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## **ORIGINAL ARTICLE**

# **Crystallographic characterization of naturally occurring aragonite and calcite phase: Rietveld refinement**



## Md. Sahadat Hossain<sup>a</sup>, Samina Ahmed<sup>a,b,\*</sup>

<sup>a</sup> Institute of Glass & Ceramic Research and Testing, Bangladesh Council of Scientific and Industrial Research (BCSIR), Dhaka 1205, Bangladesh <sup>b</sup> BCSIR Laboratories Dhaka, Bangladesh Council of Scientific and Industrial Research (BCSIR), Dhaka 1205, Bangladesh

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#### **KEYWORDS**

X-ray diffraction; Phase analysis; Eggshells; *Pila globosa*  **Abstract** This research has comprehended the crystallographic characterization of two naturally occurring calcium carbonates phases *e.g.* aragonite and calcite in *Pila globosa* (*P. globosa*) and eggshells respectively. The tools employed to confirm the phases of aragonite and calcite were X-ray diffractoion (XRD) and Fourier Transform Infrared (FT-IR) spectroscopy. Several important crystallographic parameters like crystallite size, lattice parameters, dislocation density, crystallinity index, microstrain, volume of the unit cell, relative intensity of a certain plane, preference growth, and specific surface area were taken into account while assessing the desired aragonite and calcite phases. A number of well-known models e.g. Straight-line model of the Scherrer model, the Monshi-Scherrer model, the Williamson-Hall model, the Sahadat-Scherrer model, and the three-peak model aided the estimation of crystallite size. In all the cases, the observed crystallite size of calcite was larger than that of aragonite. The percentage of calcite and aragonite in eggshell and *P. globosa* were assessed by Rietveld refinement method. Observed results revealed that 97.4% calcite and 2.6% aragonite phases are present in eggshell while in *P. globosa* these percentages exist inversely, i.e. 93.2% aragonite and 6.8% calcite phases.

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#### 1. Introduction

\* Corresponding author.

E-mail address: shanta\_samina@yahoo.com (S. Ahmed). Peer review under responsibility of King Saud University. Production and hosting by Elsevier.



The demand for calcium-based compounds is increasing day by day due to its huge potential in numerous industrial applications. Among various applications, some notable fields include determination of carbon-14 [1], removal of toxic heavy metals [2], formation of hydrogarnet [3], synthesis of pure hydroxyapatite [4], scale structure [5], hyperphosphatemia [6], oxidation agent [7], extracellular lead ion removal [8],

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etc. These diverse uses of calcium carbonate made this material special for further research. Since the application fields are expanding, exploring of new sources of calcium carbonate has become as the demand of time. Synthetically prepared calcium carbonate has received significant attention for various applications and hence,  $CaCO_3$  enriched different natural resources are widely used as the source material for synthesize.

Hitherto, widely reported natural sources of calcium carbonate are eggshells [9], crab shells [10], marbles, limestones, gypsum waste, high calcium fly ash, and hard shells of shellfish such as pearls, oysters, snails, and shrimps [11]. However, since impurity is a concern for natural sources, all the natural sources cannot be used for research purposes where high purity stands as a pre-requisite. Consequently, researchers are adopting various purification practice. Eggshells and snail shells which comprise high calcium content are two important and widely available natural sources of calcium carbonate. Eggshells contain nearly 95% calcium carbonate and are widely used for various types of applications. On the other hand, snail shells also contain high percentage of calcium carbonate (nearly 97%). Nevertheless, three polymorphs of calcium carbonate: (a) calcite, (b) aragonite, and (c) vaterite are in existence naturally. Calcite and aragonite are the stable forms of calcium carbonate while the vaterite is the unstable one. Accordingly, depending on the phases, the solubility of calcium carbonate in water varies. For instance, calcite and aragonite possess lower solubility in water than the vaterite, and this consequence is the outcome of variation in crystal structure. Having the space group R-3c (#167), calcite belongs to the rhombohedral crystal system while aragonite is the member of orthorhombic crystal system with space group Pmcn (#62). On the other hand, crystal system of vaterite is hexagonal and the space group is P63/mmc. Such dissimilarity in crystal structure administers their non-identical characteristics, e.g. density of aragonite, calcite, and vaterite varies folowing a decreasing pattern: 2.94 g/m<sup>3</sup> > 2.71 g/m<sup>3</sup> > 2.65 g/m<sup>3</sup>. [12–14].

