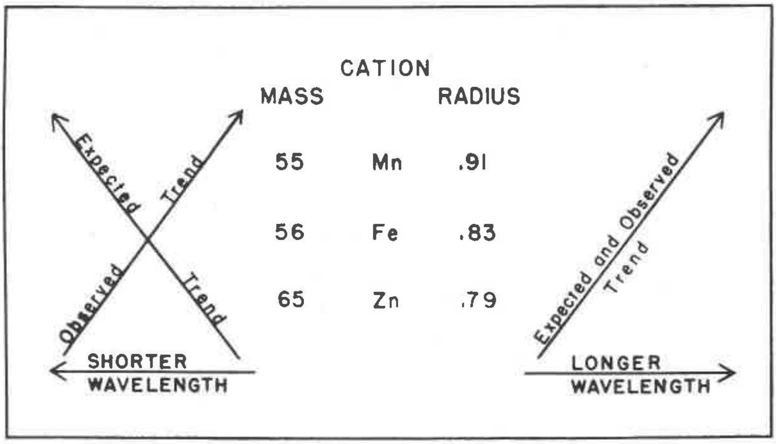


FIG. 11. Effects of cation mass and radius on Mn-, Fe- and Zn-carbonate absorptions.

these authors dismiss the probability of a mass effect, the data presented here indicate that any effect of cation-mass change may be masked to a large degree by the effect of cation-radius change; hence, a correlation between mass and absorption wavelength (or frequency) is not ordinarily apparent. Furthermore, contrary to their findings which indicate that there is little change in spectral frequency with transition from aragonite to calcite, significant variations have been noted in this study which may be related to differences in geometrical distribution of the calcium ions about the molecular oxygen atoms.

Although the present data suggest that atomic mass may affect the vibration frequency, a closer examination of the problem indicates that a direct comparison between the various cations involved is not valid because of differences in electronic structure. In this respect, a study of other properties dependent on the structure of the outer electrons of the atoms and which show periodicity is revealing. For example, the ionization potentials of Mg, Ca, Sr and Ba, which are a measure of the polarizing force of the ions, vary systematically whereas those of Fe, Mn and Zn do not conform to this series. Thus, Mg may be compared with Ca because of a similarity in electronic configuration, but Ca cannot be compared with Fe, Mn or Zn. Marked differences in the ionization potentials are related to the fact that all of the alkaline earth elements contain octets of electrons in s and p orbitals whereas Fe and Mn have incomplete d orbitals, and Zn has a complete M shell. Because ionic dimension is also a function of electronic structure a valid correlation of this property may be made only for those elements which exhibit a repetition of the configurations of the outer electrons. Comparisons between elements having similar ionic radii but belonging to different Periodic Groups should, therefore, be avoided.

TABLE 2. INFRARED WAVELENGTHS CORRESPONDING TO THE V_1 VIBRATION MODE

Mineral	Locality	Wavelength (microns)
Aragonite	Horschenz, Bohemia	9.22
Aragonite	Guanajuato, Mexico	9.23
Strontianite	Oberdorf, Austria	9.33
Strontianite	Westphalia, Germany	9.31
Witherite	Cumberland, England	9.42
Witherite	Lancashire, England	9.42
Creussite	Lone Elm, Mo.	9.50
Cerussite	Sardinia, Italy	9.50

It is probable that real systematic trends for ionic-radius and vibration-frequency phenomena will be obtained only for elements which exhibit periodicity in electronic structure. This assumption may lead to a better understanding of the factors governing changes in absorption spectra.

On re-examinating the spectral data from this standpoint we may conclude that the trend lines are valid only between points representing Ca, Sr and Ba in the aragonite group and Mg and Ca in the calcite group. Whether a join can be drawn between Mn and Fe is problematic inasmuch as it remains to be demonstrated whether frequency changes will vary in an ordered manner with the filling of the 3d orbital of the transition elements. The Mn, Fe and Zn plots should, therefore, be read independently. Under this circumstance, the position of the Mn-Fe-Zn join should not be interpreted as supporting the existence of a mass effect. Similarly, one would not expect the Pb plot to coincide with the Ca-Sr-Ba intercept or to be related to the mass of the atoms. The anomalous position of the Pb plot is probably attributable to the electronic configuration of lead which differs markedly from that of the alkaline earth group elements. Weir and Lippincott (1961) have interpreted the anomalous positions of the $PbCO_3$ bands to be caused by the greater covalency of the Pb—O bonds. However, if we accept the ionization potentials of ultimate electrons as a measure of the polarizing force, then a comparison of the ionization potentials of Mg, Pb and Ca and the vibration frequencies of the respective carbonates of these elements would lead one to expect an increase in the vibration frequency of $PbCO_3$ with respect to aragonite. This is obviously not the case. However, ionization potentials of elements of different periodic groups are not strictly comparable, and, therefore, no prediction can be made as to the differential effects of the electronic structures of lead and the alkaline earths on the vibration spectra of their compounds.

The data obtained in this study indicate that: (1) differences in coordination between the carbonate ion and the external cations produce a measurable change in the frequencies of the internal vibrations; (2) the frequencies of the various vibration modes of the carbonate ion are sensitive to cationic substitution; (3) frequency changes may be correlated with variation in the ionic radius of the extra-molecular cation but this relation may be dependent on the electronic periodicity of the elements; (4) in accordance with the interpretation advanced by Weir and Lippincott (1961), variations in the C—O distance within the carbonate ion should be expected, the bond length increasing as the molecular vibration frequency decreases; (5) when two different cations are present, such as in dolomite, the frequency modifications caused by cation-radius differences may be averaged, provided that all carbonate ions have identical environments; (6) mass effects attributable to extra-molecular cations may exist but are not unambiguously demonstrated.

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