PHASE STUDY OF RAPANA VENOSA SHELLS FROM THE BLACK SEA

Janna Mateeva, Albena Yoleva, Stoyan Djambazov

University of Chemical Technology and Metallurgy
8 Kliment Ohridski blvd., 1756, Sofia, Bulgaria
E-mail: bkrr@uctm.edu

Received 18 May 2022
Accepted 29 September 2022

ABSTRACT

Sea shells contribute to large amounts of waste. Reuse and recycling of such waste can be an excellent alternative to disposal. Recycling sea shells waste offers many benefits and has potential applications in various fields. Some applications are up-to-date, well-established, widely used, large-scale and sustainable. On the other hand, there are many more strategies that have not yet been fully explored or commercialized. Growing global research shows significant potential for the use of sea shells such as regulators of soil acidity, catalysts for biodiesel production, adsorbents to remove toxic metals from wastewater, building materials, calcium supplements, biomaterials, antibacterial protection, bone implants, etc. The present study represents a phase investigation of Black Sea Rapana venosa shells with a view to their possible application.

Keywords: Black Sea, Rapana venosa shells, phase study, calcite, aragonite, calcium oxide, functional biomaterials.

INTRODUCTION

Sea shells are often dumped on beaches, which leads to their pollution. Reuse and recycling of such waste can be an excellent alternative to disposal. The material of the sea shell attracts attention due to its high content of calcium carbonate, low price and availability provided by the rapidly growing seafood industry. Numerous articles on shell valorization have been published in recent decades, citing a number of potential applications that could alleviate the burden of shellfish on aquaculture and food producers, and in some cases provide economic as well as environmental benefits [1 - 8]. Alternative materials, such as sea shells, are increasingly believed to reduce the exploitation of natural limestone reserves, one of the most exploited resources on the planet. In this sense, the recovery of marine shell waste is a useful strategy for both sustainable resource management and reduced waste storage. So far, the use of sea shells has been limited to a few well-established and sustainable applications (soil balms, cheap adsorbents, calcium supplements, building materials, etc.) [9 - 16]. Sea shells are functional biomaterials and some studies have investigated their use as fillers. Also, $CaCO_3$ in rapan shells can be converted into a source of CaO which exhibits strong antibacterial activity. The antibacterial activity of calcined shells is mainly due to the alkaline effect caused by the hydration of CaO. The most widely discussed biomedical use for them is in bone and tissue reconstruction [16 - 21]. The $CaCO_3$ powder coating has been shown to have osteogenic properties and to act as a substrate on which new osteoblasts can grow and release bone [8]. Researchers have suggested that the $CaCO_3$ shell may be converted to calcium phosphate (hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$), which is a major mineral component and component of human bones [22].

The purpose of this paper is a phase study of Black Sea shells Rapana venosa (Neogastropoda, Muricidae).

EXPERIMENTAL

The Black Sea Rapana venosa used for our study are shown in Fig. 1. Rapan shells were ground in a ball mill to determine their chemical and mineral composition using the following methods of analysis: Chemical analysis (ICP-AES after alkaline melting and acid dissolution), X-ray diffraction (DRON 3M diffractometer) with Cu Kα radiation (wavelength 1.7903 Å), 28 mA current and 40 kV voltage), Infrared spectroscopy (IR) (apparatus "Perkin-Elmer Spectrum 1000" in the area 4000 cm^{-1} - 400 cm^{-1}). For monitoring the changes that occur when heating the shells, in porcelain crucibles were placed 20 grams of powdered shells and heated at different temperatures from 500°C to 1000°C for 1 hour at maximum temperature. The samples were examined by using XRD.

Fig. 1. Rapan shells from the Black Sea.

RESULTS AND DISCUSSION

The chemical composition of rapan shells is given in Table 1. The chemical composition of rapan shells shows that they are composed of 98 % $CaCO_3$. Fig. 2 shows the X-ray diffraction pattern of powdered rapan shells. The predominant crystalline phase is calcite. The other phase that is detected is aragonite. In Fig. 3 is given IR spectrum of rapan shells. IR analysis proves the presence of $CaCO_3$. The infrared absorption of $CaCO_3$ is associated with the following bands 2874 cm^{-1} (C = O), 1795 cm^{-1} (C = O), 1474 cm^{-1} (CO_3^{2-}), 875 cm^{-1} (CO_3^{2-}), and 712 cm^{-1} (CO_3^{2-}).