However, no significant evidence or crystallographic characterization of naturally occurring calcite and aragonite phases of calcium carbonate is available which limits the investigation of its further potential applications. It is well-known that the properties of crystalline materials depend completely on the crystal structure. Hence, here in this research work we have attempted to comprehend the crystallographic characterization of two naturally occurring calcium carbonates phases *e. g.* aragonite and calcite in *Pila globosa* (*P. globosa*) and eggshells respectively. Further more, the percentage of calcite and aragonite in eggshell and *P. globosa* were quantified by Rietveld refinement method.

#### 2. Materials and methods

#### 2.1. Materials

Eggshells were collected from neighboring restaurants of the Bangladesh Council of Scientific and Industrial Research (BCSIR), Dhanmondi, Dhaka, Bangladesh whereas the *P. globosa* shells were collected from nearby fields of Mirzapur, Tangail. Distilled water was used throughout the research work.

#### 2.2. Software

A number of software were used for precise analysis of the data which are: 'PowdLL converter' was used to convert XRD files for the 'X'pert Highscore Puls' software where data were matched with the data of the Crystallographic open database (COD) and quantification of phases were performed.

- (i) 'Smart Lab Studio II' facilitated the Rietveld refinement with the help of the PDF 4+ (2021) standard database, and "Match-3" was used with COD;
- (ii) 'Origin Pro' and 'Excell-2019' were utilized for plotting XRD and FT-IR data. On the other hand, 'Excell-2019' was used for constructing the graphs of different model equations; and
- (iii) The references of this manuscript were inserted using 'Zotero' software.

# 2.3. Processing of waste materials to synthesize calcite and aragonite

Prior to use, the collected eggshells were boiled for 5 h using distilled water and then the inner membrane was carefully removed by hand. These cleaned shells were then dipped into acetone for another 5 h which facilitated the removal of any trace level presence of the organic parts. After applying an oven drying approah for 6 h at 105°C, the eggshells were finely ground with the aid of high-speed ball mill (Model: Pulverisette 5 classic line Planetary Ball Mill) for 4 h. The powdered sample was then stored in a polyethylene bag for further analysis. On the other hand, after collecting the P. globosa shells, the inner soft part was removed carefully. The hard part which mainly contains calcium carbonate was then processed using analogous acetone dipping procedure coupled with drying and ball milling. This finally processed powder of P. globosa shells was then stored similarly for further analysis.

#### 2.4. X-ray diffraction analysis

A Rigaku Smart Lab XRD was employed to analyze the phases of naturally occurring aragonite and calcite. The data were collected in the 20 range of 15 to 70° maintaining 0.01 steps. Standard silicon reference was engaged to calibrate the machine prior to the sample analysis. The anode material was made of copper, and CuK $\alpha$  ( $\lambda = 1.54060$  Å) radiation was the main reflecting ray. The machine was operated at 23 °C temperature which was maintained with an external water circulating system fixing the water flow rate of 4.6-4.8 L/min. The required voltage and current for the X-ray production from the copper anode were 40 kV and 50 mA, respectively. The Bragg-Brentano parafocusing geometry mode was chosen during data collection as well as calibration. To filter out the  $\beta$ -ray of copper K-shell, a Ni-K $\beta$  filter was placed in front of the detector. A pdf + 4 2022 software was appended with the Smart Lab Studio II to analyze the recorded data.

#### 2.5. FT-IR analysis

An attenuated total reflection (ATR) containing FT-IR machine (IR-Prestige 21, Shimadzu, Japan) was utilized to identify the functional groups of the natural calcium carbonates. The data were collected within the range of 500– $3000 \text{ cm}^{-1}$  wavenumber maintaining a spectral resolution of 4 cm<sup>-1</sup> and an average of 30 scans.

