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INFRARED STUDY OF ARAGONITE AND CALCITE

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ABSTRACT

The fundamental vibration spectra of aragonite and calcite in the 2- to 15-μ region of the infrared have been described in previous investigations. Recently run curves, however, cast doubt on the assignment of absorption bands in the 11- to 12-μ range. Investigation of the spectra of some 20 mineral specimens indicates that the band at 11.65 μ is specific for aragonite wheras the band at 11.41 μ is caused by calcite. Five of the specimens studied yield spectra with both bands, suggesting that natural aggregation of the two minerals is a rather common occurrence.

In artificial mixtures, the intensity ratio of the bands at 11.41 and 11.65 μ is found to be approximately proportional to the ratio of concentration of aragonite and calcite in a given sample. However, considering the range in absorption intensity inherent in different specimens, the method as now applied yields at best semiquantitative data accurate to within 10 percent (absolute) of the mineral content in the specimen. Spectrograms obtained on recent and fossil invertebrates suggest application of the method to the study of the composition of calcareous shells.

INTRODUCTION

The fundamental infrared vibration spectra of carbonate minerals and compounds in general have been studied by numerous investigators for correlation of theoretical and empirical frequency data and for purposes of identification. Absorption characteristics were described initially by Morse (1907), and subsequent determinations of normal vibration modes were made by Schaefer and Schubert (1916), Schaefer, Bormuth and Matossi (1926), and Menzies (1931). Surveys of infrared spectra of various species including aragonite and calcite can be found in more recent papers of Adler *et al.* (1950), Hunt, Wisherd and Bonham (1950), Keller, Spotts and Biggs (1952), Miller and Wilkins (1952), and Huang and Kerr (1960).

The major absorption bands of carbonate spectra in the 2- to 15-μ wavelength region have been attributed to the fundamental vibrations of the carbonate radical, CO_3^{2-}, and various bands have been assigned to correspond to the vibrations of the carbon and oxygen atoms along crystallographic axial directions.

Theoretically, the number of atoms (N) which participate in vibrations within a radical should govern the number of permissible normal modes of vibration. In the CO_3^{2-} group, after consideration of the possible degrees of freedom of the atoms and the radical itself, these are restricted to 3N-6 or 6 modes. Fewer than the expected number of frequencies are generally observed in the calcite group because of the double degeneracy of two of the six frequencies, thus limiting to four the number of fundamental absorption bands characteristic of these minerals. The frequencies correspond, according to assignments reported by Herzberg (1945, p. 178), to a symmetric stretching, v_1; an out-of-plane bending, v_2; a doubly degenerate asymmetric stretching, v_3; and a doubly degenerate planar bending, v_4. The relative motions of the carbon and oxygen atoms for the internal modes of the CO_3^{2-} radical are depicted by Bhagavantam and Venkatarayudu (1939). The symmetric oscillation represented by v_1 is reported to be infrared inactive, hence only three fundamentals are ordinarily encountered. These have been recorded for various calcite-group minerals in the regions of absorption at approximately 7 $\mu(v_3)$, 11–12 $\mu(v_2)$ and 13–15 $\mu(v_4)$.

According to Halford (1946), six radical frequencies are permitted in carbonates of the aragonite group owing to removal of the degeneracies prevalent in v_3 and v_4 in the calcite group; however, the additional bands are found only if the splitting can be resolved. Splitting of v_4 is observed in aragonite and strontianite, but the band has not been resolved in witherite and cerussite spectra.

Further study of aragonite and calcite in the infrared wavelength region was prompted by differences in the data on aragonite reported by Hunt, Wisherd and Bonham (1950) and Huang and Kerr (1960). Several of the aragonite spectra which they obtained show two absorption bands in the 11-μ region whereas only a single band appears in other aragonite spectrograms. Since the v_2 mode is not degenerate, the doublet observed cannot result from splitting and another explanation for its appearance has been sought.

Data obtained in this investigation indicate the true nature of the 11-μ doublet. In addition, the application of infrared spectroscopy to the semiquantitative determination of aragonite and calcite in natural intergrowth of the two minerals is demonstrated.

ACKNOWLEDGMENTS

The samples analyzed were obtained from several sources. Most of the mineral specimens were generously donated by Dr. George Switzer of the National Museum, Washington, D. C. The Livermore and Alameda County samples are identical to those previously analyzed by Huang and Kerr (1960) and are from the mineral collections of Columbia University. Samples of calcareous shells were contributed by Norman F. Sohl of the U. S. Geological Survey.

The assistance of numerous personnel of the Analytical Laboratory of the U. S. Geological Survey, Washington, D. C., in providing equipment and supplies for this study is gratefully acknowledged. We are particularly indebted to Dr. Irving Breger for making available the infrared spectrophotometer.

EXPERIMENTAL PROCEDURE

Samples were prepared for infrared analysis by the potassium bromide pressed-pellet technique. All sample material was ground to pass a 325-mesh screen. Approximately 0.85 mg of sample powder was mixed and reground with about 300 mg of reagent-grade potassium bromide and the mixture pressed in a tool-steel die at roughly 16,000 psi. The pellets, which measure approximately 12 mm in diameter and 0.4 mm in thickness, yield well-resolved absorption spectra. The ease of preparing samples in this manner facilitates the use of the infrared method for both qualitative and semiquantitative analyses.

The spectra were obtained with a Perkin-Elmer recording infrared spectrophotometer Model 21 using sodium chloride optics. To reduce the effects of water in KBr in the spectra and to increase relative transmissivity in the sample beam, a pure KBr pellet is placed in the reference beam of the instrument.

All curves have been calibrated against a reference standard of polyethylene. Accuracy of wavelength measurement is generally dependent on the width of absorption peaks. Where the bands are fairly sharp, a precision of 0.01 μ is obtainable; however, in many cases, it is difficult to estimate band position closer than $\pm 0.02\ \mu$.

The complete spectrograms of aragonite and calcite obtained in the 2- to 15-μ region on samples pressed in KBr are shown in Fig. 1. Absorption bands caused by water in KBr and possibly CO_2 are marked with an asterisk. Similar experimental procedures were maintained for both qualitative and semiquantitative analyses.

