

Mineralogical changes and structural transformation of rhombohedral calcite to orthorhombic aragonite upon grinding of recently excavated natural sedimentary calcitic crystal

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Abstract : Spectroscopical characterisation of natural sedimentary calcitic limestone crystal from Thalaiyuthu mines of Tamilnadu is carried out using FTIR technique. The results show the presence of calcite as major mineral, quartz, feldspar, gibbsite as minor minerals, kaolinite and nacrite as accessory minerals. The change in behaviour of all the minerals at various grinding periods are documented and discussed. The structural transformations from rhombohedral calcite to orthorhombic aragonite is completed by 240 hrs hand-grinding. The formation of new minerals are discussed. The unidentate and bidentate formations of calcite are identified with the help of doubly degenerative asymmetric stretching vibration (ν_1).

Keywords : Limestone, calcite, grinding and FTIR.

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1. Introduction

The present study was initiated to examine the practical application of infra-red spectroscopy to carbonate mineralogy, particularly used in the branch of analytical mineralogy. The important minerals of precipitate sediments are the carbonates such as calcite, aragonite and dolomite. In defining and describing carbonates and its properties, more emphasis will be placed on its physical and chemical than on its geological characteristics. Fossiliferous, marine sedimentation in oceans and freshbodies of water, consisting of shells and skeletons of plants and animals, were gradually accumulated through deposition, layer upon layer to form in some instances, massive beds of calcium carbonate. Sometimes this precipitation is indirect through the intermediary of plant and animal organisms [1].

Natural calcite and aragonite in limestones are being studied everywhere as these form basic material for manufacture of cement, white washing powder, wall painting and industrial pollution control. Therefore, the study of this material in various aspects gains importance in research.

Burns and Bredig [2] have been discussed the conversion of aragonite to calcite by grinding in a laboratory mortar. Acampora *et al* [3] studied the formation of heterogeneous solid solution by grinding mixture of KCl and KBr. Jamieson [4] and Goldsmith and Graf [5] have reported some reactions produced in carbonates by grinding. Bradley *et al* [6] studied the effects of grinding on dolomite and clay minerals. Adler and Kerr [7] have outlined a semiquantitative method for the infra-red determination of calcite-aragonite ratios in shell material and they have shown that there are four fundamental absorption bands (1423 cm^{-1} , 1083 cm^{-1} , 874 cm^{-1} , 712 cm^{-1}) in the spectra of carbonates, the frequencies of which correspond to particular deformational modes of the CO_3^{2-} ion.

In the present study, the behaviour of calcite in limestone are concerned by grinding method for different hours. This work describes the formation of new minerals upon grinding the limestone which contain natural mixtures of calcite and clays. The minerals and process are determined using FTIR techniques.

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2. Material and methods

The samples used in this study are naturally grown well-crystallized calcite limestones collected from Thalaiyuthu mines of Tirunelveli district, Tamilnadu. Thalaiyuthu is located about a distance of 6 km north of Tirunelveli and 5 km from south of Nanjankulam. It is represented in the survey of toposheet number in 58 H/P and lies between latitude 77°43' E and longitude 8°47' 30" N.

The samples are usually subjected to various pre-treatments in order to remove organic matter and certain other materials to improve the quality of the spectrum. Wet grinding is carried out by placing 5–10 mg of the sample in an agate mortar along with 10–15 drops of ethanol. The samples are ground most preferably by hand, avoiding vigorous rotatory motion until ethanol evaporates completely and sieved through various grain size meshes (44, 53, 74, 88, 95, 105 μ). These sieved samples are then mixed with KBr in the ratio of 1 : 20, 1 : 30, 1 : 40 and 1 : 50. Out of these various grain-sized samples with various ratios of KBr, the 53 μ sample with 1 : 20 ratio shows more absorption bands in the IR spectra. By choosing this 53 μ grain-sized sample, it is then grounded for various time intervals using agate mortar by hand-grinding method. The grinding time extends upto 240 hrs (10 days). The spectra are recorded for ten grounded samples (*i.e.* 0 hour – 240 hrs) at an interval of 24 hours. All these IR spectra were measured using Nicolet Avator 360 series FTIR spectrometer. The instrument wave number ranges from 4000 cm^{-1} to 400 cm^{-1} with an accuracy of 0.01 cm^{-1} and resolution of $\pm 1 \text{ cm}^{-1}$.