#### 3. Results and discussion

#### 3.1. Phase and crystallographic analysis

As illustrated in Fig. 1, the XRD patterns are characteristic of the naturally occurring aragonite and calcite phases. Clearly, the XRD diffractograms of calcite and aragonite are in well agreement with the standard ICDD database card No:# 00–005-0586 and card no.:# 00–005-0453 respectively. The XRD of naturally occurring calcite exposed reflections at 20 positions 23.13 {01.2}, 29.42 {10.4}, 31.55{00.6}, 36.25 {11.0}, 39.50 {11.4}, 43.27 {20.2}, 46.89 {02.4}, 47.60 {01.8}, 48.49 {11.6}, 57.51 {11.2}, 59.94 {11.9}, 64.45 {30.0}, and 65.51 {00.12}. Such observation strongly supports the existence of calcite phase by 100% in the eggshell. However, since a number of literatures explain the crystallographic parameters of the naturally occurring calcite phase from the eggshells, here we

Fig. 1 X-ray diffraction pattern of calcite and aragonite of natural sources.

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have limited the explanations regarding this calcite phase of eggshells. On the other hand, *P. globosa* shells originated aragonite phase shows the reflections at 20 positions 26.18, 27.22, 31.09, 32.76, 33.09, 36.12, 37.87, 38.42, 41.42, 42.86, 45.86, 48.31, 50.12, 52.42 and 52.88 which are symbolic for the respective planes (111), (021), (002), (121), (012), (200), (112), (130), (211), (220), (221), (041), (132), (113) and (231). The recorded XRD reflections of the aragonite phase of *Pila globosa* shells were indistinguishable from the ICDD database assigned for the aragonite phase. The XRD pattern confirmed the presence of aragonite phase in the *P. globosa* shells.

Nevertheless, in order to explore further crystallographic analysis, crystallite size, lattice parameters, dislocation density, crystallinity index, microstrain, and volume of unit cell were estimated with the aid of equations 1-5 [15,16].

Crystallite size, 
$$Dc = \frac{K\lambda}{FWHM.cos\theta}$$
 (1)

Dislocation density, 
$$\delta = \frac{1}{(D_c)^2}$$
 (2)

Lattice parameter equation (rhombohedral),  $(\frac{1}{d_{rr}})^2$ 

$$=\frac{4}{3}\left(\frac{h^2+hk+k^2}{a^2}\right)+\frac{l^2}{c^2}$$
(3)

Lattice parameter equation (orthorombic),  $\frac{1}{r^2}$ 

$$=\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$
(4)

Microstrain, 
$$\varepsilon = \frac{FWHM}{4\tan\theta}$$
 (5)

Crystallinity index, 
$$CI = \frac{H_1 + H_2 + H_3}{H_1}$$
 (6)

where, FWHM = full width at half maxima (in radian); Scherrer's constant K = 0.94;  $\lambda$  = wavelength = 0.15406 nm;  $\theta$  = diffraction angle; a, b, c, and h, k, l = lattice parameters and plane of crystals, respectively; H = peak height.

The crystallite sizes of the naturally occurring calcite and aragonite samples were estimated employing equation (1) and the measured values were 110, and 34 nm, respectively. The dislocation density, microstrain and crystallinity index of the calcite phase of naturally occurring crystals were 0.068, 0.063, and 1.142, respectively and these values were calculated employing equations (2), 5, and 6. Using the above equations, the dislocation density, microstrain, and crystallinity index for aragonite phase were calculated as 0.94, 0.23, and 1.88, respectively. The lattice parameters of the calcite crystals were obtained from equation (3) and the values were: a = 4.97 Å, b = 4.97 Å, and c = 16.98 Å. These values matched very well with the standard ICDD database. The lattice parameters of the aragonite phase were measured engaging equation (4) and the values were a = 4.97 Å, b = 7.97 Å, and c = 5.74 Å, and identical results were documented in the ICDD database.

The plane of the crystals which is preferred by the natural phenomena can be predicted by the growth preference of the crystal plane and this can be estimated from the relative



intensity of the crystal plane. The relative intensity (RI) of a plane can be assumed from another three strong peak intensities. For the case of the calcite phase, the relative intensity of the (104) plane was calculated with respect to (113), (202), and (110) planes. To estimate the preference growth, initially, the relative intensity of the standard sample was measured for the same planes. For the calcite phase, equation (7) was used [17].

