Infrared and atomic mineral analysis of some oyster shells

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An attempt has been made to calculate the calcite-aragonite ratios and atomic mineral composition of some Oyster shells of Indian origin by spectroscopic techniques. A correlation is obtained between the calcitic structure and the magnesium concentration of these shells. However, the strontium concentration is found to be nearly the same in all these shells while the barium concentration is very low.

1. Introduction

The study of the crystal structure and the chemical composition of shells is of interest to the biologists as well as geologists because of the reason that these factors give valuable information regarding the environments in which these animals live, namely, the temperature, the pressure and the salinity The crystal structures of these shells also show considerable variation with age. Hence, the study of the crystal structures, will also throw light on the age of the specimens. Earlier studies of the crystal morphology of calcium carbonate deposits in these shell specimens and other animal species were carried out by many workers using different techniques. Powder X-ray crystallographic methods were used by Bevelander & Benzar (1948) and Lutts *et al* (1960a). Turekian & Armstrong (1960c) employed the X-ray diffraction methods to study the calcite-aragonite ratios and the variation of the trace elements like magnesium, barium and strontium in the case of about hundred molluscan shells. The scanning electron microscope technique was used by Wada (1961a).

Recently, Compere & Bates (1973) analysed the calcium carbonate structure in some molluscan shells through infrared spectroscopy. They observed that the infrared methods have the advantage of being faster and less tedious than the X-rays and or the electron microscope techniques and has about the same quantitative accuracy as the powder X-ray diffraction methods.

The study of the atomic mineral constitution of these shells gives additional information on the crystal structure of calcium carbonate present in the shells Such studies were carried out by Turekian & Armstrong (1960b), Boggild

(1930), Chave (1954), Thomson & Chow (1955), Lowenstam (1961b) and Odum (1951a and 1951b).

The present study deals with the infrared spectroscopic analysis and the atomic mineral analysis of some oyster shells of Indian origin.

2. EXPERIMENTAL

Samples used in the present study were collected from the Marine Biological Research Station, Annamalai University, Portonovo. They are one specimen each of *Pinctada vulgaris*, *Tridacna* sp. *Ostrea* sp, (Fossil), *Placuna* sp, two freshly collected specimens (No. 5, 6) of the *Crassostrea madrasensis* and two specimens of the same species *Crassostrea madrasensis* collected a few years back. (No 7, 8).

The infrared spectra of the mother-of-pearl layer of these shells were recorded using Perkin Elmer Grating Spectrograph (No. 237-B) in the region 400—1300 cm^{-1} with KBr pellets.

The atomic spectra of these shells were recorded using 'Hilger and Watts' (No. E/495306/57225) high dispersion spectrograph and Ilfor N-40 photographic plates. The region recorded being 3800 to 5100 A. Similarly the Hilger and Watts high dispersion quartz spectrograph (No. E/498306/57928) and Agfa-Gevaert plates were used to record the spectrum in ultraviolet region. Drilled spectroscopically pure copper rods were used as electrodes.

The wavelengths of the spectral lines were calculated using Hartmann's formula. Comparing the wavelengths and their intensity estimates with the standard wavelengths reported in the M.I.T. Table (1939), the various elements present in the shells were identified. The persistent lines (Brode 1962) made use of for the identification of elements like calcium, strontium, barium and magnesium are as follows :