3. Results and discussion

In our early work [8], the presence of minerals and temperature effects of twelve different limestones collected from Tirunelveli district of Tamilnadu were discussed. From these, one sample was selected for the present study and FTIR spectrum was recorded which is shown in Figure 1 (0 hour). The observed absorption frequencies are tabulated in Table 1. From this table, it is observed that calcite is the major constituent. The other minerals such as kaolinite, nacrite are accessory minerals, feldspar and quartz are impurity minerals. Then the sample was subjected to hand-grinding using agate mortar. The FTIR spectra of grounded samples were recorded for every 24 hours upto 240 hrs and are shown in Figure 2. The observed absorption frequencies are listed in Table 1.

The frequency assignments reported by Herzberg [9] for carbonate minerals are a symmetric stretching ν_1 (1083 cm^{-1}); an out of plane bending ν_2 (909–833 cm^{-1}); a doubly degenerative asymmetric stretching ν_3 (1420–1480 cm^{-1}); a doubly degenerate planar bending ν_4 (769–666 cm^{-1}). But the symmetric oscillation represented by ν_1 is reported to be infrared inactive for calcite; hence only three fundamental modes are ordinarily encountered.

In the present investigation, the IR spectrum of '0' hour sample shows major proportion of calcite having the absorption bands at approximately 1422 cm^{-1} , 875 cm^{-1} , 712 cm^{-1} , and minor bands at 1799 cm^{-1} , 2515 cm^{-1} , 2590 cm^{-1} , 2872 cm^{-1} , 2981 cm^{-1} . According to Ramasamy *et al* [8] and Prost *et al* [10], the OH peaks observed at 3727 cm^{-1} , 3430 cm^{-1} and 2923 cm^{-1} in 0 hour spectrum are due to the presence of kaolinite. It is also noted that the presence of a band at 3640 cm^{-1} be ascribed inter

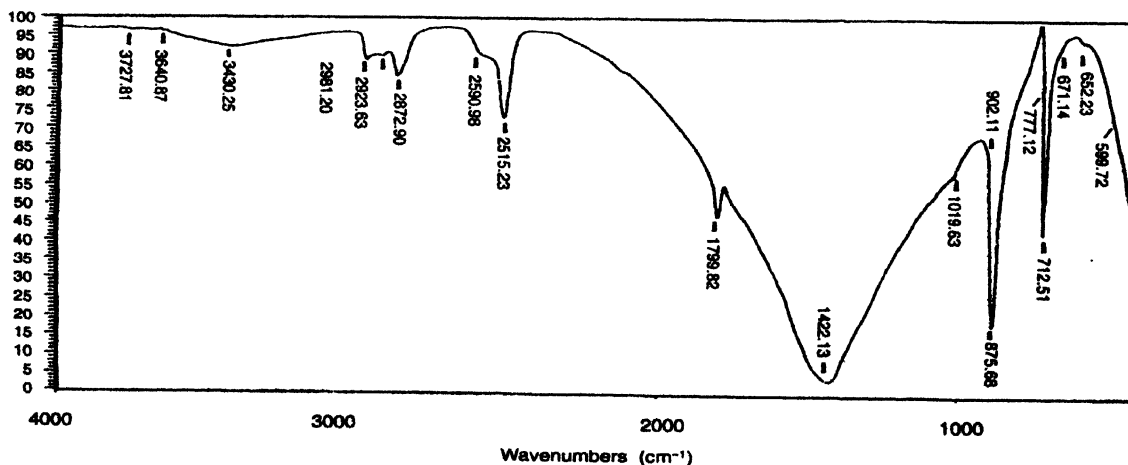


Figure 1. FTIR spectrum of calcitic limestone at 0 hr.

Table 1. Observed absorption frequencies (cm⁻¹) from FTIR spectra at various grinding hours.