Relative intensity, RIcalcite = 
$$\frac{\mathbf{I}_{(104)}}{\mathbf{I}_{(113)} + \mathbf{I}_{(202)} + \mathbf{I}_{(110)}}$$
 (7)

The relative intensity of the naturally occurring aragonite for (111) plane was explored in relation to the (021), (012), and (221) planes. A similar mathematical expression (equation (8)) of equation (7) was employed for the natural and standard aragonite phases.

Relative intensity, RIaragonite = 
$$\frac{I_{(111)}}{I_{(021)} + I_{(012)} + I_{(221)}}$$
 (8)

The calculated relative intensities of calcite and aragonite for (104) and (111) planes were 3.5637, and 0.74, respectively whereas the corresponding standard relative intensities of calcite (card No:# 00–005-0586), and aragonite phase (card no.:#00–005-0453) were 2.0 and 0.61. The preference growths of the calcite and aragonite were estimated by equation (9) [16].

Preference growth, P = 
$$\frac{Relative intensity_{sample} - Relative intensity_{standard}}{Relative intensity_{standard}}$$
(9)

Consequently, the growth preferences of calcite and aragonite along (104) and (111) planes were 0.78 and 0.21. The positive values of the preference growth along (104) and (111)planes carried good evident to be the favored growth by the natural phenomena. It can be predicted from the positive values that the formation process of calcite and aragonite in the natural system is thermodynamically stable.

By considering the density of the standard database and using the measured crystallite size, the specific surface area of the calcite and aragonite were computed engaging equation (10) [18].

Specific surface area, 
$$S = \frac{6 \times 10^3}{\rho \times D_c}$$
 (10)

The computed values of the specific surface areas of the calcite and aragonite were 18.45, and 63.97  $m^2/g$ , respectively.

The volume of the unit cell was calculated from equation (11) for the crystal of naturally occurring calcite which belongs to the R3c (167) space group [19].

The volume of the calcite unit cell, 
$$V = \frac{\sqrt{3}}{2} \times a^2 c$$
 (11)

Equation (11) carried the same notation as described for the lattice parameters of crystal, and the measured volume of calcite was  $363 \text{ Å}^3$ .

The orthorhombic unit cell of aragonite crystals belongs to the Pmcn (#62) space group, and the assigned unit cell volume mathematical expression is illustrated in equation (12) [19].

The volume of the orthorhombic unit cell, V = abc (12)

The naturally occurring unit cell volume of the aragonite phase of *P. globosa* shell is 227.36  $\text{\AA}^3$ .

#### 3.2. Crystallite size calculation

#### 3.2.1. Liner straight-line method of Scherrer's equation

The Scherrer equation was reformed to determine crystallite size and the simplest model is the Liner straight-line model of Scherrer's equation (LSLMSE). The Scherrer equation was shuffled to predict the crystallite size more precisely considering all the generated peaks in the XRD pattern. The crystallite size ( $D_L$ ) was measured utilizing equation (13), and the details are documented elsewhere [20].

Liner straight – line model, 
$$\cos \theta = \frac{K\lambda}{D_c} \times \frac{1}{\beta} = \frac{K\lambda}{D_L} \times \frac{1}{\beta}$$
 (13)

This equation carried the conventional notation of crystallography. To calculate the crystallite size, this equation was compared with the linear straight-line equation (y = mx + c). Plotting  $\cos \theta$  (in degree) and  $\frac{1}{\beta}$  (in radian) in the y-axis and the x-axis, respectively, a straight line was drawn. A detailed procedure of this model was explained elsewhere [20]. Two graphs were built for the calcite and aragonite and presented accordingly in Figs. 2 and 3. The crystallite sizes utilizing this model are inscribed in the respective Figure. The crystallite sizes calculated from this model are too large (2310 and 462 nm) which made this model invalid for the natural calcite and aragonite phase of calcium carbonate.

#### 3.2.2. Monshi-Scherrer model

Moshi-Scherrer Method is widely recognized as the modified Scherrer formula which was constructed by reordering and



**Fig. 2** Crystallite size of calcite (eggshell) using Liner straightline method of Scherrer's equation.



**Fig. 3** Crystallite size of aragonite (*Pila globosa* shell) using Liner straight-line method of Scherrer's equation.

putting logarithm on each side of the Scherrer equation. The crystallite size  $(D_{M-S})$  was computed from the Monshi-Scherrer formula by engaging equation (14), and the details of the model were reported in several literatures [21,22].