Calcium : 4455.9, 4435.7, 4425.4, 4318.7, 4226.7, 3968.5 and 3179.3 Å

Strontium : 4607.3, 4215.5 and 4077.7 Å
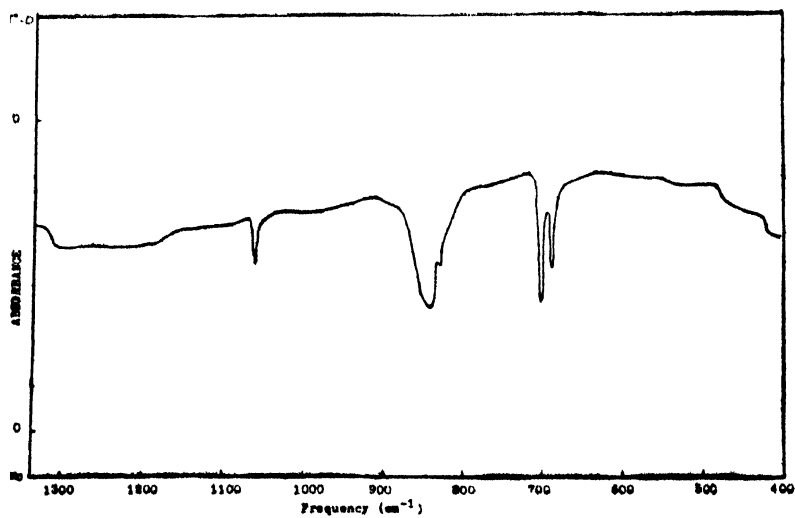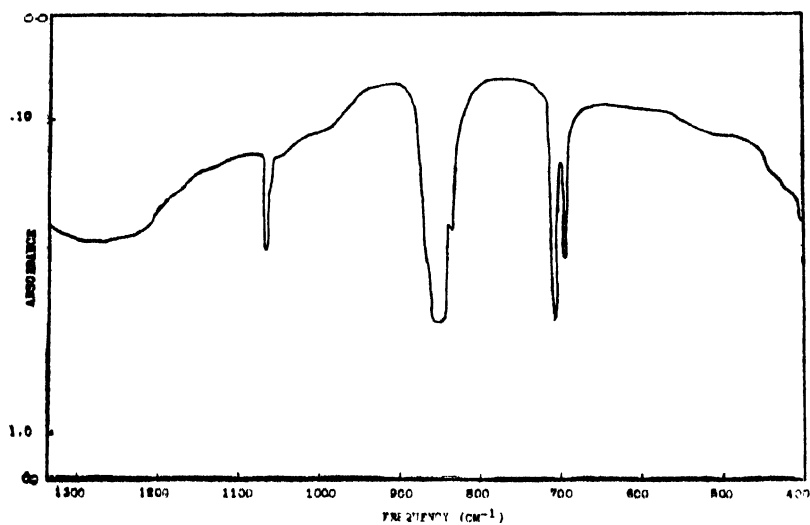
Barium : 4554 Å

Magnesium : 2852.13, 2795.5 and 2802.7 Å.