0 hr	24 hrs	48 hrs	84 hrs	96 hrs	120 hrs	144 hrs	168 hrs	192 hrs	240 hrs
-	-	-	-	-	-	-	-	-	3794.05 (mk)
3727.81 (K)	3729.57	3729.95	3728.43	3728.21	3726.63	3728.20	3729.96	3729.66	3726.58 (mk)
3640.87 (N)	3646.49	3644.81	3641.62	3648.51	3642.36	3646.06	3643.02	3642.72	3642.86 (N)
-	-	-	-	-	-	-	-	-	3667.63 (mk)
3430.25 (K)	3429.65	3430.54	3429.24	3428.94	3429.88	3429.12	3396.32	3396.67	3396.22 (mk)
2981.20 (C)	2980.76	2981.56	2980.94	2981.00	2983.30	2983.49	2982.00	2979.37	2979.73 (C)
2923.63 (K)	2923.63	2924.73	2924.96	2924.65	2924.54	2924.67	2925.19	2925.38	2924.79 (mk)
2872.90 (C)	2872.93	2873.27	2873.36	2873.30	2873.34 (C)	2856.57 (Ar)	2855.95	2855.79	2854.81 (Ar)
2590.98 (C)	2589.83	2589.44	2589.66	2589.13	2588.52	2588.67 (C)	-	-	-
-	-	-	-	-	-	-	2558.46 (Ar)	2559.63 (Ar)	-
-	-	-	-	-	-	-	2651.24 (Ar)	2651.13 (Ar)	-
2515.23 (C)	2514.93	2514.99	2514.94	2514.84	2515.15	2517.25 (C)	2521.24 (Ar)	2521.93 (Ar)	2521.20 (Ar)
1799.82 (C)	1797.17	1797.35	1796.67	1796.38	1796.24	1794.31 (C)	1788.18 (Ar)	1787.01 (Ar)	1786.26 (Ar)
1422.13 (C)	1427.17	1425.11	1421.38	1424.62	1417.99	1422.14	1422.24 (C)	-	-
-	-	-	-	-	1479.81 (Ar)	1481.18	1480.63	1480.45 (Ar)	1485.90 (Ar)
-	-	1084.58 (Ar)	1084.37	1084.58	1083.07	1082.39	1082.49	1081.53 (Ar)	1087.04 (Ar)
1019.63 (Al)	1023.49 (An)	1021.43	1023.69	1023.72	1024.52	1025.57	1024.75	1022.55	1024.57 (An)
902.11 (G)	902.52 (G)	901.13	902.49	902.52	902.27	903.25	908.26	911.09	-
875.68 (C)	877.10	877.14	877.08	877.02	877.11	877.64	878.61 (C)	-	-
-	857.82 (Ar)	858.07	858.02	857.36	856.80	857.22	857.12	857.26 (Ar)	857.59 (Ar)
777.12 (Q)	777.30	780.83	777.50	780.09	779.05	779.39	781.59	780.92	779.70 (An)
712.51 (C)	712.92	713.17	713.12	713.15	713.18	713.13	713.42	710.36 (Ar)	709.88 (Ar)
-	-	-	-	-	-	-	699.27	699.77	699.86 (Ar)
671.14 (Q)	671.25	668.55	670.32	668.24	666.29	667.84	671.68	672.31	669.86 (An)
652.23 (Al)	652.32	653.02	652.52	652.55	655.50	652.69	656.60	650.12	648.92 (An)
599.72 (Q)	599.72	600.38	595.70	579.23	600.80	600.22	599.79	600.52	596.59 (Q)
-	-	-	-	-	-	-	471.02 (An)	467.95	467.36 (An)
-	-	-	-	-	-	-	-	-	408.20 (An)

K - Kaolinite; N - Nacrite; C - Calcite; Ar - Aragonite; Q - Quartz; Al - Albite; An - Anorthite; G - Gibbsite; mK - meta-Kaolinite

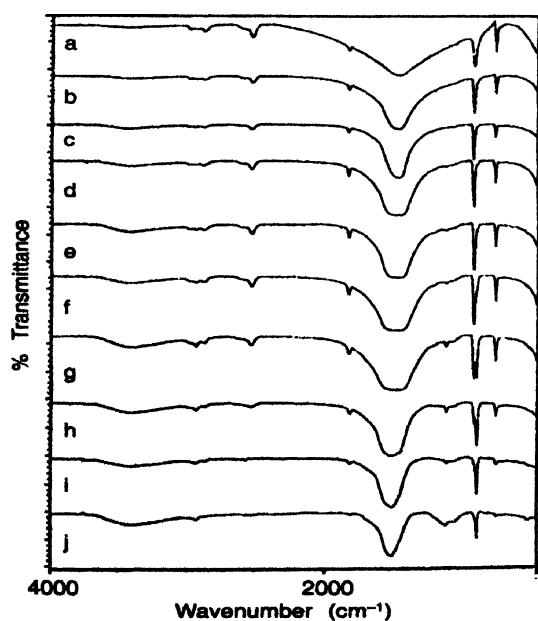


Figure 2. FTIR spectra of calcitic limestone at (a) 0 hr, (b) 24 hrs, (c) 48 hrs, (d) 84 hrs, (e) 96 hrs, (f) 120 hrs, (g) 144 hrs, (h) 168 hrs, (i) 192 hrs and (j) 240 hrs.