Monshi – Scherrer model, 
$$\ln \beta = \ln \frac{1}{\cos \theta} + \ln \frac{K\lambda}{D_{M-S}}$$
 (14)

By plotting  $\ln \beta$  in the y-axis, and  $\ln \frac{1}{\cos \theta}$  in the x-axis, graphs were constructed which were illustrated in Fig. 4 for the calcite and Fig. 5 for the aragonite phase. A very reasonable crystallite size was found for each sample of calcite and aragonite phase which are registered in the respective illustration.

#### 3.2.3. Williamson-Hall plot

The XRD peak broadening occurs for three reasons such as crystallite size, instrumental effects, and intrinsic strain of crystal. The Williamson-Hall model was designed to estimate crystallite size ( $D_{W-H}$ ) and strain ( $\varepsilon$ ) considering the intrinsic strain and the mathematical expression is given in equation (15) [23,24]. This model was documented in detail previously [22].

Williamson – Hall model, 
$$\beta_{\text{total}} \cos \theta = \frac{K_B \lambda}{D_{W-H}} + 4\varepsilon \sin \theta$$
 (15)

Figs. 6 and 7 represent the illustration of the calcite and the aragonite phases, respectively as accomplished by applying the Williamson-Hall plot containing crystallite size and intrinsic strain. The strain in the case of calcite was negative which carried evidence of the compressive strain inside the eggshells. But, the aragonite phase was under tensile stress resulting in a positive value.



Fig. 4 Crystallite size of calcite (eggshell) from Monshi-Scherrer model.



Fig. 5 Crystallite size of aragonite from Monshi-Scherrer model.



**Fig. 6** Crystallite size and intrinsic strain of calcite utilizing Williamson-Hall plot.



**Fig. 7** Crystallite size and intrinsic strain of aragonite utilizing Williamson-Hall plot.

#### 3.2.4. Sahadat-Scherrer model

Very recently, to calculate the crystallite size more accurately, another modfied model named as Sahadat-Scherrer model was built minimizing the shortcomings of the previously mentioned models and the detail of this model is publicized in the literature [15]. The mathematical equation of this model is presented in equation (16) which was constructed from the basis of the Scherrer equation. In this model, all the peaks of the calcite and aragonite were considered like the previously mentioned models but the difference was to build another straight line passing through the origin. The straight line passing through the origin leads the model to be more accurate. To plot a graph from this model,  $\cos\theta$  was plotted on the y-axis and 1/FWHM was plotted on the x-axis. An intercept passing through the origin was constructed after building a straight line. This intercept was matched with the y = mx equation and crystallite size was computed.

Sahadat – Scherrer model, 
$$cos\theta = \frac{K\lambda}{D_{S-S}} \times \frac{1}{FWHM}$$
 (16)

Figs. 8 and 9 visualize the crystallite sizes (inscribed inside the figure with respective equations) estimated from the Sahadat-Scherrer model of calcite and aragonite, respectively.

#### 3.2.5. Three peaks model

A minor modification of the Scherrer equation was employed to measure crystallite size where three strong peaks needed to be considered and the details of this model were documented in the literature [15]. The mathematical expression of this model is expressed in equations 17–20 where the notation carried the conventional significance. Here, the average reflection angle, full width at half maxima, and wavelength were considered.

$$\theta_{Average} = \frac{\theta_{peak-1} + \theta_{peak-2} + \theta_{peak-3}}{3}$$
(17)

$$\lambda_{\text{Average}} = \frac{\lambda_{\text{K}-\alpha \, 1} + \lambda_{\text{K}-\alpha \, 2}}{2} \tag{18}$$

$$FWHM_{Average} = \frac{FWHM_{peak-1} + FWHM_{peak-2} + FWHM_{peak-3}}{3}$$
(19)

Three peaks model, Daverage = 
$$\frac{K\lambda_{average}}{FWHM_{average}cos\theta_{average}}$$
 (20)

The average crystallite size of three strong peaks of calcite and aragonite are 65 and 35 nm, respectively.