The optical densities of the lines were determined using Hilger and Watts Spectrophotometer (No. FR 300-2/61228) in conjunction with a densitometer (Serial No. 5103; Model 501 M) Photovolt Corporation, New York city, U.S.A.
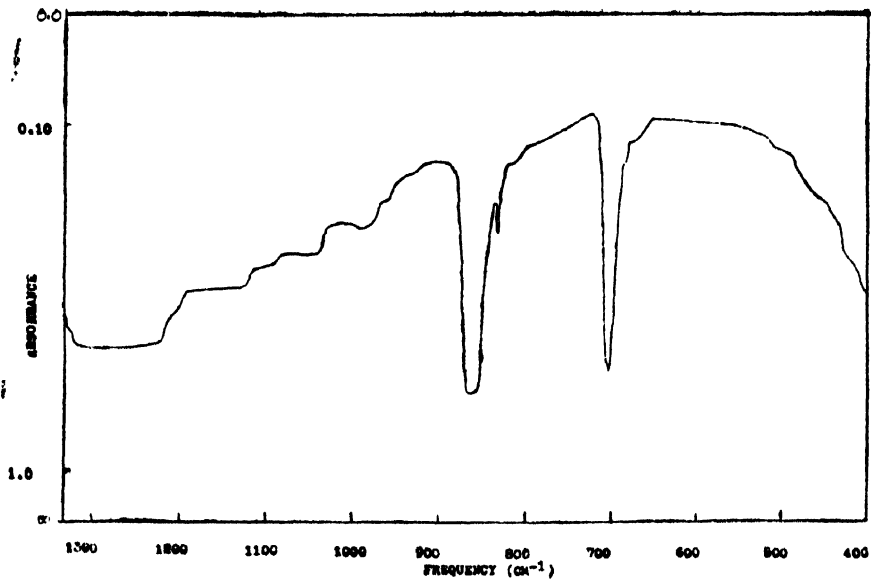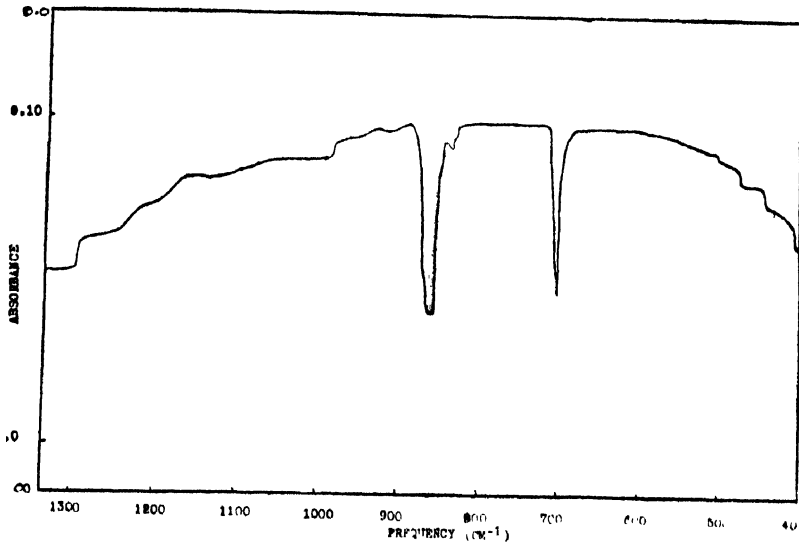
3. RESULTS AND DISCUSSION

(a) *Infrared analysis* :

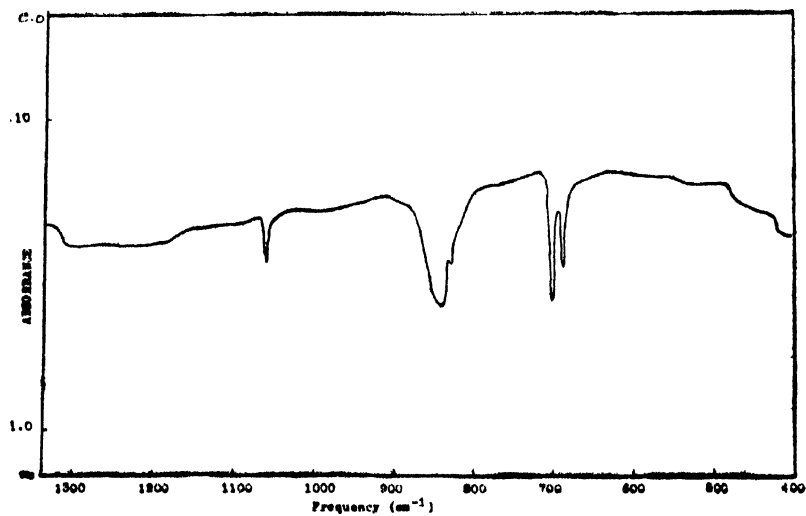The infrared spectra of the various shell specimens are given in figures 1 to 8.

