Effect of grinding on the crystal structure of recently excavated dolomite

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Transmission FTIR technique was used to identify the minerals in recently excavated dolomites and study the structural changes of dolomite upon grinding at various grinding periods. KBr pressed disk technique was found to be very useful for a routine characterization of minerals, for examination of structural modification of dolomite and formation of new minerals during grinding. These minerals and processes were also determined using XRD and SEM analysis. The minerals which were formed upon grinding dolomite, were aragonite, anorthite, metakaolinite and periclase.

Keywords: FTIR, Dolomite, XRD, SEM

1 Introduction

Dolomite is one of the most available abundant form closely followed by calcite, vaterite and comparatively rare aragonite in the sedimentary formation. The occurrence and origin of dolomites have been a subject of interest for over six decades now and probably no other mineral has attracted as much speculation regarding its origin as dolomite. Limestones, dolomites and marbles play an important role in the development of countries which dispose significant confirmed reserves of high quality carbonates. More carbonate rocks are used as dimension or decorative stones; they may be crushed and used as aggregates, concrete ingredients, ballast, animal supplements, soil conditioners, lime production, etc.; they may be ground and used as inert fillers and extenders in numerous industrial products (i.e., paper, glass, plastics and rubber). Dolomite may be considered as a concentrated source of chemical MgO and magnesium metal. They may be used in alloys, die casting, desulphurisation of iron and steel, refractories, pharmaceuticals, glass industry, fertilizers, etc. The dolomite problems have been studied and reviewed by Last1 and Warren2. The main facts of the problem are: (a) it has not been possible to synthesize dolomite under normal sedimentary conditions, inspite of a simple decomposition, CaMg(CO3)2, (b) it is relatively rare in modern sediments, despite its abundance in ancient rocks and (c) the understanding of the inorganic and organic geochemical factors conducive to form dolomite are still largely unresolved. Hence, the study of dolomite gains importance in research.

The IR and XRD spectra have been utilized for the analysis of carbonates by chemists and mineralogists3-8. Adler and Kerr9 and Ghosh10 used the characteristic IR spectra of minerals and rocks for identification of known minerals and mixtures. Adler and Kerr9 have explained a semi quantitative method for the infrared determination of calcite-aragonite ratios in shell materials. The main undesirable impurities in the carbonate rocks are silica, Na2O and alumina. These impurities combine with calcium oxide under grinding to form a slag, which reduce the particle size, pore volume and the amount of available active lime11. Such impurities either occurred in the matrix or came from the material in the crevices and other strata excavated along with limestone. Samples were chosen from quarries in which these impurities were low.

The applicability of infrared spectroscopy to carbonate mineralogy, particularly used in the branch of analytical mineralogy has been studied. The formation of new minerals upon grinding the dolomitic limestone which contain natural mixtures of dolomite and clay has been investigated. The minerals and process are determined with FTIR, XRD and SEM techniques.

2 Materials and Methods

Ten well crystallized recently excavated natural dolomites from Tirunelveli district, Tamilnadu, India, were investigated. The chemical compositions of the samples were determined by the standard analysis12. Its chemical composition in oxide wt% is: MgO-21.03±0.02, CaO-28.94±0.04, SiO2-1.92±0.03,
Fe₂O₃·0.70±0.02, Al₂O₃·0.25±0.05, Na₂O·0.22±0.02, loss of ignition 46.94. The study area lies between North latitudes 8°36′-8°57′ and East longitudes 77°33′-77°51′ falls in the toposheet numbers 58H/9, 58H/10, 58H/13 and 58H/14.

The Nicolet Avatar 360 series FTIR spectrophotometer was used for recording the IR spectra of the samples. The instrument wave number ranges from 4000 to 400 cm⁻¹ with an accuracy of ±0.01 cm⁻¹ and resolution of ±4 cm⁻¹. The instrument was calibrated with the spectra of a standard polystyrene film at room temperature. Every time, before the spectrum of the sample was obtained, the spectrum of the polystyrene film was obtained and checked for the accuracy and transmittance.

The samples were subjected to various pre-treatments in order to remove organic matter and certain other materials to improve the quality of the spectrum. Wet grinding was carried out by placing 5 to 10 mg of the sample in an agate mortar along with 10 to 15 drops of ethanol. The samples were ground most preferably by hand, avoiding vigorous rotatory motion until ethanol evaporates completely. All the ground samples were then sieved through various size meshes 53, 74, 88 and 105 µm. Each grain size sample was mixed with KBr at various ratios 1:10, 1:20, 1:30, 1:40 and 1:50. The pellets were prepared and the spectra were recorded. The maximum absorption and a large number of peaks were observed for the 53 µ grain size samples in the ratio of 1:20 (sample-KBr). A pellet measures 1mm in thickness and 13 mm in diameter. For each sample three pellet specimens were prepared and the spectra were recorded in the region : 4000 to 400 cm⁻¹ at 0 hr (53 µm) as well as higher grinding periods. The pellet specimen containing well resolved maximum number of peaks was taken for the analysis.

