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Special properties of the bivalve shell in the sea of Vietnam

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KEYWORDS

Bivalve shell
Oyster shell
Mussel shell
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Cockle shell
Sea snail shell
Structure
Mineral composition

ABSTRACT

This paper presents the results of an investigation to identify differences in chemical composition, mineral composition, and structure of the bivalve shell under the same living conditions of VietNam's marine environment. The bivalve mollusc shells presented by the research team in this paper include: Pacific Oyster shell, sea Oyster shell, Clam shell, Mussel shell, Cockle shell, sea snail shells. These studies are compared with the properties of limestone due to the similar $CaCO_3$ content. Based on the special characteristics of the bivalve shells. This research provides suitable direction for their practical application.

1. Introduction

According to statistical documents, bivalve shells are raised in many countries around the world: China, Malaysia, Indonesia, the Philipines, Taiwan, Korea, Japan, and Vietnam. China has the largest bivalve shells production in the world. On average, 1 kg of molluscs produces 370 to 700 g of shell [1]. The total amount of Oyster shell wastes is estimated at 300,000 tons/year in China [2], while the amount of bivalve shells in Taiwan exceeds 160,000 tons/year [2]. On average, approximately 10 million tons of bivalve shell is disposed of in landfills per year [2]. The chemical composition of the bivalve shell contains CaCO3 and negligible amounts of other components [3]. Bivalve shell exists in three polymorphic forms depending on the conditions they live in, including: Aragonite (needle-shaped), Vaterite (spherical), and Calcite (rhombic), with Calcite being the most thermodynamically stable form. Vaterite and Aragonite can easily undergo metamorphism and transform into the more stable polymorphic form of Calcite [4]. Bivalve shells have many different applications in industries such as: food, pharmaceuticals [5], cosmetics, Raw material for cement production [6], water purification [7], and environmental engineering [8]. Vietnam is a country with more than 3,610 km of coastline and over 3,000 diverse large and small islands. Provinces along the coast and islands have developed aquaculture industries, especially bivalve molluscs such as:

- Pacific Oysters (Province of Quang Ninh, Hai Phong, Khanh Hoa),
- Clams (mainly raised in the Province of Nam Dinh, Thanh Hoa, Nghe An, Ha Tinh,
- Cockles, Mussels and snails (mainly harverted from natural environment.

Bivalve molluscs are cultured for 5-6 months, then they are then harvested and sent to processing factories to obtain their meat, which is either exported or consumed domestically, while their shells are discarded. According to statistics, during the Oyster harvest season (April-October every year) in Quang Ninh province, approximately 400 to 450 tons per day of Oyster shells are discarded [9]. Additionally, industrial factories the process Clams and snails generate several hundred tons of garbage per day from the north to the south. Although living in the same marine environment, each species has a different process of forming its shell structure. The following research results provide details on the composition and structure of bivalve shells in marine environmental conditions in Vietnam, and suggest the application of bivalve shells in construction materials.

2. Methodology and materials used in the study

2.1. Methodology

- The chemical composition of bivalve shells was analyzed using an Arl Thermo instrument (Germany) by X-ray fluorescence (XRF);
- The mineral composition of the bivalve shells was analyzed using a D8-advance Bruker instrument (Germany) with X-ray diffraction (XRD);
- The structure and morphology of the bivalve shells was determined using a Jeol JMS 6490, scanning electronic microscope (SEM) (Jeol, Japan).

2.2. Materials

The study includes the following types of bivalve shells: Pacific Oysters (TBD Oysters) were taken in Van Don - Quang Ninh province; Clam shells were taken in Hau Loc - Thanh Hoa province; Sea Oysters, sea snails, Mussel shells, and Oysters were quarried in Ky Anh - Ha Tinh province, and Limestone from Phu Thanh- Hoa Binh province. Images of the bivalve shells used in the study are provided in Figures 1 to 6.

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Figure 1. Pacific Oyster shells.

Figure 2. Clam shells.

Figure 3. Sea Oyster shells.

Figure 4. Sea Snail shells.

Figure 5. Mussel shells.

Figure 6. Cockle shells.

3. Results and discussion

The bivalve shells collected in the laboratory were washed to remove soil, moss, and any remaining meat, and then dried at a temperature of 100 degrees Celsius.

3.1. Chemical composition

The results of the chemical composition analysis of bivalve shells by X-ray fluorescence (XRF) method are given in Table 1.

Table 1. The chemical Composition of bivalve shells and Limestone.