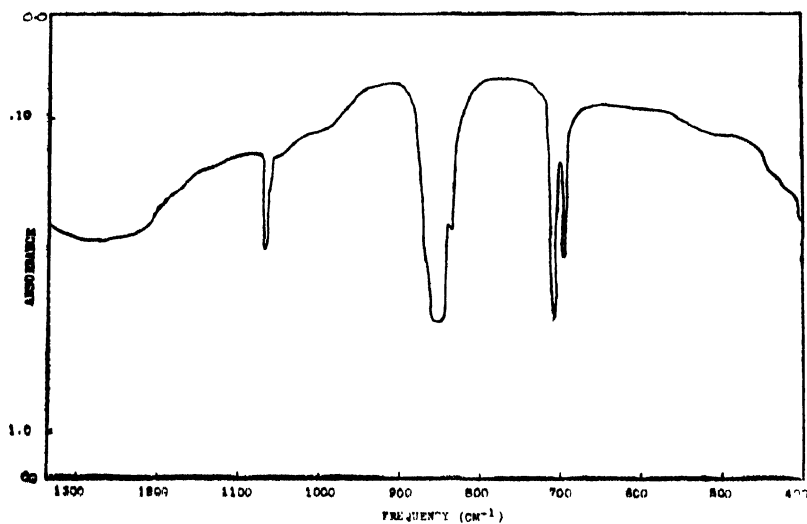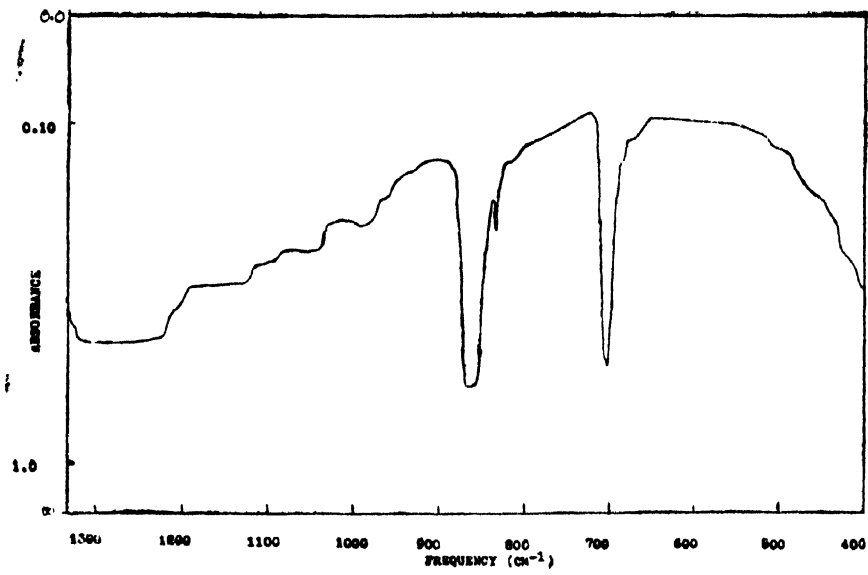## 3. RESULTS AND DISCUSSION