QUALITATIVE EXPERIMENTAL OBSERVATIONS

In attempting to reconcile differences in the infrared absorption measurements of aragonite obtained in earlier investigations (Adler *et al.*, 1950; Hunt *et al.*, 1950; Keller *et al.*, 1952; and Huang and Kerr 1960), it has been found necessary to re-examine the spectra of aragonite and its dimorph calcite. Absorption maxima reported in earlier investigations of aragonite and calcite are listed in Table 1. Major differences in these spectra appear in the 11-μ region where both single and double bands have been reported. Since the shorter wavelength band recorded for some aragonites (11.40 to 11.42 μ) coincides with the non-degenerate v_2 fundamental of calcite, it was believed that this band might be caused by calcite rather than aragonite. This suspicion was strengthened by the observed broadening in the suspect spectra of the dense 7-μ

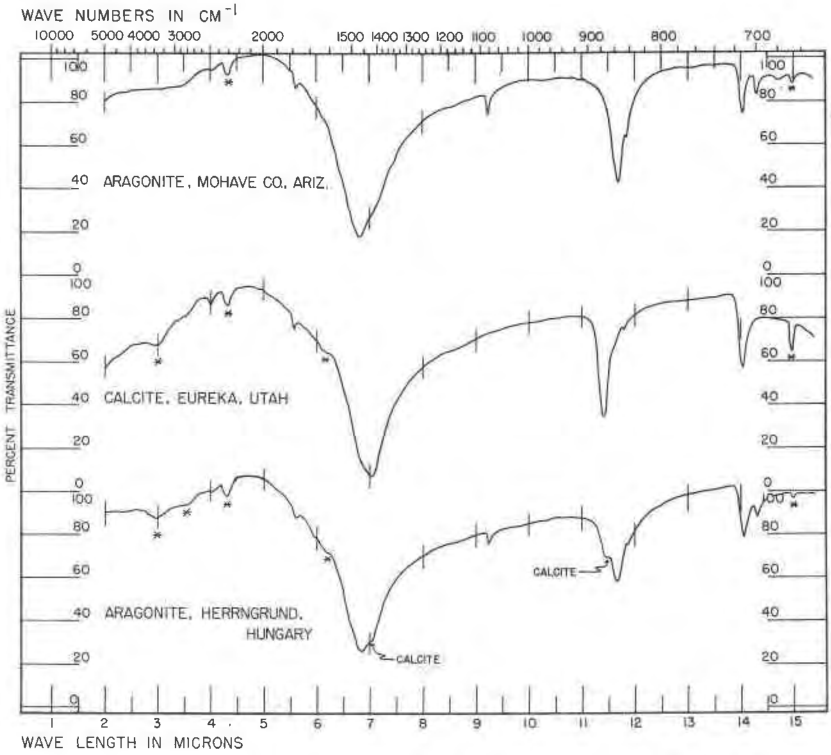

FIG. 1. Spectra of aragonite and calcite pressed in KBr.

band of aragonite to include the calcite absorption position. These observations prompted further investigation of the absorption spectrum of both substances.

The major features of the spectra of four aragonite (curves 1, 2, 3 and 4) and two calcite specimens (curves 9 and 10) are shown in Fig. 2. The spectra of four other samples (curves 5, 6, 7 and 8), identified as aragonite by their museum labels but apparently containing intergrown calcite, are also shown.

Table 2 gives the positions of the absorption bands found in this study for various specimens of aragonite and calcite. The spectra of aragonite (Figs. 1, 2 and 3) are characterized by strong absorptions at approximately 6.80 μ, 11.65 μ, 14.04 μ and 14.30 μ, which correspond to the fundamental vibrations of the CO_3^{2-} radical. Bands of lesser intensity appear at 4.02 μ, 5.61 μ, 9.23 μ and 11.84 μ. The 14.30-μ band, which is prevalent in the spectra of aragonite but absent in calcite, is probably caused by a splitting of the v_4 fundamental of the carbonate radical

TABLE 1. SPECTRAL POSITIONS OF INFRARED ABSORPTION BANDS OF ARAGONITE AND CALCITE RECORDED IN PREVIOUS INVESTIGATIONS

Wave-length Region, Microns	Aragonite 1	Aragonite 2	Aragonite 3	Aragonite 4	Calcite 1	Calcite 2	Calcite 3	Calcite 4
4		4.02		3.93–3.95		4.02		3.92–3.93
5		5.58		5.53–5.55		5.58		5.50–5.52
6–7	6.8	6.95	6.66	6.70–7.00	7.0	6.95	6.8–7.0	6.97
9				9.22				
11		11.40		11.40–11.42	11.45	11.40	11.33–11.43	11.40–11.42
	11.60	11.65	11.64	11.63		11.80		
14	14.05	14.02	14.12	14.03	14.05	14.02	14.05	14.02–14.03
	14.30	14.30	14.41	14.30				

1. Adler *et al.* (1950).
2. Hunt *et al.* (1950).
3. Keller *et al.* (1952).
4. Huang and Kerr (1960).

which is doubly degenerate in aragonite. Absorptions of the split mode have been reported at 711 cm^{-1} (14.06 μ) and 706 cm^{-1} (14.16 μ) by Bhagavantam and Venkatarayudu (1939) and at 14.06 μ and 14.17 μ

TABLE 2. POSITION OF ABSORPTION BANDS OBSERVED IN THIS STUDY

Locality	4μ	5μ	ν_3	ν_3	9μ	ν_2	ν_2	11μ	ν_4	ν_4
Aragonite										
Mohave Co., Ariz.	4.01	5.61	6.81	—	9.23	—	11.70	11.85	14.04	14.31
Guanajuato, Mexico	4.02	5.61	6.79	—	9.23	—	11.64	11.83	14.04	14.31
Girgenti, Sicily	4.03	5.60	6.80	—	9.23	—	11.64	11.83	14.04	14.30
Leadville, Colo.	4.00	5.61	6.80	—	9.24	—	11.65	11.84	14.04	14.31
Horschenz, Bohemia	4.00	5.60	6.80	—	9.22	—	11.65	11.82	14.02	14.31
Aragonite and Calcite										
Alameda Co., Calif.	4.00	5.56	(6.79–7.05)		9.22	11.40	11.59	—	14.02	14.29
Livermore, Calif.	4.01	5.59	(6.78–7.02)		9.22	11.42	11.64	—	14.03	14.29
Herrngrund, Hungary	4.00	5.62	(6.78–7.03)		9.24	11.43	11.65	11.83	14.04	14.30
Sacramento, Colo.	4.02	5.60	6.79–7.02		9.23	11.44	11.69	11.84	14.05	14.32
Calcite										
Black Hills, S. Dak.	4.00	5.56	—	7.05	—	11.41	—	11.79	14.03	—
Eureka, Utah	4.01	5.57	—	7.03	—	11.41	—	11.79	14.04	—
New Mexico	4.00	5.56	—	7.20	—	11.40	—	11.78	14.02	—