Chemical composition	Limestone, %	Pacific Oyster shell,%	Sea Oyster shell,%	Clam shell,%	Sea Snail shell,%	Mussel shell,%	Cockle shell,%
MKN	42.59	43.66	42.70	44.60	46.10	46.90	44.40
SiO_2	1.56	1.51	1.21	0.17	0.30	0.28	0.28
Fe_2O_3	0.17	0.10	0.000513	0.000404	0.000904	0.000805	0.000805
Al_2O_3	0.35	0.11	0.28	0.000201	0.14	0.13	0.12
CaO	53.04	51.94	53.80	53.80	50.60	51.50	53.80
MgO	0.2	0.20	0.0	0.11	0.45	0.00	0.00
SO_3	0.00	0.54	0.47	0.21	0.28	0.22	0.26
K_2O	0.02	0.06	0.00031	<0.0001	0.11	<0.0001	0.000215
Na_2O	0.01	0.40	0.46	0.53	0.77	0.41	0.68
TiO_2	0.02	0.08	0.00	0.00	0.00	0.00	0.00
Cl^-	-	-	0.00073	0.000163	0.28	0.000167	0.000358
P_2O_5	-	-	0.000565	0.000118	0.000684	0.000612	0.000229
ZnO	-	-	<0.0001	<0.0001	0.000164	0.000155	0.000160
SrO	-	-	0.15	0.29	0.19	0.31	0.21

Based on the analysis results of Table 1, we have plotted the CaO and MKN values in Figures 7 and 8.

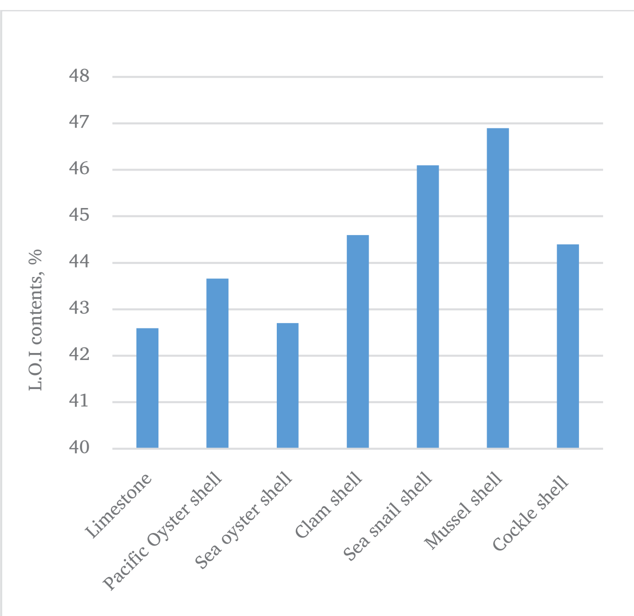


Figure 7. L.O.I contents of bivalve shells.

The results of chemical composition analysis of six types of bivalve shells showed that each type has a different chemical composition. Clam shells, sea oysters, and cockle have the highest CaO contents, accounting for 53.80% and CaO contents equivalent to Phu Thanh Limestone (53.04%). The lowest CaO content is found in Pacific oyster Shell, sea Snail Shells, and mussel Shells (50 - 51%). Other compositions such as K_2O, Na_2O, TiO_2, Cl^-, P_2O_5, ZnO, and SrO have negligible content.