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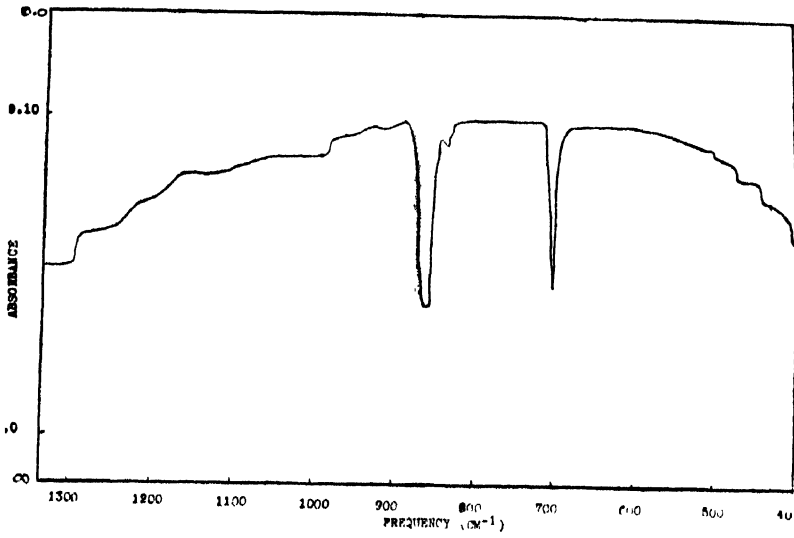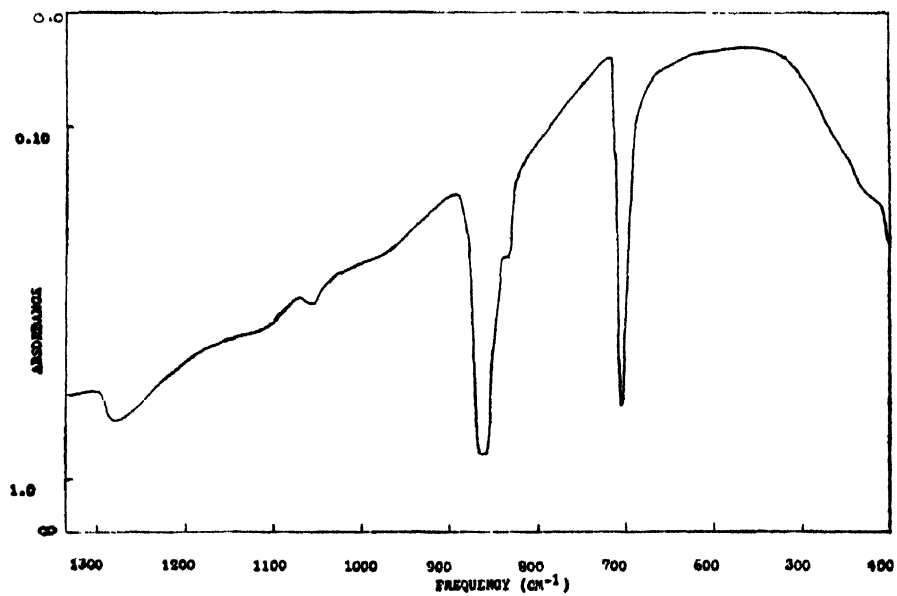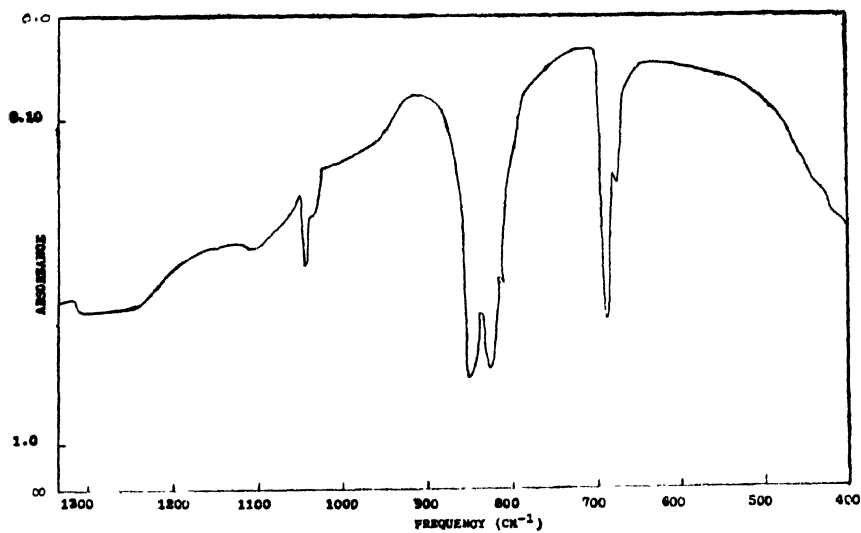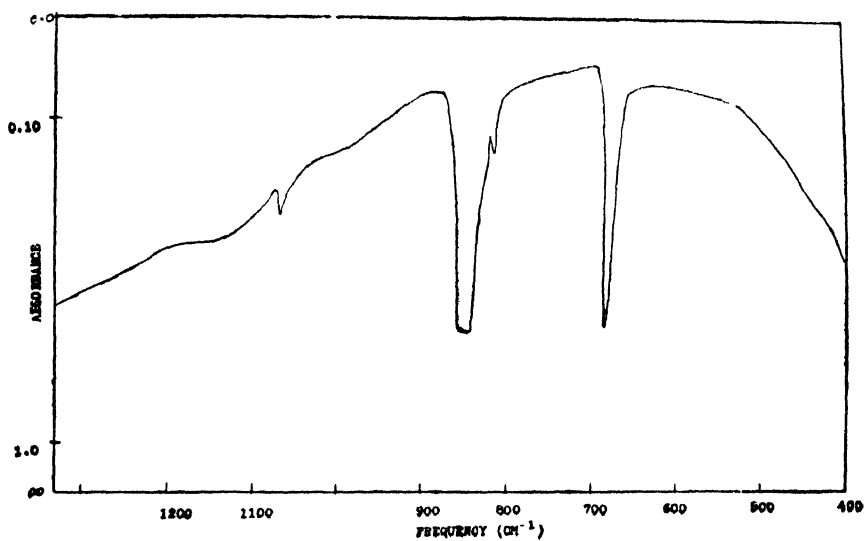
The infrared spectra of pure calcite and pure aragonite have the following characteristic absorption bands (Flugge 1958) :