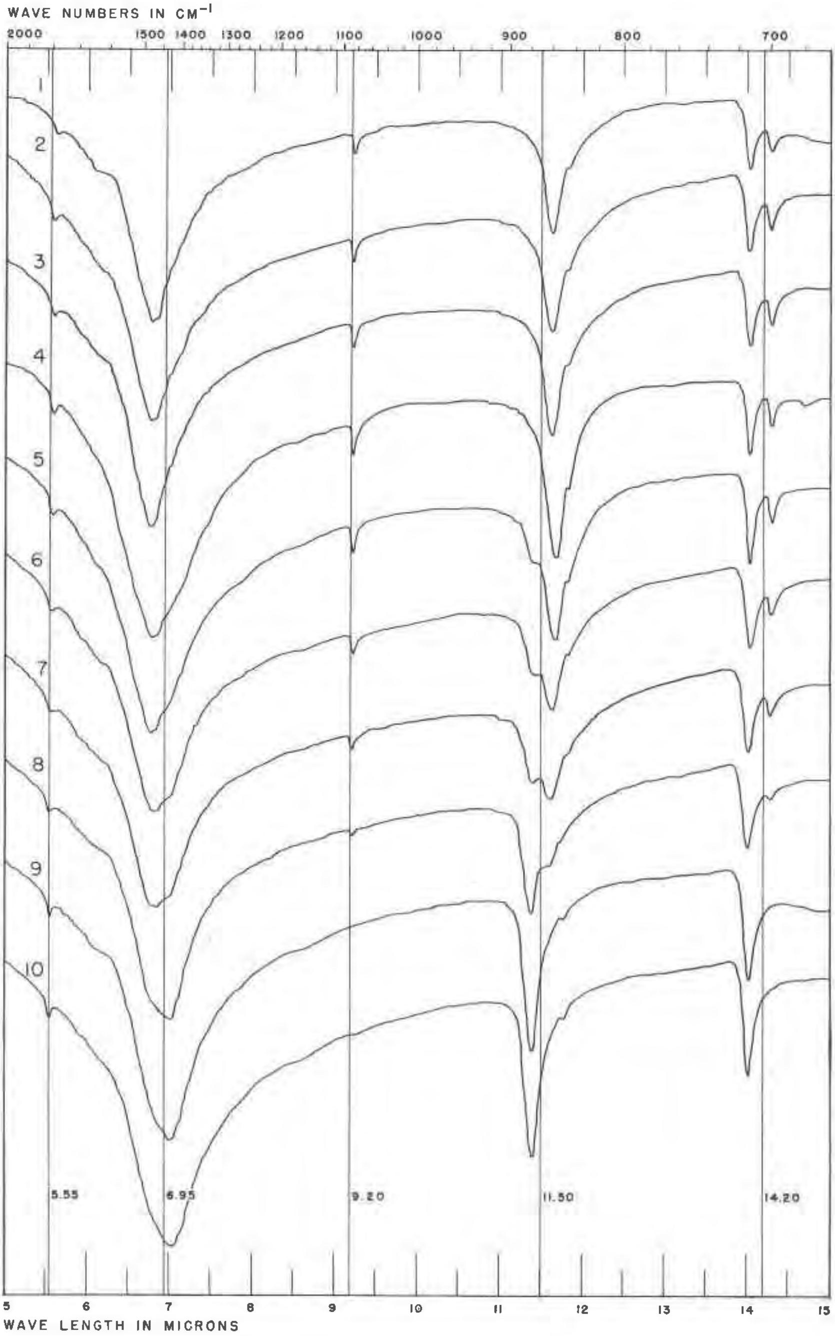

FIG. 2. Infrared spectra of aragonite and calcite. Aragonite: (1) Leadville, Colorado (USNM-80361), (2) Girgenti, Sicily (USNM-104620), (3) Guanajuato, Mexico (USNM-C2085), (4) Mohave Co., Arizona (USNM-R127); aragonite and calcite: (5) Sacramento, Colorado (USNM-69188), (6) Herrngrund, Hungary (USNM-R2534), (7) Alameda Co., Calif.; (8) Livermore, Calif.; calcite: (9) Eureka, Utah (USNM-R2334), (10) Black Hills, So. Dakota (USNM-R2332).