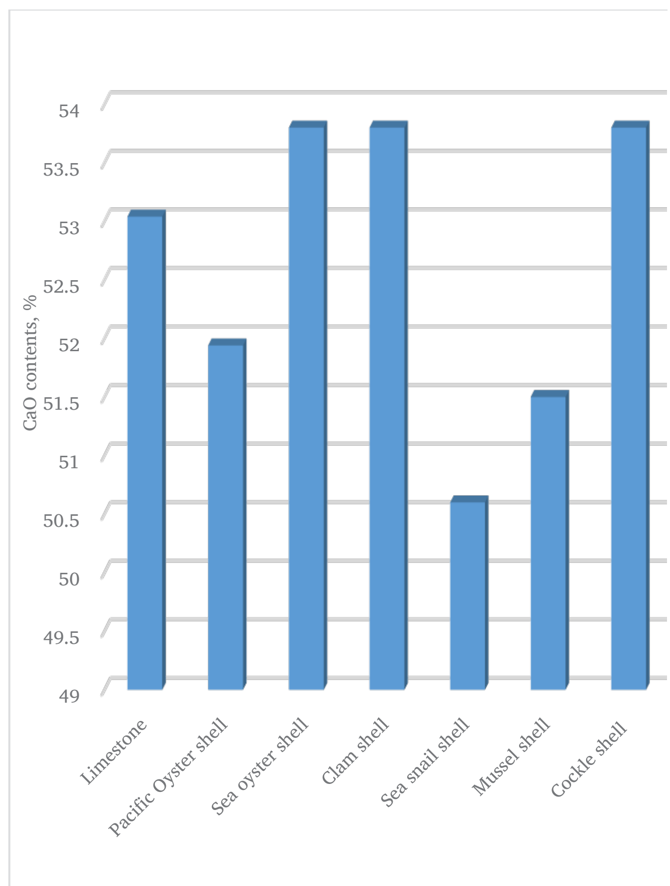


Figure 8. CaO contents of the bivalve shells.

3.2. Mineral composition

The analysis results of bivalve shells are given in Figure 9.

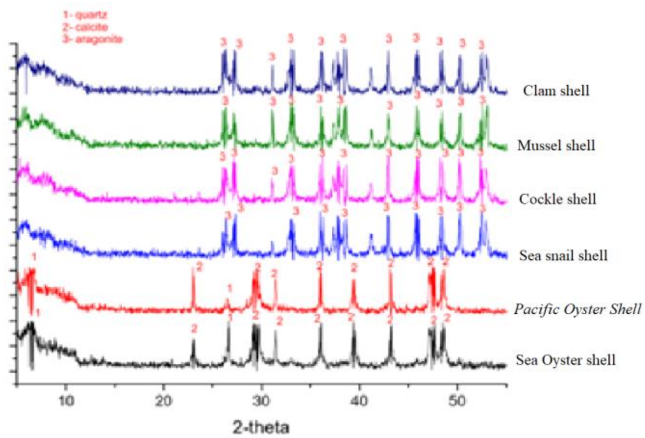


Figure 9. XRD results of bivalve shells.

Based on the XRD results of bivalve shells, we have the follwing comments:

a. Pacific Oyster Shell

Pacific Oysters are Oyster varieties imported from Australia but cultured and transplanted as seeds to adapt to the living conditions in Vietnam's sea. The XRD analysis results of TBD Oyster shells are shown in Figure 9, the mineral composition is mainly calcite with the following special peaks: d = 3,03275; 2.84217;2,49261; 2.09263; 1.91154.

b. Sea Oyster shell

Sea Oysters live naturally in the Vietnamese sea. Sea Oyster shells are about 1/3 -1/5 smaller in size compared to Pacific Oysters shells. The results of the XRD analysis of Oyster shells are shown in Figure 9, and the mineral composition is mainly Calcite with the following special peaks: d = 3.85351; 3,03144; 2,49226; 2.28137; 1.91141; 1.87418.

Sea Oyster shells contains many impurities, so the XRD analysis results show the presence of minerals such as Quartz (SiO_2), Labradorite (Na 0.34 Ca 0.66 Al 1.66Si 2.34O8); Mordenite (Ca. 0.41Al 0.98Si 5.03 O.12(H_2O) 0.465 and Aldermanite - Mg. 5Al .12(PO_4)8 .(OH)22. 32 H_2O.

c. *Clam shell*

The XRD analysis results of Clam Shells are shown in Figure 9, and the main mineral composition is Aragonite with the following special peaks: d= 3.3955; 2.70089; 2.3728; 1.9767; 1.7430.

d. Mussel shell

The results of the XRD analysis of Mussel shells are shown in Figure 9, and the main mineral composition is Aragonite with the following special peaks: d= 3.3905; 2,7000; 1.9761; 1.4732. Additionally, there are Calcite minerals at d = 3.03514 and Yeelimite minerals at d = 3.7566. The presence of Yeelimite minerals may indicate the presence of moss impurities clinging to the Mussel shells.

e. Cockle shells

The results of the XRD analysis of Cockle shells are shown in Figure 9, and the main mineral composition is Aragonite with the following special peaks: d= 3.3964; 2.7025; 2.3734; 1.9771; 1.7444. There is also the presence of Yeelimite mineral at d = 3.7566. The appearance of Yeelimite mineral may indicate the presence of moss impurities clinging to the Cockle shells.

f. *Sea snail shells*

The results of the XRD analysis of sea snail shells are shown in Figure 9, and the main mineral composition is Aragonite with the following special peaks: d = 3.3943; 2.7008; 2.3714; 1.9771; 1.7444. There is also the presence of Yeelimite mineral at d= 3.7566. The appearance of Yeelimite mineral may indicate the presence of moss impurities clinging to sea snail shells.