Calcite   :   876 and 714 cm^{-1}
                 Shoulder at 848 cm^{-1}.

Aragonite :   1080, 857, 714 and 698 cm^{-1}
                 Shoulder at 842 cm^{-1}.

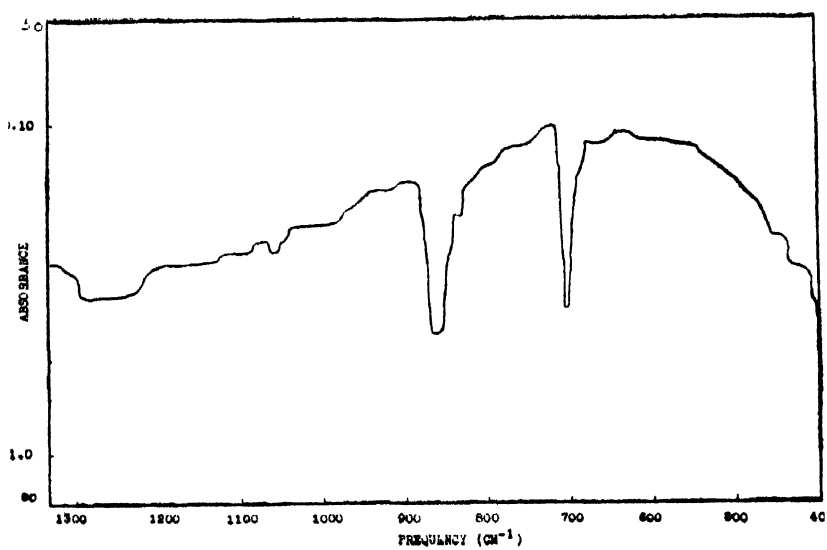From these spectra it is possible to distinguish between calcite and aragonite. The percentage of aragonite in these specimens can be obtained by determining the integrated intensity ratios of the 698 cm^{-1} and 1080 cm^{-1} bands of aragonite in these spectra and comparing them with the integrated intensity raio of the same bands in the spectrum of pure aragonite.

From the figures, it is seen that the specimens of *Ostrea* sp, *Placuna* sp, and three specimens of *Crassostrea madrasensis* do not have any absorption at 1080 and 698 cm^{-1} which hows that they are purely calcitic. But the *Pinctada vulgaris*, *Tridacna* sp and *Crassostrea madrasensis* (No. 8) specimens are having absorption bands at 1080, 855, 714 and 698 cm^{-1}. The percentages of aragonite present in these samples were calculated. They are summarized in table 1.