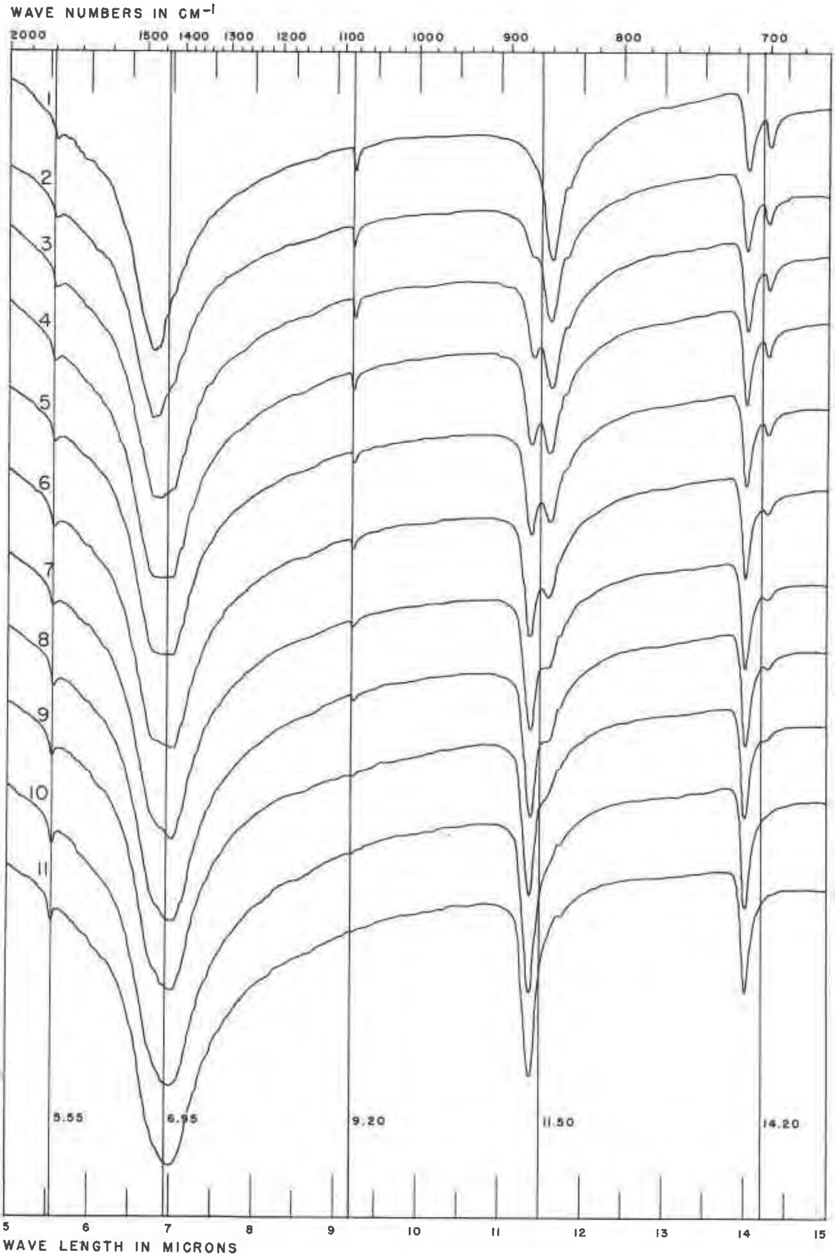

FIG. 3. Infrared spectra of prepared aragonite-calcite mixtures. End members: (1) Aragonite, Horschenz, Bohemia (USNM-R12050), (11) Calcite (Iceland spar), New Mexico (USNM-106158); mixtures in weight per cent aragonite: calcite: (2) 90:10, (3) 80:20, (4) 70:30, (5) 60:40, (6) 50:50, (7) 40:60, (8) 30:70, (9) 20:80, (10) 10:90.

by Schaefer and Matossi (1930, p. 340). The corresponding bands were found in this study at 14.04 μ and 14.30 μ.

The calcite spectra in Figs. 1, 2 and 3 show major absorptions at approximately 7.03 μ, 11.41 μ and 14.03 μ and minor bands at 4.00 μ, 5.56 μ and 11.79 μ. With the exception of the absorption bands at 9.23 μ and 14.30 μ, all major calcite bands have corresponding bands in the aragonite spectrum.

It is noted that the band at 9.23 μ nearly coincides with the frequency corresponding to the v_1 fundamental given by Herzberg (1945) as 1063 cm^{-1} and by Bhagavantam and Venkatarayudu (1939) as 1084 cm^{-1}. The appearance of this band in spectra of aragonite suggests that the structural change in the transformation from calcite to aragonite is sufficient to activate this mode.

Curves 5, 6, 7 and 8 in Fig. 2 show varying degrees of absorption at about 11.4 and 11.6 μ. The band at 11.4 μ conforms in position to the corresponding band in curves 9 and 10 which is characteristic of calcite.

Similarly, there is close correspondence between the band at 11.6 μ in curves 5 to 8, inclusive, and that in curves 1, 2, 3 and 4 which represent aragonite. In comparing the two bands in question in curves 5, 6, 7 and 8, it is apparent that the relative intensities vary inversely for a given spectrum, *i.e.*, as the 11.4-μ band increases in intensity the 11.6-μ band decreases simultaneously. Considering this variation in intensity in light of the fact that the spectra were obtained on identical amounts of sample material, the two bands may be explained by an intergrowth of aragonite and calcite, with aragonite predominant in sample 5 and calcite in sample 8. This conclusion is supported by *x*-ray analyses which confirmed the presence of both minerals in each of the four samples, and also by comparison of these curves with the spectra in Fig. 3 which were obtained on artificial mixtures of aragonite and calcite.

It is worthy of note that optical examination may be inadequate in determining the purity of carbonate mineral specimens. Re-examination of specimens of so-called aragonite from Alameda Co., and Livermore, California, by *x*-ray diffraction and infrared analysis indicate that both calcite and aragonite are present, whereas optical determinations reported previously by Huang and Kerr (1960) suggest only the presence of aragonite.

Broadening of the absorption peak in the 7-μ region to include both the aragonite and calcite band positions appears also to be related to intergrowth of the two minerals. When one mineral predominates in an aggregate the broadening diminishes and a "shoulder" appears on either the shorter or longer wavelength side adjacent to the peak of the major mineral. A possible interpretation of this phenomenon as caused by the removal in aragonite of the degeneracy of the v_3 funda-