Thermal treatment of rapan shells at different temperatures from 500°C to 1000°C shows that

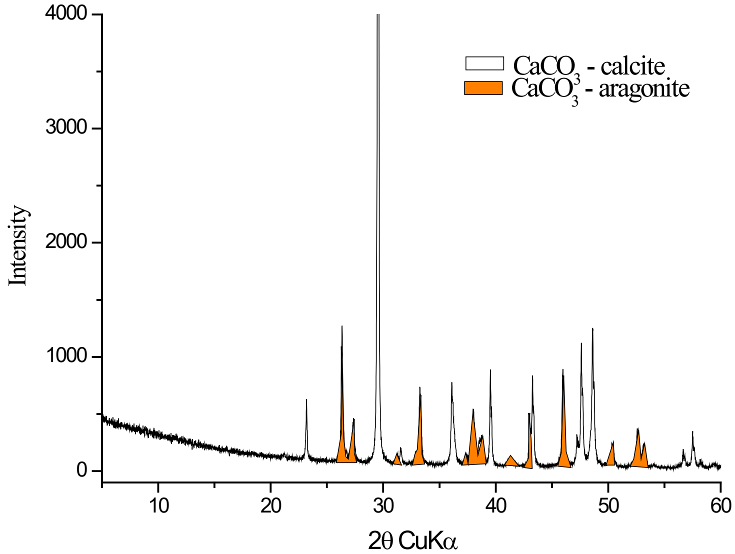

Fig. 2. XRD of powdered rapan shells.

Table 1. Chemical composition of rapan shells.

Oxides, mass %	Al_2O_3	CaO	MgO	Fe_2O_3	K_2O	Na_2O	SiO_2	TiO_2	LOI
Rapan shell from Black Sea	0.28	54.75	0.24	0.13	0.05	0.05	1.20	0.02	42.76

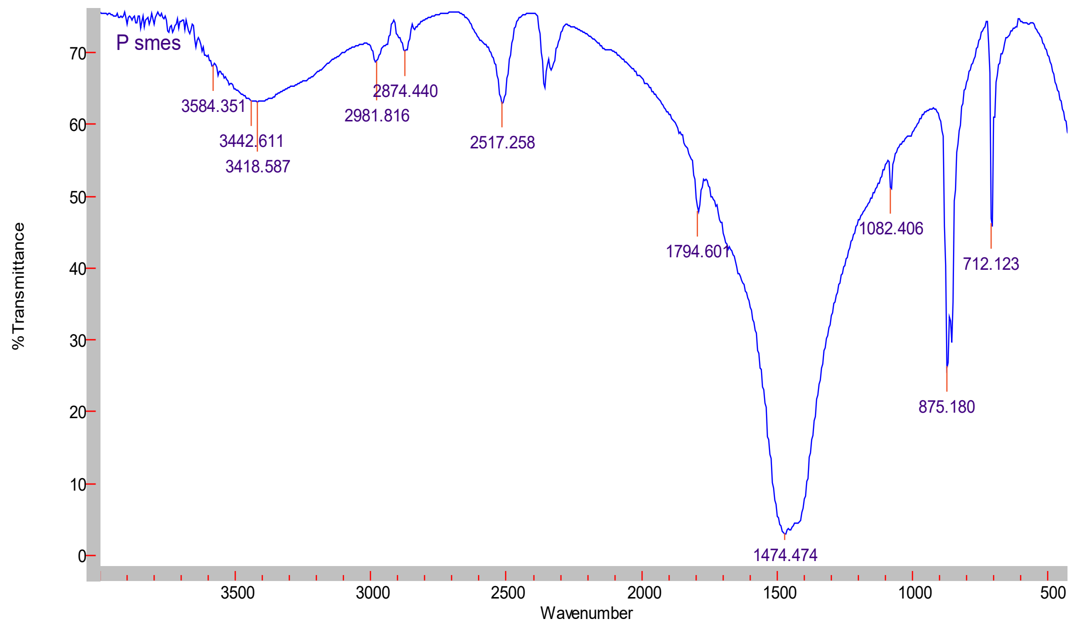

Fig. 3. IR spectroscopy of powdered rapan shells.