layer hydroxyl bonding of nacrite, stacking in the kaolinite structure which in turn, associated with calcite [11,12]. With the view of Russell [11] and Hlavey *et al* [13], the appearance of weak peaks at 777 cm⁻¹, 671 cm⁻¹ and 599 cm⁻¹ denotes the presence of quartz. The band observed at 1019 cm⁻¹, 652 cm⁻¹ and 902 cm⁻¹ indicates the presence of albite and gibbsite, respectively.

Mineralogical changes and structural transformation of rhombohedral calcite to orthorhombic aragonite upon grinding :

During grinding, the following observations were made. There is no change in the position of weak peaks at 599 cm⁻¹, 671 cm⁻¹ and 777 cm⁻¹ upto 240 hrs grinding.

The peak 712 cm⁻¹ is present upto 240 hrs with decrease in its intensity. This clearly confirms the disorderedness in the calcite structure. From 0 hr to 144 hrs, a gradual decreasing trend is observed. After that (192 hrs), there is a sudden decrease in its intensity. At the same time in 168 hrs, a new weak peak is appeared at 699 cm⁻¹.

The intensity of a peak at 875 cm^{-1} slowly decreased and finally disappeared at 192 hours grounded spectrum. At the same time, a new weak peak appeared at 24 hrs spectrum at 857 cm^{-1} . The intensity of this peak increases slowly upto 240 hrs. From this, it is observed that the intensity of peak at 857 cm^{-1} increases as the intensity of peak at 875 cm^{-1} decreases. These changes are due to the formation of aragonite.

The presence of a peak at 902 cm^{-1} in all the grounded spectra, shows no change in position and intensity upto 144 hrs. At 168 hrs, this peak is shifted to 908 cm^{-1} and finally disappeared at 240 hrs. At the same time, a new peak at 471 cm^{-1} at 168 hrs and 408 cm^{-1} at 240 hrs are observed. Thus, the appearance of 408 cm^{-1} and disappearance of 908 cm^{-1} at 240 hrs indicates the formation of new mineral anorthite. This means, calcium carbonate along with quartz reacts with aluminium bearing mineral gibbsite ($\text{Al}(\text{OH})_3$) to form calcium aluminium silicate (anorthite; $\text{CaAl}_2\text{Si}_2\text{O}_8$). During the formation of this mineral, intensity of quartz peaks decreased. This indicates the loss of quartz when reaction takes place.

As far as a peak at 1019 cm^{-1} (0 hr) is concerned, there is a slight shift in peak position at 24 hrs spectra to 1023 cm^{-1} . Above 24 hrs, the shape of this peak is slowly changed and the intensity increased after 144 hrs spectra. This shifts and increase in intensity also show the formation of new mineral anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$).

It is also observed that there is a new peak of 1084 cm^{-1} due to symmetric stretching (ν_1) after 24 hrs spectra. The intensity of this peak increases gradually upto 240 hrs. According to Herzberg [9], the appearance of this band in the spectra suggests that the structural change in the transformation of calcite to aragonite is sufficient to activate this mode (ν_1). For aragonite, this mode is IR active but not for calcite.

A broad peak observed at 1422 cm^{-1} (ν_3) due to doubly-degenerative asymmetric stretching of calcite mineral at 0 hr spectrum is slowly narrowed upto 96 hrs. After that, invisible splitting occurs at 120 hrs upto 144 hrs. At 168 hrs, the peak is visibly splitted into 1422 cm^{-1} and 1480 cm^{-1} . Then the peak appears narrower and there is a loss in intensity at 192 and 240 hrs. According to Adler and Kerr [7], the broadening of a peak at 1422 cm^{-1} in 0 hr, is due to the mineral prevailing low pressure during the formation. However, the narrowing of this peak is due to the mineral prevailing high pressure during grinding. From the splitting of this vibrational

mode in calcite, one can infer that the carbonate groups become increasingly distorted in this phase with high compression. The pressure effects of some carbonates made by William [14] supports these changes. With the view of Adler and Kerr [7], the visible appearance of a peak at 1480 cm^{-1} at 192 hrs, are due to the complete formation of aragonite structure. Due to increasing disorderedness with high compression in rhombohedral calcite, the structure is changed into orthorhombic aragonite.