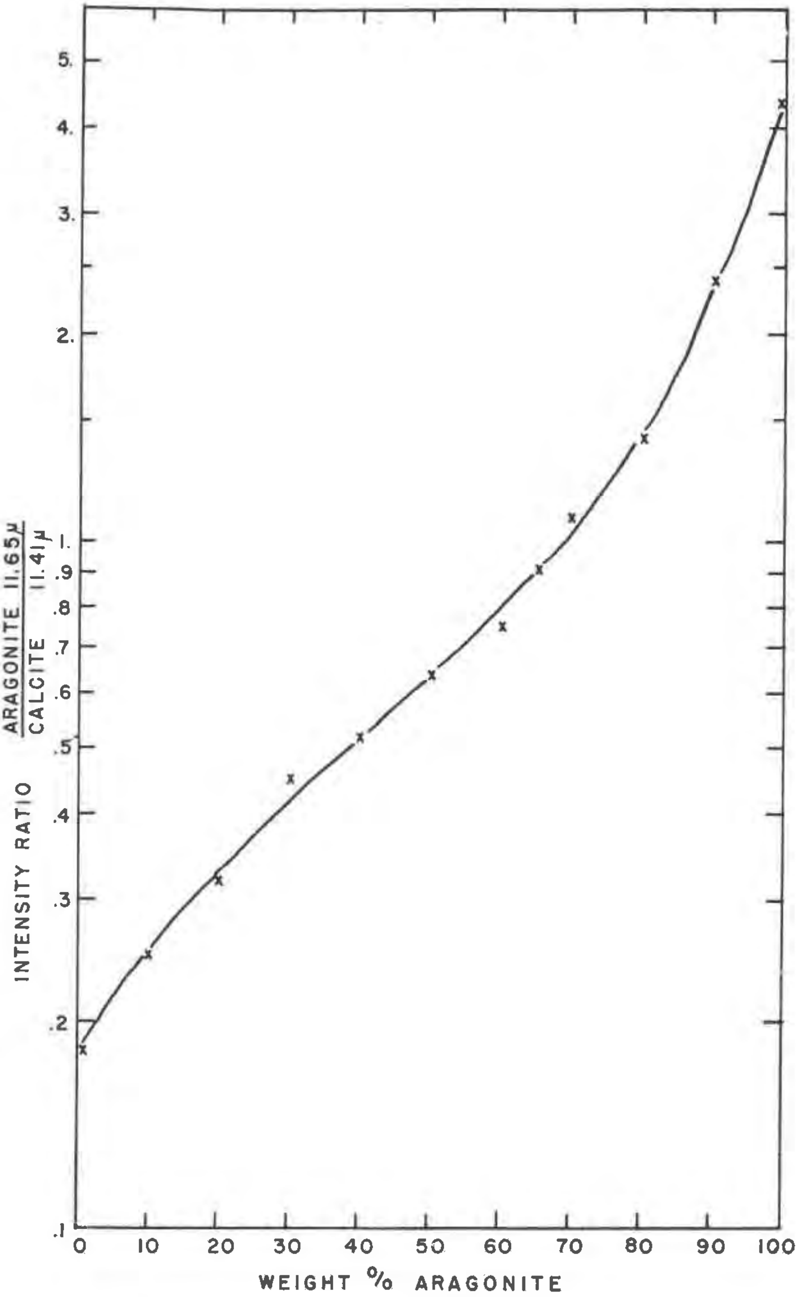

FIG. 4. Ratio of the intensities of aragonite and calcite absorption bands in the 11–12 micron range plotted against the percentage of aragonite in prepared aragonite-calcite mixtures.

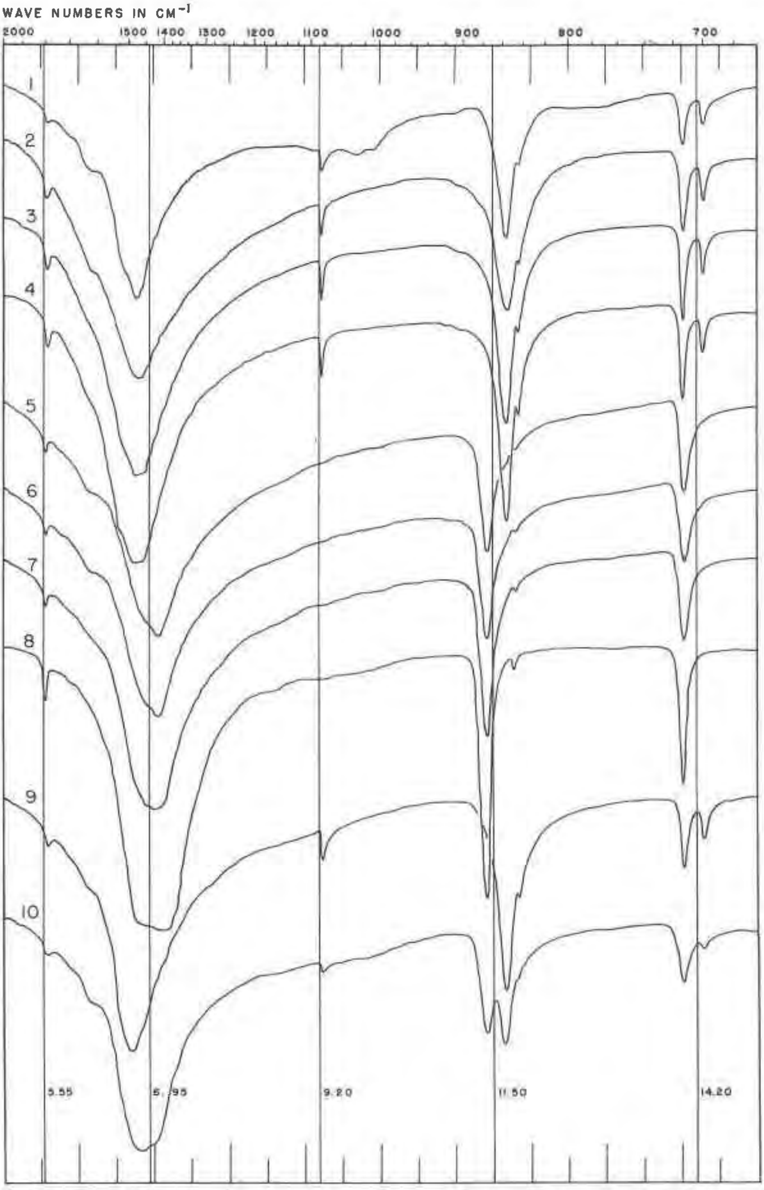

FIG. 5. Infrared spectra of aragonite and calcite varieties. Aragonite: (1) ktypeite, Madagascar (USNM-93948), (2) zeyringite, Flatschach, Austria (USNM-R2548), (3) erzbergite, Erzberg, Austria (USNM-114166), (4) flos ferri, Corinthia, Austria (USNM-R2545); calcite: (5) schaumkalk, Harima, Japan (USNM-61492), (6) calcareous tufa, Bear Spring, Mont. (USNM-18648), (7) calcareous tufa, Pierce Co., Wash. (USNM-14499), (8) chalk, Dover, Eng. (USNM-2932); miscellaneous: (9) oolitic calcite (aragonite) Hot Springs, Mont. (USNM-45998), (10) oolitic limestone, Pyramid Lake, Nev. (USNM-35306).