Table 1. Calcite-aragonite ratios, the barium, strontium and magnesium concentrations in ppm of calcium in some oyster shells

Specimen	Calcite-aragonite ratio	Concentration in ppm		
		Ba.	Sr.	Mg.
1 *Pinctada vulgaris*	100 per cent aragonite	135	2219	650
2. *Tridacna* sp	100 per cent aragonite	76	2274	1650
3. *Ostrea* sp	100 per cent calcite	83	2178	2150
4. *Placuna* sp	100 per cent calcite	78	2894	3750
5. *Crassostrea madrasensis*	100 per cent calcite	69	2450	3500
6. *Crassosrea madrasensis*	100 per cent calcite	49	2836	3150
7. *Crassostrea madrasensis*	100 per cent calcite	45	1680	1250
8. *Crassostrea madrasensis*	70 per cent aragonite	45	2848	600

The mother-of-pearl layers or the nacreous layers of the Japanese pearl oysters (*Pinctada martensii*) were studied through X-ray diffraction methods by Shozo Tanka *et al* (1960b). They reported that the nacreous layer of the shell contains only aragonitic structure. Horigarchi (1959) and Wada (1961b) also observed that the nacreous layer of the Japanese pearl oyster is aragonitic and the prismatic layer is calcitic. These observations essentially confirm our findings from infrared analysis.

The hundred per cent calcitic nature of the fossil *Ostrea* sp obtained in the present analysis agrees very well with the observations of Compere & Bates (1973) on the same fossil *Ostrea* sp which they reported as entirely calcitic.

In the spectrum of the operculam or the base portion of the freshly collected *Crassostrea madrasensis* specimen (figure 6) it is observed that in addition to the absorption bands at 877 and 714 cm $^{-1}$ there is a weak band near 1080 cm $^{-1}$. This band arises due to the totally symmetric A_{1g} vibration in calcite. The presense of the weak band may be due to rotational disordering leading to a reduction in site symmetry to C_3 from D_3 in this specimen (Ross 1972).

One of the main features observed in the spectra of the aragonite specimens is that the bands at 855 cm $^{-1}$, due to the out-of-plane bending vibration (v_2) of the carbonate ions, are split. The splitting of the v_2 band was attributed to the coupling between the vertical neighbour carbonate ions by Decius *et al* (1963a). But in the spectrum of the 70 per cent aragonite *Crassostrea madrasensis* specimen in addition to the aragonite bands, the 877 cm $^{-1}$ band of calcite is also present. This 877 cm $^{-1}$ band is due to the presence of about 30 per cent of calcite. The spliting of the v_2 band at 855 cm $^{-1}$ is also observed in this specimen because of the presence of about 70 per cent of aragonite.

X-ray diffraction analysis of the *Crassostrea virginica* by Watabe & Simkiss (1963b) shows that it is calcite. In the present investigation it is observed that three of the four *Crassostrea madrasensis* specimens are made up of calcite only. But only one specimen deviates from this in that it has got 70 per cent of aragonite. This rather high concentration of aragonite may be due to the presence of the prismatic layer powders in the mother-of-pearl layer which is not probably well defined in this specimen. Further, the specimen did not have any definite separable layer. This may be due to some defect in the growth of the shell. Majority of the specimen was in the form of powder.

(b) *Atomic mineral analysis*

The most probable elements in these shells are found to be calcium, strontium, magnesium and barium. In addition to these elements traces of iron, manganese and chromium also present in these samples as is evident from the presence of persistent lines at 4583.4, 4048.8, 3748.26, 3745.56, 3581.2, 2413.3, 2408.88 and 2382.04 Å of iron, 4289.72, 4274.8, 4254.35, 2843.2 and 2835.63 Å of chromium and 4034.49, 4033.07 2605.7, 2593.73 and 2576.10 Å of manganese.

For the quantitative estimation of the elements, the procedure adopted was as follows. The optical densities of the characteristic lines of calcium (4578.6 Å), strontium (4607.3 and 4077.7 Å) and barium (4554 Å) determined in order to estimate the barium and strontium concentrations. For the determination of magnesium concentration, the optical densities of calcium (3009.2 Å) and magnesium (2779.8 Å) lines were used.