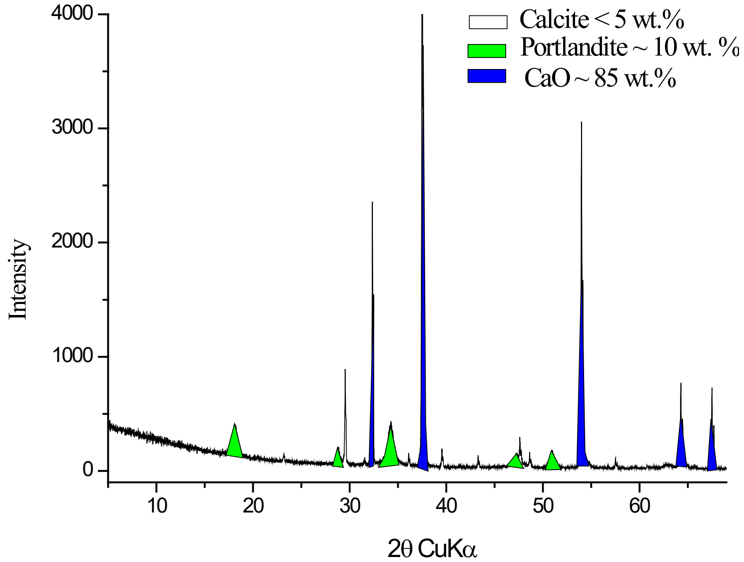

Fig. 4. XRD of powdered rapan shells calcined at 900°C, 1 hour.

decarbonization of calcium carbonate begins after 800°C. The diffraction patterns of the calcined shells at 900°C and 1000°C are given in Figs. 4 and 5. It can be seen that at 900°C most of the carbonate is decarbonized to CaO, and at 1000°C there is almost complete decarbonization of calcium carbonate. The diffractograms also show small amounts of portlandite $Ca(OH)_2$.

It was visually established that the rapan shells are made up of two different phases. One phase is white in color and the other phase is orange. The two phases are shown in Fig. 6. The next step of the study was to part these phases by crushing and separating. Then the two phases were ground separately in a ball mill. The orange phase is more difficult to mill due to its higher hardness. Their phase composition was determined by using X-ray diffraction. Figs. 7 and 8 show the diffractograms of the white and the orange phases. They contain calcium carbonate, but in different polymorph modifications. The white phase is composed of calcite and the orange phase of aragonite.

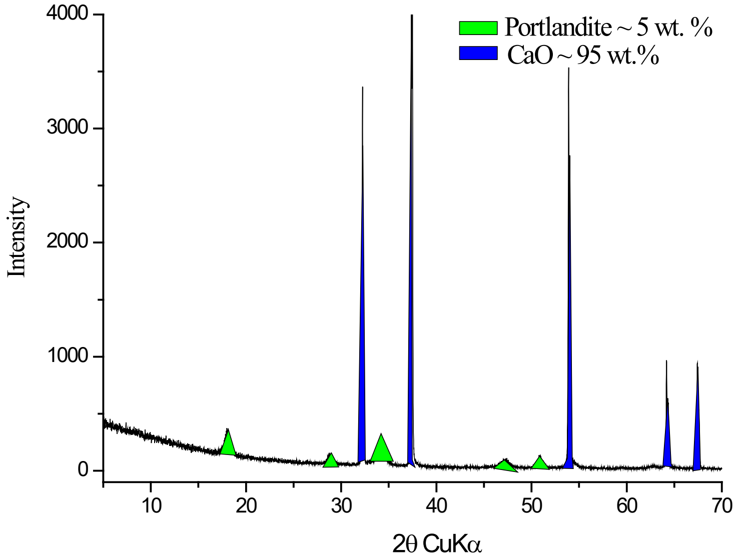

Fig. 5. XRD of powdered rapan shells calcined at 1000°C, 1 hour.

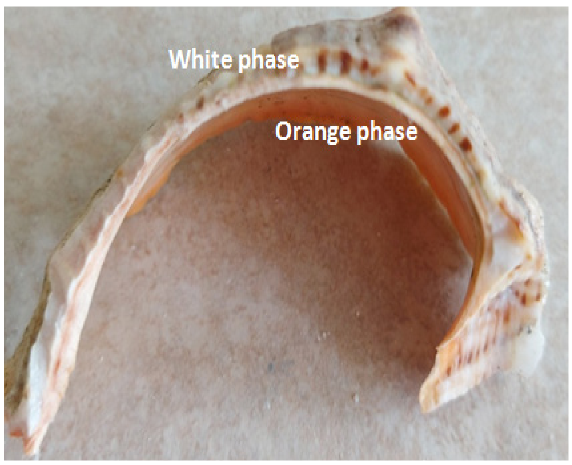

Fig. 6. White phase and orange phase in the rapan shell.