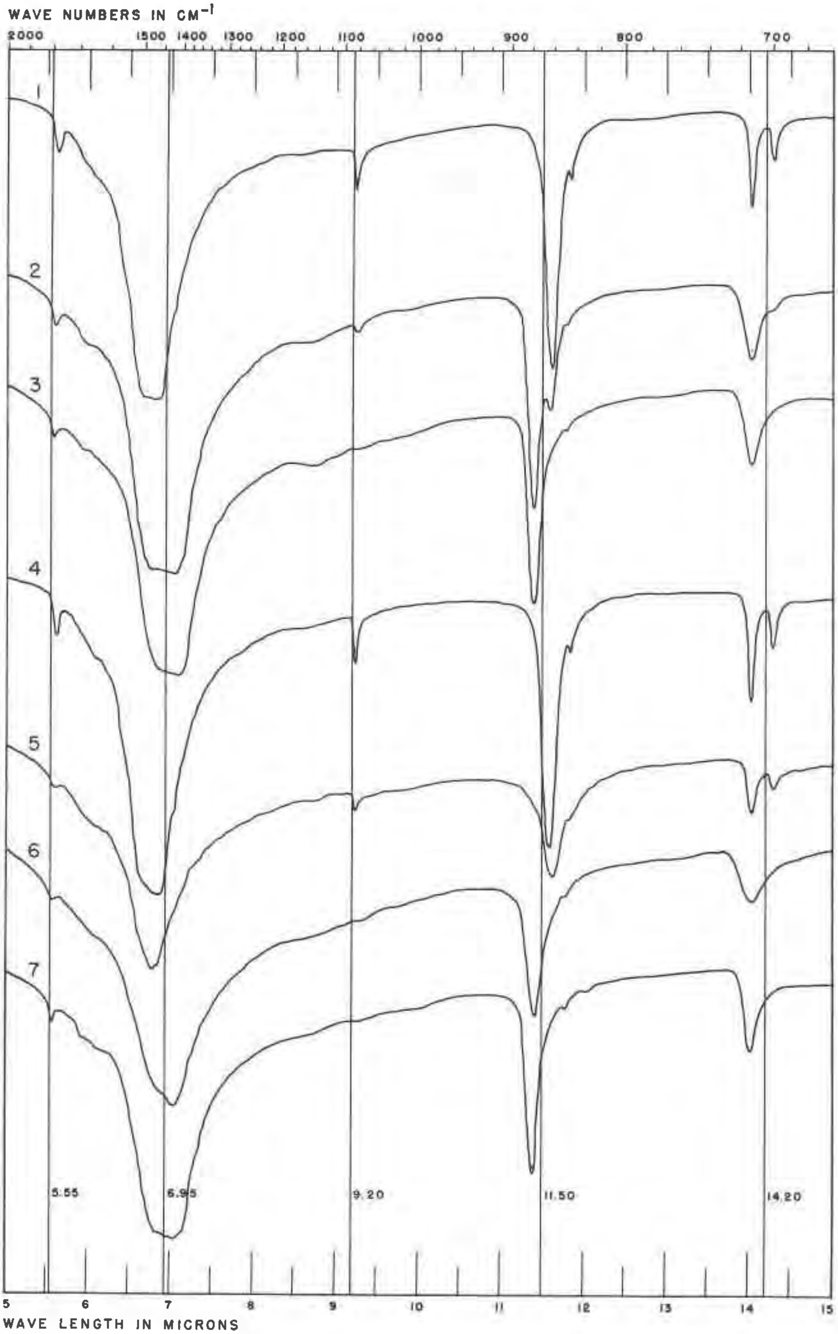

FIG. 6. Infrared spectra of recent invertebrate shells. (1) *Strombus gigas* (gastropod), (2) *Nerita* (gastropod), (3) *Pecten* (pelecypod), (4) *Arca* (pelecypod), (5) *Spirula* (cephalopod), (6) *Echinus millaris* (echinoderm), (7) *Ostrea* (pelecypod).

mental with resultant resolution of the split modes does not seem to be valid in spite of the supporting indication from apparent resolution of the split bands in the spectrum of the isostructural orthorhombic carbonate, cerussite, obtained by Huang and Kerr (1960). The invalidity of this assumption is indicated by the absence of such resolution in spectra of aragonite which show no evidence of calcite by *x*-ray analysis or by absorption at 11.4 μ.

The dependence of peak broadening at 7 μ on the presence of an aggregate of the two minerals is, furthermore, apparent from inspection of the curves in Fig. 1, 2 and 3. The broadening reaches a maximum when the approximate ratio of aragonite to calcite approaches 1:1, and diminishes as the composition of the mixture approaches each end member. In no case does the individual band peak for aragonite (6.80 μ) or calcite (7.03 μ) shift from its characteristic position as has been observed for solid solutions of the carbonates (Adler *et al.*, 1950). The broadening constitutes, rather, a merging of the two peaks to form a single broad band which consists of the two superimposed absorptions. The "shoulder" results from incomplete resolution of the minor peak. Since the width of the peak at 7 μ is also sensitive to mineral concentration, as shown in curve 5 of Fig. 7, intense absorption must be avoided when utilizing this band for interpretative purposes.

The 9.23-μ and 14.30-μ bands are particularly diagnostic for aragonite. The intensities of these peaks vary with the amount of aragonite in the sample. These absorptions provide additional criteria for recognizing aragonite in spectra of single minerals or mixtures.

In the light of the spectra obtained in the current study it may be concluded that the 11.4-μ band previously assigned to aragonite (Hunt *et al.* 1950; Huang and Kerr, 1960) is caused by calcite as an impurity, and that the 11.6-μ band is solely definitive of aragonite. That the relative intensities of the two bands are indicative of the relative concentrations of the two minerals is clearly illustrated in Fig. 3 which shows the effects of change in composition on band intensity for artificial mixtures of aragonite and calcite. Broadening of the absorption maxima in the 7-μ region may also be related to intergrowth of aragonite and calcite, but this criterion is less reliable owing to the sensitivity of this band to sample concentration.

SEMIQUANTITATIVE APPLICATIONS

In addition to its useful application in qualitative identification, the absorption of aragonite and calcite in the 11-μ region has been considered from the aspect of yielding quantitative information.