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The working curves essential for the estimation of these elements were given by Turekian & Armstrong (1960c). These curves were drawn by taking parts per million of the elements in the abscissae and ratio of the optical densities of the barium, strontium and magnesium lines to that of calcium line as ordinates. The amount of these elements present in the shells can be determined from their optical density ratios.

The barium content of the shells was determined by finding the optical density ratios of 4554 Å barium linex and 4578.6 Å line of calcium and using them in the working curves given by Turekian and Armstrong (1960c). The amount of barium present in all the shells are listed in table 1. It is evident from the table that the barium concentration in these shells is very low. Similar observation was made by Turekian and Armstrong who pointed out that the low concentration of barium is a consequence of the low barium concentration in the ocean.

For the estimation of strontium content in these shells, the strontium lines of 4607.3 Å and 4077.7 Å were used for optical density determination. The 4607.3 line could not be used directly as its intensity was very high and the ratio of optical densities of strontium and calcium exceeded 1, hence making it impossible to use the working curve given by Turekian and Armstrong (1960c). Self absorption of this line was assumed to be the reason for the high intensity whenever the strontium concentration exceeds 650 ppm.

To overcome this difficulty, the 4077 7 Å strontium line was made use of and the ratio of the optical densities of this line and the 4554 Å line of barium was determined. Knowing this ratio and the ppm of barium in that particular shell, the parts per million of strontium in that shell was determined. This procedure can be written in the form of an equation

$$\frac{Sr}{Ca} = \frac{D\ 4077.7\ Å}{D\ 4554.0\ Å} \times \frac{D\ 4554.0\ Å}{D\ 4578.6\ Å} \qquad (1)$$

The strontium concentration in these shells obtained through the above procedure was only approximate. The exact amounts of strontium were computed by taking into consideration the 4607.3 Å line which was used in the working curves of Turekian and Armstrong. The optical density ratio of 4607.3 Å and 4578.6 Å lines was found out in all the shells. Comparing this ratio with the ratio obtained for the 4077.7 Å and 4578.6 Å lines, the parts per million of strontium in these shells was computed. These values are given in table 1.

By finding the optical density ratio of the 2779.8 A magnesium line and 3009.2 A calcium line and using the working curve, the magnesium contents of the shells were estimated and summarized in table 1.

In the present work it is found that the calcitic shells, namely, *Ostrea* sp, *Placuna* sp, *Crassostrea madrasensis* are rich in magnesium except the specimen No. 7. The aragonitic shells comparitively low concentration of magnesium. The concentrations are 650, 1650, 600 ppm respectively for *Pinctada vulgaris*, *Tridacna* sp and also a *Crassostrea madrasensis* specimen.

Similar observations were made by Boggild (1930) who suggested that all the aragonite shells are low in magnesium and calcitic shells are more complicated; some species have little magnesium; others have much. Chave (1954) reported that in the case of bivalves and gastropods the magnesium content is usually found to be greater as the proportion of calcite is increased. But Horiguchi (1959) and Wada (1961b) reported that the magnesium content of calcitic prismatic layer of *Pinctada martensii* (Japanese pearl oyster) is lower than that of aragonite nacreous layer. That means there are some exceptions to the general observation that calcitic shells are rich in magnesium. Turekian and Armstrong also reported some exceptions in the magnesium content of about hundred molluscan shells analysed by him.

Strontium content of these shells lies in the region 2500 ppm. The aragonitic as well as calcitic shells are found to contain more or less the same amount of strontium. But Thompson & Chow (1955) and Harris (1965) pointed out that the strontium content of aragonitic shells is generally higher than that in the calcitic shells. In the present study, only one calcitic *Crassostrea madrasensis* specimen was found to contain relatively lower amount of strontium, namely, 1680 ppm. Hence it is not possible to arrive at any definite correlation between the strontium concentration and aragonitic structure in the oyster shells of Annamalainagar region. But in the case of magnesium contact in these shells such a correlation exists between the concentration and calcitic structure. The calcitic shells are having greater amount of magnesium than the aragonitic shells.

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