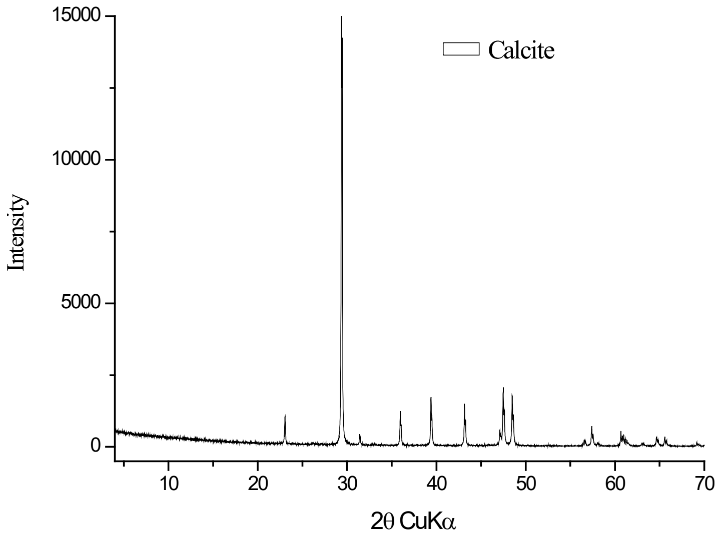

Fig. 7. XRD of the white phase in the rapan shell.

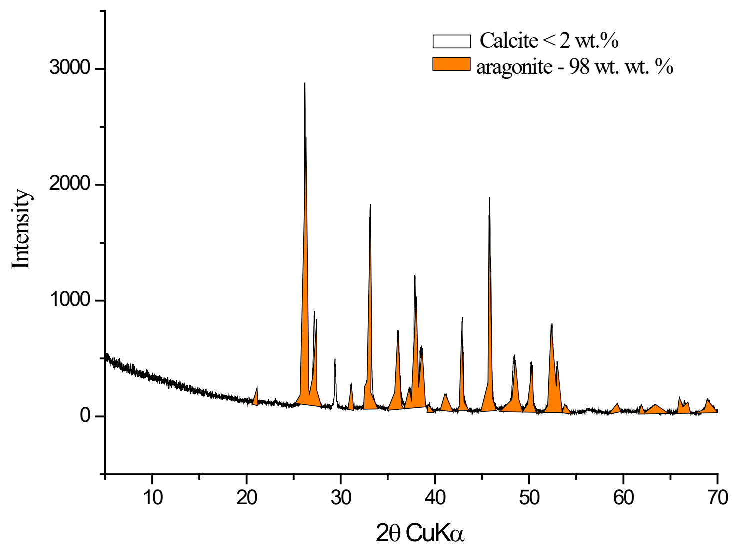

Fig. 8. XRD of the orange phase in the rapan shell.

CONCLUSIONS

Rapana venosa shells from Black Sea have been shown to contain 98 % $CaCO_3$. They contain two separate phases, one outer white phase of calcite (hard but brittle material) and the other inner orange phase with higher hardness containing aragonite. It was proved that the $CaCO_3$ from which the rapan shells are made begins to decarbonizes after 800°C and has been completely decarbonizes at 1000°C to CaO. One of the possible applications of rapan shells from Black Sea can be as an alternative source of biogenic calcite and bio calcium oxide for use in medicine, pharmacy and food industries.