The X-ray patterns of the powdered samples were recorded at RT (0 hr, 53 µm) and at various grinding hours using Joel-JDX 8030 diffractometer having a curved graphite crystal diffracted monochromator, with a source of CuKα (λ=1.5406 Å) at 40 V and 20 mA, Ni filter and NaI(Tl) scintillation detector cooled by liquid nitrogen. During the recording of the diffractogram, a narrow slit of 0.1mm was used with a scanning speed of ½°/min and a time constant of 2 sec. The sample was firmly pressed into an aluminium holder, with an area of 30 mm x 30 mm. The diffraction patterns were obtained over the 2θ values in the region 20°-90°. The estimated error in the lattice parameters is of the order of 0.0005 Å. The experimental pattern was compared with the patterns obtained from the JCPDS database. SEM microphotographs were recorded for the sample (0 hr, 120 hr and 264 hr) using JEOL SEM model, JSM-5610 LV with an accelerating voltage of 20 V, at high vacuum (HV) mode and secondary electron image (SEI).

3 Results and Discussion

3.1 FTIR analysis

The FTIR spectra of all the ten samples (53 µ) were recorded and analysed. All the spectra showed similar peaks. The representative FTIR spectrum is shown in Fig. 1(a) and the absorption frequencies are presented in Table 1. The present results are in good agreement with the absorption frequencies, reported by Adler and Kerr, Ghosh and Russell. The absorption peaks observed in the spectrum indicate the presence of dolomite (major), kaolinite, feldspars and talc.

The frequency assignments reported by Hertzberg for carbonate minerals are a symmetric stretching, ν₁; an out-of-plane bending, ν₂; a doubly degenerate asymmetric stretching, ν₃; and a doubly degenerate planar bending ν₄. But the symmetric oscillation
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D — Dolomite; Or — Orthoclase; Al — Albite; K — Kaolinite; ** — Tale; Ar — Aragonite; An — Anorthite; ? — Periclas; mK — meta Kaolinite
In the present case, there is no splitting of the formation of rock or if the same peak is splitted, mineral might have been received low pressure during the mineral had received high pressure during the formation of rock. This suggests that the structural transformation of dolomite to aragonite is sufficient to activate this mode ($\nu_1$). For aragonite, this mode is IR active but not for dolomite. At 96 hr, there is an appearance of a peak at 858 cm$^{-1}$ which might be due to the penetration of aragonite formation. At 120 hr, two new weak peaks appeared at 701 cm$^{-1}$ and 712 cm$^{-1}$ which belongs to $\nu_1$ mode for aragonite. The peaks at 2921 cm$^{-1}$ and 3408 cm$^{-1}$ belonging to kaolinite are shifted to 2929 cm$^{-1}$ and 3421 cm$^{-1}$, respectively at 144 hr which may be due to formation of metakaolinite. The shifting of peak position from 2524 to 2533 cm$^{-1}$ at 192 hr shows the structural changes of dolomite to aragonite. The shifting of the peak from 1018 cm$^{-1}$ to 1023 cm$^{-1}$ at 192 hr and increasing intensity in further periods of grinding show the formation of new mineral anorthite: (CaAl$_2$Si$_2$O$_6$).

A broad peak observed at 1437 cm$^{-1}$ ($\nu_5$) due to doubly degenerative asymmetric stretching of dolomite mineral at 0 hr spectrum is slowly increasing in intensity up to 192 hr and visibly shifted into 1460 cm$^{-1}$, which is due to the formation of aragonite structure. Then the peak appeared narrower and there is a decrease in intensity at 288 hr. According Adler and Kerr, the narrowing of this peak suggested that the mineral had received high pressure during grinding. From the shifting of this vibrational mode in dolomite, one can infer that the carbonate groups become increasingly distorted in this phase with high compression. The pressure effect of carbonates made by William supported these changes. Due to this increasing disorderedness with high compression in rhombohedral dolomite, it gets changed to orthorhombic aragonite.