#### 3.2.6. Functional groups analysis

An FT-IR machine was engaged to identify the functional groups of calcite and aragonite, and only CO<sub>2</sub> group is IR active in these compounds. There are four vibrational modes (symmetric stretching, asymmetric stretching, and two bendings) of the carbonate group, and three of them are IR active. The out-of-plane bending vibration  $(v_2)$  of calcite  $(CO_2)$ appeared at 875 cm<sup>-1</sup>, and the degenerate bending mode of  $CO_2$  appeared at 711 cm<sup>-1</sup>. For the presence of calcium carbonate in eggshells, a peak appeared at 1406 cm<sup>-1</sup>, but in the P. globosa shells, two adjacent peaks were noticed at 1455 and 1470  $\text{cm}^{-1}$ . The aragonite phase generated peaks at 1082 cm<sup>-1</sup> for symmetric stretching vibration  $(v_1)$  and at 853 cm<sup>-1</sup> for out-of-plane bending vibration (v<sub>2</sub>) [25]. Only the aragonite phase represented the symmetric stretching vibration while this peak was absent in the case of calcite. This peak is normally used for the separation of the aragonite and the calcite phases. The v2 mode was present for both of the compounds, but the calcite phase revealed this a little bit higher wavenumber  $(875 \text{ cm}^{-1})$  than that of the aragonite phase (853 cm<sup>-1</sup>). A similar peak of degenerate bending mode like the calcite was also noticed for the aragonite phase at



Fig. 8 Crystallite size of calcite utilizing Sahadat-Scherrer model.



Fig. 9 Crystallite size of aragonite utilizing Sahadat-Scherrer model.

711 cm<sup>-1</sup>. In addition to this, another peak was visualized at 702 cm<sup>-1</sup> for the doubly degenerate aragonite phase (v<sub>4</sub>). The literature also described similar types of peaks [26–29]. Fig. 10 illustrates the FT-IR spectra of calcite and aragonite phases from naturally occurring eggshells and *P. globosa* shells.

#### 3.2.7. Rietveld refinement of calcite and aragonite phase

When we are talking about the natural sources of calcite and aragonite, there may be a combination of the mentioned phases as the other most abundant phase (vaterite) of calcium



Fig. 10 FT-IR of calcite and aragonite.

carbonate is unstable. As there was no significant intense peak combination to easily separate each phase. To overcome this limitation, Rietveld refinement was performed to quantify the aragonite phase in the eggshell (calcite) and the calcite phase in the *P. globosa* (aragonite). This refinement is widely applicable if it is difficult to separate the diffraction peaks in a registered pattern. Rietveld refinement was performed to evaluate the quantity of calcite and aragonite phases in two naturally occurring calcium carbonates, and in addition to this quantification, lattice parameters such as a, b, c,  $\alpha$ ,  $\beta$ , and  $\gamma$ were also refined. Lattice volume and strain percentage were also measured. Supplementary Figs. 1 and 2 represent the calcite and aragonite which were experienced for Rietveld refinement. The number of points is crucial for the Rietveld refinement [30] here 5,500 points ( $2\theta = 15$  to 70° and steps of 0.01°) were considered for the quantification of phases. The quantification of the natural eggshells phase using Rietveld refinement was 97.4% calcite phase and 2.6% aragonite phase. On the other hand, the P. globosa contained 93.2% aragonite phase and 6.8% calcite phase. From this phase quantification, it was assumed that the natural source of calcite and aragonite contained other phases. All the resulting data from Rietveld refinement are registered in Table 1. A small variation was noticed among the lattice parameters of the calcite phase between the eggshells and P. globosa. Lattice volume and strain percentage were also very close to each other for the calcite phase in eggshells and P. globosa shells. But, in the case of the aragonite phase in eggshell and P. globosa, a significant variation was noticed. The lattice parameter values of b and c presented a noticeable difference from each other and also from the standard (as described previously). There was a very close relationship according to the standard values of lattice parameters and volume of the aragonite phase in the P. globosa shells but deviation was noticed in eggshells. The lattice volume of the aragonite phase has differed abnormally in eggshells and P. globosa shells which resulted from the change of lattice parameters more precisely for b and c. Each phase retained the strain percentage whether it was eggshells or P. globosa shells. The strain in the calcite phase whether from eggshells or P. globosa was three times higher than the aragonite phase. The eggshells contained about 97% of calcite with a three times higher strain percentage which made contraction of lattice volume of the aragonite phase. But, in the case of P. globosa, though the calcite retained its higher strain percentage, the amount of calcite was low which could not influence sufficiently for too much lattice contraction. The higher strain percentages of the calcite phase in eggshells were also visualized in the XRD pattern showing Rietveld refinement of eggshells (more clearly presented in supplementary Fig. 1). The volumes of the unit cell of aragonite in eggshells and *P. globosa* shells were 182.97 and 227.102 Å<sup>3</sup>, respectively. The contraction of unit cell volume has occurred where the percentage of the aragonite phase was lower (2.6% in eggshells). A similar trend of unit cell volume was also visualized for the case of the calcite phase in the eggshells (367.36 Å<sup>3</sup>) and the *P. globosa* (367.01 Å<sup>3</sup>). The higher percentage of a phase in a combined-phase compound may hinder the uniform expansion of a lesser phase percentage which ultimately shortens the lattice parameters and consequently reduced unit cell volume is obtained.