The combinational modes of vibration ($\nu_1 + \nu_3$) appearing at 1799 cm^{-1} in 0 hr, is not at all changed upto 144 hrs. After that, this peak is shifted to 1788 cm^{-1} without change in its intensity. The appearance of this new peak (1788 cm^{-1}) at 168 hrs also suggests the structural transformation of calcite. At 168 hrs, it is also observed that there is a sudden decrease in intensity of the combinational mode band ($\nu_1 + \nu_3$) appearing at 2515 cm^{-1} . This indicates the disorderedness in the rhombohedral structure [15].

The OH peak observed at 2590 cm^{-1} , shows no change in peak position and shape upto 144 hrs. After 144 hrs, the intensity decreases and the peak is splitted into two peaks (2558 and 2651 cm^{-1}). This trend indicates the disorderedness in the calcite structure and formation of a new structure. According to Herzberg [9], the appearance of these two peaks suggests the formation of aragonite.

As far as the peak at 2872 cm^{-1} , 2923 cm^{-1} and 2981 cm^{-1} are concerned, there is no change in the peak value and intensity upto 96 hrs. After that, it varies with intensity. At the same time, value of 2872 cm^{-1} is changed to 2856 cm^{-1} . All these changes are due to structural variation in the calcite. At 144 hrs, there is a sudden increase in intensity of a peak at 2923 cm^{-1} with respect to other two peaks. This is due to formation of meta-kaolinite.

The intensity of the OH peak belonging to kaolinite mineral (3430 cm^{-1}) is gradually increased upto 240 hrs. But there is a shift in the peak position (3396 cm^{-1}) at 168 hrs onwards. This change is due to the formation of meta-kaolinite. The peaks observed at 3640 and 3727 cm^{-1} have no change upto 240 hrs. But, at 240 hrs, two new peaks 3667 and 3794 cm^{-1} appeared. These are due to the completion of the formation of meta-kaolinite.

From overall observations, the peaks observed for rhombohedral calcite is slowly transformed into orthorhombic aragonite from 48 hrs onwards. The process

is completed at 192 hrs. At the same time, the formation of new minerals are started. According to Russell [11], the appearance of the peaks at 2624, 2550, 1788, 1474, 1083, 857, 712 and 699 cm^{-1} are due to the presence of aragonite. In the present study, all these peaks appeared at 192 hrs. With the view of Herzberg [9], the observation of a single peak at 1422 cm^{-1} belonging to doubly-degenerative asymmetric stretching vibrations (ν_3) upto 96 hrs, are due to presence of unidentate formation of calcite. From 120 to 168 hrs, the splitting of same mode (ν_3) like 1417 cm^{-1} and 1479 cm^{-1} are due to bidentate formation of calcium carbonate, that is of both calcite and aragonite nature. Then the appearance of a single peak at 1480 cm^{-1} in 192 hrs, indicates complete formation of aragonite.

4. Conclusion

FTIR spectroscopy has been used satisfactorily to characterise the calcium carbonate in two different structures. The transformation of rhombohedral calcite to orthorhombic aragonite was completed at 192 hours grinding.

The formation of anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) was visibly identified at 240 hrs due to reactions taken place between quartz (SiO_2), calcite (CaCO_3), gibbsite ($\text{Al}(\text{OH})_3$) and albite ($\text{NaAlSi}_3\text{O}_8$). At 168 hrs, a new mineral metakaolinite is also formed. With the help of doubly-degenerate asymmetric stretching vibration (ν_3), the type of formation of calcium carbonate was also identified (unidentate and bidentate). Thus, a systematic study of carbonate decompositions could give some information during grinding as the equilibrium for carbonate systems are known. A grinding of mixtures can be used in a

rough way to amplify our knowledge of miscibility in some solid systems in which no experimental work has been performed. Finely-ground materials used for solution calorimetry etc., should be carefully examined for phase changes and degradation effects.

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