In the present study 11 samples were prepared to illustrate the rela-

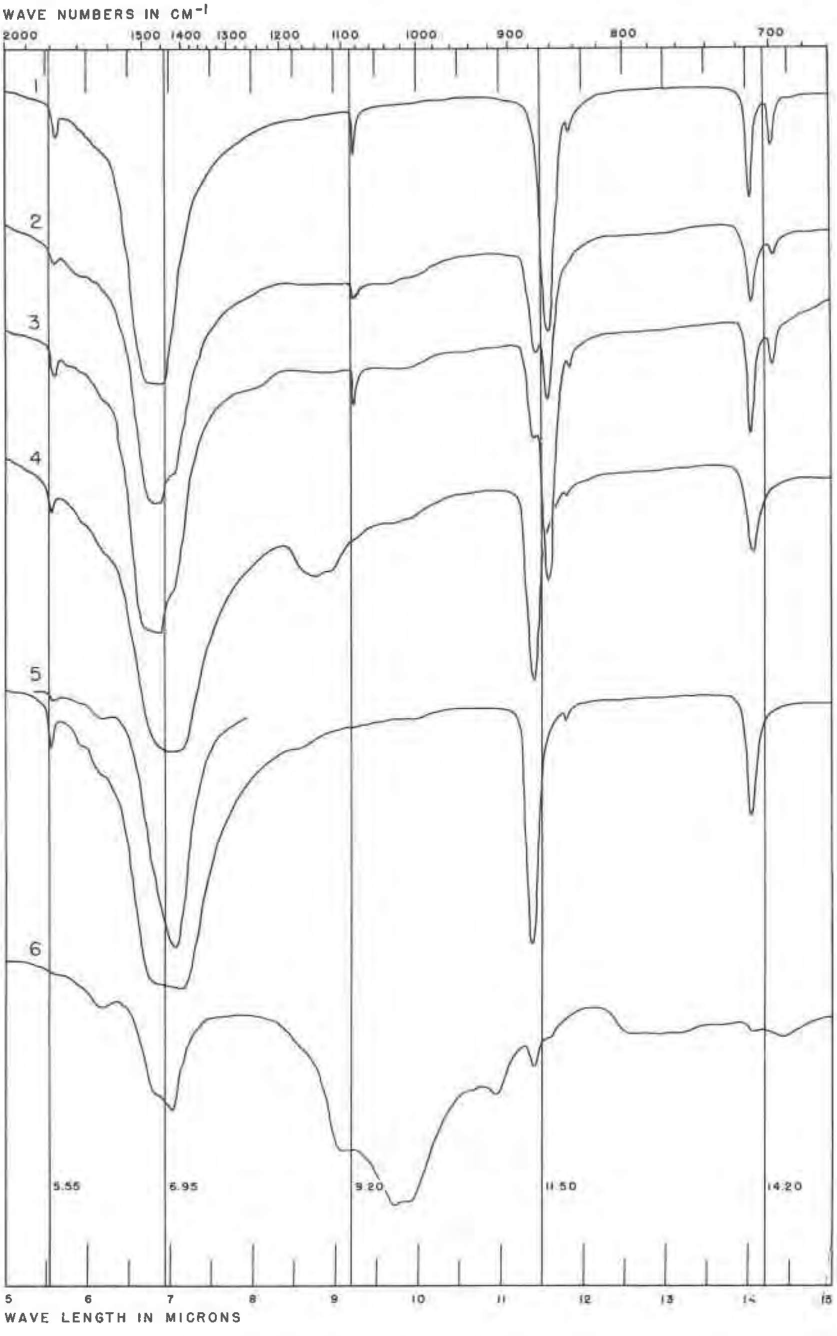

FIG. 7. Infrared spectra of fossil invertebrate shells. (1) *Eutrephoceras* (cephalopod), (2) *Lima* (pelecypod), (3) *Pecten* (pelecypod), (4) *Ostrea* (pelecypod), (5) *Anomia* (pelecypod), (6) *Lithophaga* (pelecypod).

tionship between infrared spectral changes and composition of artificial mixtures of aragonite and calcite. The materials for the synthetic mixtures were obtained from a cleavage specimen of the Iceland spar variety of calcite, which shows no detectable aragonite in the *x*-ray spectrum, and from an optically clear crystal of aragonite from the Horschenz locality near Bilin, Bohemia, which is likewise devoid of any detectable calcite. Samples of the two minerals were prepared in proportions of 10, 20, 30, 40 and 50 per cent by weight of each component using procedures previously described. For all mixtures and the end members, 0.85 mg of sample material was used; the infrared spectra are shown in Fig. 3.

The lower limits of apparent detectability of aragonite and calcite in aggregates are defined by the resolution achievable for their 11.65-μ and 11.41-μ bands, respectively. The infrared absorption caused by 10 per cent by weight of aragonite in a calcite matrix is barely shown by a slight inflection at 11.65 μ in the calcite band. Under present experimental conditions, this represents the minimal amount that yields an apparent inflection in the curve. Calcite is also apparent at 10 per cent concentration in an aragonite matrix by a slight absorption at 11.41 μ on the high-frequency limb of the aragonite band, but its presence can be recognized in slightly lower amounts. For practical purposes 10 per cent by weight is the approximate lower limit at which aragonite and calcite are apparent in natural or artificial aggregates using routine sample preparation and instrument operation methods. At higher concentrations the bands become more intense and are useful for estimating the relative amounts of each mineral present.

By using the spectra in Fig. 3 for measurement of the ratio of the intensity of the 11.65-μ band peak of aragonite to the 11.41-μ band peak of calcite, the calibration curve shown in Fig. 4 was obtained. Intensity measurements were made from a baseline constructed by extending the straight-line portion of the spectrum at 10.8 to 11.05 μ laterally across both bands. Null points for zero concentration of aragonite and calcite were obtained at the intersection of the curve of the pure specimens with the 11.65-μ and 11.41-μ lines, respectively.

Although the intensity ratio obtained is proportional to the ratio of concentration of aragonite and calcite in a given sample, measurements on test samples show that the calibration curve is sensitive to sample weight changes and is dependent on the particular materials comprising the mixture. Therefore, calibration data cannot be extrapolated in a purely quantitative manner to other calcite-aragonite aggregates.