At 240 hr, the OH peak observed at 2898 cm$^{-1}$ completely disappeared which indicates the disorderedness in the dolomite structure and complete formation of aragonite. The combinational modes of vibration ($\nu_1 + \nu_3$) appearing at 1793 cm$^{-1}$ in 0 hr is
not at all changed up to 240 hr. After that, this peak completely disappeared. At the same time, a new peak appeared at 1169 cm$^{-1}$, which may be due to the formation of anorthite. At 264 hr, the new peak observed at 712 cm$^{-1}$ ($\nu_4$) has disappeared, indicating the break down in the $\nu_4$ mode of aragonite structure. The disappearance of a peak 466 cm$^{-1}$ and appearance of two new peaks at 470 and 432 cm$^{-1}$ at 264 hr also indicate the formation of new mineral anorthite. The position of the peak at 1823 cm$^{-1}$ slowly shifted to lower wave number side 1812 cm$^{-1}$ at 288 hr with slight variation in intensity, which may be due to the disorderedness in dolomite structure. The presence of the peaks at 729 cm$^{-1}$ and 881 cm$^{-1}$ in 288 hr spectrum indicates the formation of periclase (MgO).

Thus, applied forces during grinding give rise to an increase in the proportion of structurally distorted dolomite. The dolomite decomposes directly to CaCO$_3$ (aragonite) accompanied by the formation of periclase (MgO) between 240 and 288 hrs. No evidence was offered for the formation of either CaO or MgCO$_3$. This supports the reaction

$$\text{CaMg(CO}_3)_2 \rightarrow \text{CaCO}_3 + \text{MgO} + \text{CO}_2$$

3.3 X-ray diffraction (XRD)

Using XRD technique, the X-ray diffraction patterns for the selected ground samples (0 hr, 72 hr, 240 hr and 288 hr) were recorded and are shown in Fig. 2. The diffractograms of the original (0 hr) and the ground samples indicate that dolomite suffers significant structural degradation. This distortion of structure induced by grinding is reflected in the line broadening and reflection shifting, as well as the reduction of peak intensities (areas). As seen from Fig. 2, the X-ray line broadening is mainly due to the lattice microstrains rather than microcrystalline size.

As the grinding hour increases, the intensity and position of reflected planes obtained for dolomite changes and finally it is transformed into aragonite. The transformation started at 72 hr and completed at 240 hr. In aragonite, even if the structural transformation takes place, the intensity of the planes is not comparable to structure of dolomite, which indicates the development of structurally deformed form of aragonite. However, the formation of new minerals such as anorthite (CaAlSi$_2$O$_6$) and periclase (MgO) is also observed through this XRD pattern. Under the condition studied, dolomite suffers significant crystal structural alteration due to the rising over the critical amount of the point defects and lattice microstrain. Milling of samples to 288 hrs, the rearrangement of crystal structure (as a secondary mechano-chemical process) causes an increase in the position of structurally undistorted aragonite.

3.4 Scanning electron microscopy (SEM)

Three samples (0 hr, 192 hr, and 288 hr) were selected for SEM analysis. The SEM micro photographs were taken and the particle sizes were noted Fig. 3. From these results, it is observed that the particle sizes are drastically changed for a grinding time of 0 to 288 hr. Initially at 0 hr, the particle sizes
are between 50 and 65 µm approximately. After grinding for 192 hr, the size gets reduced to in the range 1-2 µm. But at 288 hr, again there is a drastic reduction in particle sizes in the range 200-500 nm. At the same time, surface morphology of the particles is not clear. This indicates that the particles are not in definite structure or shape. This may be due to the change in crystalline nature.

4 Conclusions

FTIR technique has been successfully used to study the structural variation of dolomitic limestone at various grinding periods. The IR observations made through the various grinding periods showed the completion of structural changes of dolomite to aragonite at 240 hr, the transformation of kaolinite to meta kaolinite at 144 hr, the formation of new silicate mineral anorthite feldspar at 264 hr, and the formation of periclase (MgO) at 288 hr. This structural transformation was confirmed through XRD studies. Further, the study reveals that the formation of aragonite (CaCO₃) at 240 hrs is not in well ordered form, since the intensity of planes are not comparable to the JCPDS. The reason is due to the reduction of particle size at higher grinding periods. These were confirmed through SEM analysis. The surface morphology of 288 hr sample was not in definite shape indicating that the samples have almost lost its crystallinity.

Thus, grinding of carbonates could pave way for a systematic study of carbonate decomposition and can be used as a tool in understanding the solid systems where no experimental work has been carried out. This study also suggested that finely ground materials used for some applications should be carefully examined for phase changes and degradation effects experimentation.

References