There is a good relationship between the crystallite size and strain in crystals. If the crystallite size is large then the internal stress is higher and vice versa. From the literature, it was noticed that the 44% calcite phase was converted to calcium oxide within 800°C, but only 35% weight loss was reported for the aragonite phase [31-33]. But, no literature has discussed the effects of strain on calcium carbonates. From profile fitting utilizing Rietveld refinement, it was noticed that the strain percentage of calcite is much higher than that of the aragonite phase in eggshell and also P. globosa shells. This higher strain percentage may affect the conversion of calcium carbonate to calcium oxide as upon heating the molecule trends to get stress relaxation. The crystallite size of calcite was higher than that of aragonite which was calculated from a single peak using the Scherrer model, Straight line model of the Scherrer model, Monshi-Scherrer model, Williamson-Hall model, Sahadat-Scherrer model, three peak model. In addition to these models, the graphical representation of the calcite and aragonite in the XRD pattern carried good evidence of smaller crystallite size of the aragonite phase than the calcite phase. As there was a low strain percentage in the case of aragonite, higher energy was required to vibrate the molecule for representing FT-IR activity. The FT-IR spectrum of aragonite revealed the appearance of the same peak relatively higher wavenumber than that of calcite and the energy is directly proportional to the wavenumber.

#### 4. Conclusion

Waste eggshells and *P. globosa* shells can be potential natural sources of calcite and aragonite. Two different phases were identified in the natural eggshells and *P. globosa* shells utilizing

Parameters	Eggshells		Pila Globosa	
Phase	Calcite	Aragonite	Calcite	Aragonite
Percentage (quantity)	97.4	2.6	6.8	93.2
a Å	4.98707	5.06540	4.99425	4.95919
b Å	4.98707	4.76580	4.99425	7.96796
c Å	17.0559	7.57934	16.9906	5.74729
$\alpha$ (degree)	90.000	90.000	90.000	90.000
β (degree)	90.000	90.000	90.000	90.000
γ (degree)	120.000	90.000	120.000	90.000
Lattice volume $Å^3$	367.363	182.970	367.012	227.102
Strain percentage	0.153	0.0561	0.1446	0.050

 Table 1
 Generated data from Rietveld refinement for eggshell and Pila globosa.

XRD patterns with the support of FT-IR spectra. Rietveld refinement was performed for eggshells and *P. globosa* shells to quantify the amount of each phase in the natural sources. A small amount (2.6%) of the aragonite phase was quantified in natural eggshells, and 6.8% aragonite phase was in *P. globosa* shells. The crystallite size of the natural calcite phase in eggshells is relatively higher than that of the aragonite phase in *P. globosa* shells. The strain percentage in calcite is larger which ultimately affects a number of crystallographic parameters. The crystallographic analysis of the natural aragonite phase along with the natural calcite phase will open new research fields assisting in a better understanding of crystal structure.

#### Author contributions

Md. Sahadat Hossain conceived and designed the experiment, analyzed the data, wrote the original manuscript, and performed the experiment. Samina Ahmed supervised the overall work and assisted in writing the manuscript.

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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