For example, for a given suite of mixtures, varying the quantity of sample has a distinct effect on the ratios obtained. With samples of less than 0.85 mg small differences are found between actual and plotted concentrations which may be caused by inaccuracies in weight measurements. However, for a relatively large sample (2.55 mg) the plotted data deviate considerably from the measured concentration:

Sample weight (mg)	*Ar:Ca (measured)*	*Ar:Ca (plotted)*
0.50	20:80	25:75
0.50	50:50	48:52
0.50	10:90	16:84
2.55	20:80	42:58

Test samples weighing 0.85 mg, used to check the infrared method, show as much as a 10 per cent deviation in weight between measured and plotted concentration values:

Sample Material Ar:Ca	*Ar:Ca (measured)*	*Ar:Ca (plotted)*
Girgenti:Black Hills	50:50	60:40
Guanjuato:Black Hills	50:50	60:40
Alston Moor:Eureka	50:50	60:40
Alston Moor:Black Hills	80:20	81:19
Girgenti:New Mexico	80:20	84:16

Comparison of measured and plotted data for these samples indicates that the infrared method can be used to obtain semiquantitative figures accurate only to about ± 10 per cent (absolute) of the mineral content in the specimen. The agreement is satisfactory considering that the intensity of a given absorption band varies for different specimens in spite of standardization of preparation procedures. For a given calibration plot, the observed narrow scatter of points outside the line may result from inhomogeneity of sample or weighting errors but this cannot account for the major deviations observed for the test samples. The latter are apparently caused largely by inherent intensity differences in various specimens, which are especially well reflected by comparison of spectra of mineral specimens (Fig. 2 and 5) with those of similarly prepared invertebrate samples (Fig. 6 and 7) which show relatively high absorption. Inasmuch as different sample combinations can be expected to yield somewhat different ratios, calibration curves based on mixed samples can serve only a semiquantitative purpose.

The infrared method in its present state does not compete with x-ray diffraction as a quantitative technique for determining the percentage of aragonite and calcite in aggregates. However, it has the distinct advantage as a survey method of furnishing a rapid means of identifying the nature and semiquantitative composition of such mixtures, and its use may be advocated for this purpose.

SPECTRA OF ARAGONITE AND CALCITE VARIETIES

Infrared spectra of aragonite and calcite varieties based upon crystallization or mode of aggregation and chemical composition are shown in Fig. 5. No significant spectral differences between varietal specimens and the common mineral forms were observed, although several of the specimens differ from their museum labels.

Both aragonite and calcite reportedly exhibit a considerable range of compositional variation; however, small differences obtained in the varieties are not reflected in the infrared spectra which are relatively insensitive to minor compositional variations caused by solid solution. The coralloid aragonite flos ferri (curve 4), the porous form ktypeïte (curve 1), the calcareous sinter zeyringite (curve 2), and erzbergite (curve 3), yield spectra essentially identical to ordinary aragonite. Massotite (not shown) and zeyringite, strontian varieties reportedly containing a maximum ratio of Sr:Ca = 1:25, show no change from the typical aragonite spectrum, which is to be expected because compositional differences of this magnitude are not generally discernible in infrared spectra of carbonate minerals inasmuch as the magnitude of displacement of the CO_3^{2-} absorption bands by cation substitution is low.

A specimen of schaumkalk from Harima, Japan (curve 5), listed as a variety of aragonite (Palache *et al.*, 1951) but identified by the museum label as calcite, yields a spectrum characteristic of calcite. Calcareous tufa and chalk (curves 6, 7 and 8), which are varieties of calcite, yield typical calcite curves.

Specimens identified by museum label as oolitic calcite and oolitic limestone (curves 9 and 10) yield atypical calcite spectra. The spectrum of so-called oolitic calcite from Hot Springs, Montana, agrees with aragonite, whereas oolitic limestone from Pyramid Lake, Nevada, is an aggregate with the approximate ratio of Ar:Ca = 70:30. The spectrum (not shown) of thinolite, a calcite pseudomorph from Pyramid Lake, Nevada, is conformable with calcite.

INVERTEBRATE SPECTRA

Infrared spectra of both recent and fossil shells are shown in Figs. 6 and 7, respectively. The recent shells are from relatively warm environments, having been collected from the waters around Puerto Rico. The fossil shells are from the Cretaceous of Tennessee and Mississippi. Several classes of mollusks are represented in each group.

The calcareous materials deposited by the various mollusks examined consist, according to their infrared spectra, of either aragonite or calcite and in some cases are composed of both materials. Recent shells of *Strombus*, *Arca* and *Spirula* and the fossil shell of *Eutrephoceras* are dominantly aragonitic, no calcite being evident in the spectra. Fossil shells of *Lima* and *Pecten* (Fig. 7) are composed of aragonite and calcite with aragonite predominating. The approximate compositions calculated on the basis of the calibration curve in Fig. 4 are for *Lima* (curve 2), Ar:Ca = 75:25, and for *Pecten* (curve 3) Ar:Ca = 90:10. The composition of the recent *Nerita* shell is similarly determined to be Ar:Ca = 40:60. Recent shells of *Pecten*, *Echinus* and *Ostrea* (curves 3, 6 and 7, respectively) and fossil shells of *Ostrea* and *Anomia* (curves 4 and 5) yield infrared curves characteristic of calcite.

Absorption at about 8.5 μ in the curve of fossil Ostrea is caused by an undetermined impurity. The two bands shown for *Anomia* (curve 5) in the 7-μ region were obtained on samples of 0.85 and 0.425 mg. The 0.85-mg sample yields an absorption peak extending over both the aragonite and calcite positions, but better resolution was achieved by using the smaller sample.

The absorption curve obtained on a fossil *Lithophaga* specimen (curve 6) is presumably atypical for this mollusk. The sample did not possess a characteristic calcareous texture and seemed to be largely composed of mudstone. Since this is a burrowing form of pelecypod, it is quite likely that much of the shell cavity may have become filled with the surrounding sediment. The spectrum indicates the presence of carbonate by absorption at 7, 11.4 and 14 μ; however, the mineralogic composition of the carbonate is evident only to the extent that one can say it is dominantly calcite. Although the "shoulder" at about 6.8 μ may be interpreted as indicative of some aragonite, absorption in the 11- and 14-μ regions is too weak to confirm this. A considerable part of the sample is composed of non-calcareous matter which produces absorption at 8 to 11 and 12 to 13 μ. Comparison with reference spectra previously obtained by Adler *et al.* (1950) indicates that the general nature of the curve in the 8- to 11-μ region is characteristic of a clay mineral, possibly kaolinite or montmorillonite. Inasmuch as kaolinite also absorbs in the 12- to 13-μ region and montmorillonite apparently does not, the non-calcareous component of the sample is most likely kaolinite.

Although the infrared technique employed in this investigation does not achieve the quantitative accuracy attainable through *x*-ray methods, it is adequate as a survey method for obtaining an approximate quantitative determination in addition to rapidly establishing the identity of the carbonate species constituting the invertebrate shell.

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