The bivalve shells have the same living conditions in the marine environment, but they have different mineral compositions and are divided into 2 clasifications:

- Clasification 1: contains Calcite minerals similar to Limestone, such as Pacific Oyster shells, sea Oyster shells, and Mussel shells.
- Clasification 2: contains Aragonite minerals, including Clam shells, sea snail shells, and Cockle shells.

3.3. Structural shape analysis

In the world of the published results, bivalve shells were examined to determine the main minerals present, manely Calcite and Aragonite. The research team conducted a microstructure analysis of the samples using scanning electron microscopy (SEM) at magnifications of 2000 and 4000 times the follwing:

3.3.1. Limestone

The structural analysis of Phu Thanh Limestone using scanning electron microscopy (SEM) is presented in Figure 10. Limestone exhibits a complete cylindrical structure, which is typical of Calcite mineral, with an average size of 10 μm.

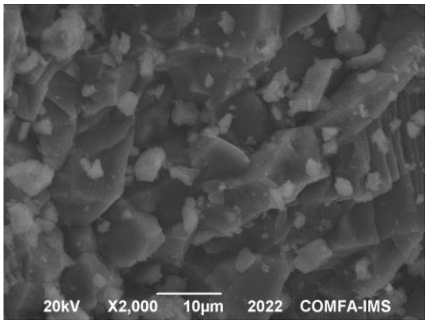


Figure 10. Scanning electron microscopy analysis (SEM) of Limestone.

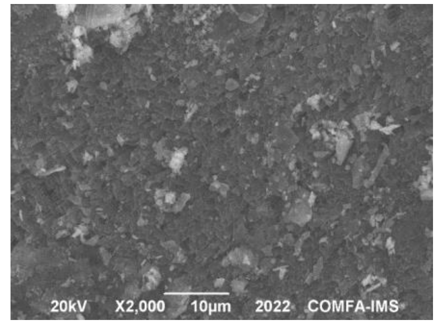


Figure 11. Scanning electron microscopy analysis (SEM) of Oyster shell.

3.3.2. Pacific Oyster shell TBD

The structural analysis of the Oyster shell using scanning electron microscopy (SEM) is presented in Figure 11. The results of the structural analysis reveal that the Oyster shell TBD primarily consists of cylindrical and plate-shaped minerals, which are typical of Calcite minerals. The structure is similar to that of Limestone. However, the average size of the Calcite minerals in TBD Oyster shells is 1µm, which is one - tenth the size of the Calcite minerals found in Limestone.

3.3.3. Sea oyster shells

Sea Oyster shells were subjected to structural analysis using scanning electron microscopy (SEM) as shown in Figure 12. The results of the structural analysis of sea Oyster shells indicate that the distribution of predominantly cylindrical minerals is stacked in a specific order, unlike the structure of TBD Oyster shells and Limestone, which is typical of Aragonite minerals. The average size of the Aragonite mineral in sea Oyster shells is 1µm.

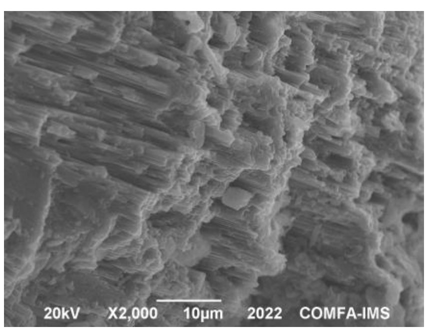


Figure 12. Scanning electron microscopy analysis of sea Oyster shell.

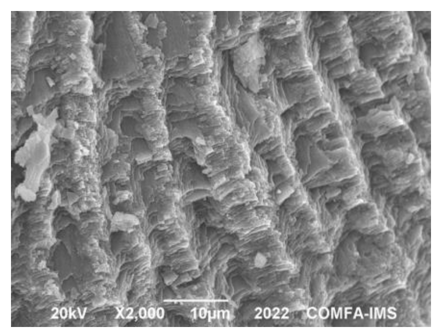


Figure 13. Scanning electron microscopy analysis of Clam shell.

3.3.4. Clam shell

The Clam shell underwent structural analysis using scanning electron microscopy (SEM) as shown in Figure 13. The results of the structural analysis revealed that the distribution of mainly cylindrical plate-shaped minerals, arraged in a specific order, was similar to that of sea Oyster shells, which is characteristic of Aragonite minerals. The average size of the Aragonite mineral in the Clam shell is 1µm.