REFERENCE

1. M.S. Clark, L.S. Peck, J. Arivalagan, T. Backeljau, S. Berland, J.C.R. Cardoso, C. Caurcel, G. Chapelle, M. De Noia, S. Dupont, K. Gharbi, J.I. Hoffman, K.S. Last, A. Marie, F. Melzner, K. Michalek, J. Morris, D.M. Power, K. Ramesh, T. Sanders, K. Sillanpää, V.A. Sleight, P.J. Stewart-Sinclair, K. Sundell, L. Telesca, D.L.J. Vendrami, A. Ventura, T.A. Wilding, T. Yarra, E.M. Harper, Deciphering mollusc shell production: the roles of genetic mechanisms through to ecology, aquaculture and biomimetics, Biological Reviews 95, 2020, 1812-1837.
2. G. Magnabosco, D. Giuri, A. Bisceglie, F. Scarpino, S. Fermani, C. Tomasini, G. Falini, New Material Perspective for Waste Seashells by Covalent Functionalization, ACS Sustainable Chem. Eng., 9, 2021, 6203-6208.
3. L. Habte, M. Khan, N. Shiferaw, A. Faroo, M.Lee, S. Jung, J. Ahn, Synthesis, Characterization and Mechanism Study of Green Aragonite Crystals fromWaste Biomaterials as Calcium Supplement, Sustainability, 12, 2020, 5062-5072.
4. M. Ravi, B. Murugesan, A. Jeyakumar, K. Raparthi, A review on utilizing the marine biorefinery waste in construction raw materials to reduce land pollution and enhance green environment, Advances in Materials Science, 21, 3, 2021, 44-62.
5. M. Jović, M. Mandić, M. Sljivić-Ivanović, I. Smičiklas, Recent trends in application of shell waste from mariculture, Studia Marina, 32, 1, 2019, 47-62.
6. Y. Hou, A. Shavandi, A. Carne, Marine shells: Potential opportunities for extraction of functional and health-promoting materials. Critical Reviews in Environmental Science and Technology 46, 2016, 1047-1116.
7. Z. Yao, M. Xia, H. Li, T. Chen, Y. Ye, H. Zheng, Bivalve shell: not an abundant useless waste but a functional and versatile biomaterial. Critical Reviews in Environmental Science and Technology 44, 2012, 2502-2530.
8. P. Morris, Report synthesising the existing and potential uses of shells as by-products of the aquaculture industry, CACHE WP6: D6.3 Final Report, Brussels, Belgium, 2017.

9. J. Morris, T. Backeljau, G. Chapelle, Shells from aquaculture: a valuable biomaterial, not a nuisance waste product. Reviews in Aquaculture 11, 2019, 42-57.
10. Y. Ok, S. Oh, M. Ahmad, Effects of natural and calcined oyster shells on Cd and Pb immobilization in contaminated soils, Environmental Earth Sciences, 61, 6, 2010, 1301-1308.
11. F. Wheaton, Review of oyster shell properties: part II. Thermal properties, Aquacultural Engineering, 37, 1, 2007, 14-23.
12. E. Zolotoyabko, B. Pokroy, Biomineralization of Calcium Carbonate: Structural Aspects. Cryst. Eng. Comm. 9, 2007, 1156-1161.
13. B. Pokroy, A., Fitch, E. Zolotoyabko, Structure of biogenic aragonite ($CaCO_3$), Crystal Growth & Design, 7, 9, 2007, 1580-1583.
14. M. Toffolo, E. Boaretto, Nucleation of aragonite upon carbonation of calcium oxide and calcium hydroxide at ambient temperatures and pressures: a new indicator of fire-related human activities, Journal of Archaeological Science, 49, 1, 2014, 237-248.
15. J. Chen, L. Xiang, Controllable synthesis of calcium carbonate polymorphs at different temperatures, Powder Technology, 189, 1, 2009, 64-69.
16. W. Sun, S. Jayaraman, W. Chen, K. Persson, G. Ceder, Nucleation of metastable aragonite $CaCO_3$ in seawater, Proceedings of the National Academy of Sciences of the United States of America, 112, 11, 2015, 3199-3204.
17. H. Nebel, M. Epple, Continuous preparation of calcite, aragonite and vaterite, and of magnesium-substituted amorphous calcium carbonate (Mg-ACC), Zeitschrift fur Anorganische und Allgemeine Chemie, 634, 8, 2008, 1439-1443.
18. A. Niida, Y. Hirose, H. Akagi, P. Wang, M. Ochi, Bone augmentation with composite of calcium carbonate of scallop shells and salmon collagen, Journal of Japanese Society of Oral Implantology 25, 2012, 3-12.
19. S. Lee, Y. Kim, R. Kim, C. Choi, Nanostructured biogenic calcite: a thermal and chemical approach to folia in oyster shell, Micron, 39, 4, 2008, 380-386.
20. M. Li, Z.T. Yao, T. Chen, Z.H. Lou, M. Xia, The antibacterial activity and mechanism of mussel shell waste derived material, Powder Technology, 264, 2014, 577-582.
21. Y. Khrunyk, S. Lach, I. Petrenko, H. Ehrlich, Progress in Modern Marine Biomaterials Research, Mar. Drugs, 18, 2020, 589-635.
22. Z. Zuliantoni, W. Suprapto, P. Setyarini, F. Gapsari, Extraction and characterization of snail shell waste hydroxyapatite, Results in Engineering, 14, 2022, 100390.