3.3.5. Mussel shell

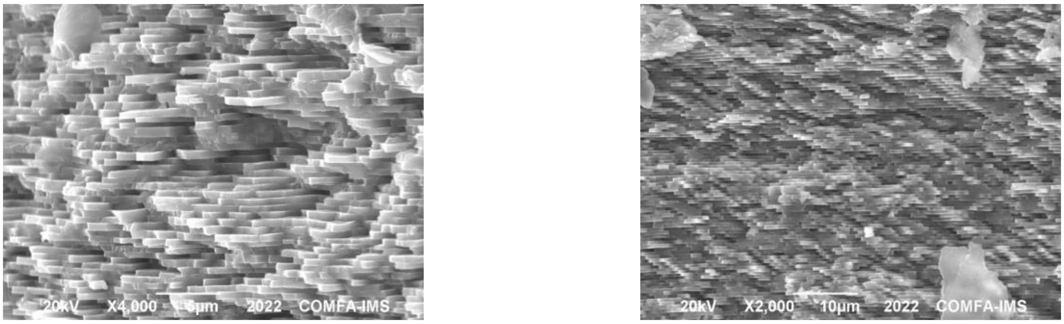
The structure analysis of the mussel shell using scanning electron microscopy (SEM) is depicted in Figure 14. The results revealed that the distribution of predominantly cylindrical minerals in the form of stacked plates appeared distinct, which is attributed to the growth process of mussels. The mineral size is very small, almost comparable to the naked eye when observed at a magnification of 2000 times. However, at a magnification of 4000 times, which is twice that of the sea oyster shell and Clam shells samples, the aragonite mineral become clearly visible with an average size of 0.1 µm.

4.3.6. Cockle shell

Structural analysis of Cockle shells (SEM) is shown in Figure 15. The results of structural analysis of Cockle shells show that the distribution of mainly cylindrical minerals is stacked in layers on the lower layer, which is typical of aragonite minerals. The average size of the aragonite mineral in Cockle shell is 1µm.

4.3.7. Sea snail shell

The structural analysis (SEM) of the sea snail shell is shown in Figure 16. The results of thestructural analysis of the snail shell indicated that the distribution of mainly cylindrical minerals is stacked in a basket-weave pattern, which is typical of the Aragonite minerals in the sea snail sehll is 1µm.



A magnification of 4000 times A magnification of 2000 times

Figure 14. Scanning electron microscopy analysis (SEM) of Mussel shell.

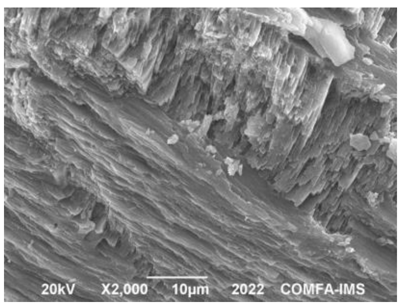


Figure 15. SEM of a cockle shell.

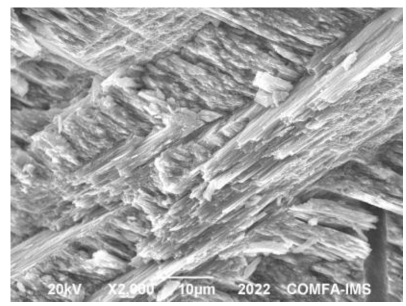


Figure 16. SEM of a sea snail shell.

5. Conclusion

- The Analysis of the chemical composition of the control sample of Limestone, TBD Oyster shells, sea Oyster shells, Clam shells, Cockle shells , Mussel shells, and sea snail shells all showed a very high CaO content (> 50%) in their composition. The CaO composition is equivalent to that of Limestone.

- The XRD analysis of bivalve shells is given as follows:

+ Pacific Oyster shell maninly consists of Calcite mineral, which is similar to the composition of Limestone mineral.

+ Sea Oyster shells have a composition of Aragonite mineral, which is a mixed of Calcite mineral.

+ Clam shells, sea snails shells, Cockle shells, and Mussel shells have a composition of Aragonite mineral .

- The structural analysis (SEM) of bivalve shells is given as follows:

+ Pacific Oyster Shell and Sea Oyster shells have the same arrangement and shape as Limestone mineral. However, the size of Pacific Oyster shells and Sea Oyster shells is 10 times smaller than the size of Limestone mineral.

+ Cockle Shells, Clams shells, Mussel shells, and Sea Snails's minerals are arranged in layers typical of Aragonite minerals, which have a size of 1 μm.

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