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Research Article

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Chemical and Mineralogical Measurements on Estuarine Clam *Meretrix casta* Shells of Yadayanthittu Estuary, Southeast Coast of India

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Abstract The present study endeavors chemical and mineralogical characteristics in *Meretrix casta* (Bivalve) shells of the Yadayanthittu estuary, Southeast coast of India. In this estuary shell specimens were collected at 100m distance in the sampling stretch. The oxides, the elements and biominerals were measured with the aid of an integrated XRF and XRD instrument. The result of oxides demonstrates that the CaO content is in high percentages (54.47), which is common in organic shells. Apart from CaO, the other reported important oxides are Na_2O, (0.697), SiO_2, (0.241), Fe_2O_3, (0.116), MgO, (0.0661) and Al_2O_3, (0.0587). The elemental concentration shows that Ca with high level of 38.95 wt%. All other reported elements are only in lesser wt %, i.e. Na, (0.517), Si, (0.113) Sr, (0.156) Fe (0.0813), Sx (0.0266), Mg (0.0399) and Al (0.0311). The XRD analysis exhibits that the *Meretrix casta* shells of the Yadayanthittu estuary is formed by aragonite (98%) and selwynite (2%) biominerals.

Keywords Yadayanthittu estuary, *Meretrix casta*, XRF and XRD, oxides, elements, biominerals

Introduction

Economically important *Meretrix casta* (Bivalvia: Veneridae) shells occur abundantly on the Southeast Coast of India. The clam shell *Meretrix casta* (Chemnitz, 1782) characterized by a thick, moderately large shell generally attain a length of about one and half inch with a brown horny periostracum when fresh but smooth and devoid of sculpture. The interior surface is white and glossy but exterior surface is pale yellowish brown, fringed with dark gray posteriorly and very faintly grayed with a grayish radial line. *Meretrix casta* is rich in nutrients, particularly proteins, fats and minerals and it's mainly used as food for a large section of poor people of the coastal tract. The hard shells are composed of high $CaCO_3$, has three Polymorphs, namely Aragonite, Vaterite and Calcite. The $CaCO_3$ is used as raw materials for manufacture of lime, cement, chemicals, fertilizers and flux material in iron and steel, ferro-alloy and other metallurgical industries [1]. Other than these, the shells are used in the biomedical field like artificial dental root implantations, orthopedic application in bone repair, etc. In medicinal field, some bivalves are used for treatment of diseases like anemia, hypertension, labour pain and constipation [2-4].

The hard calcareous shells are the results of a mineralization process, biologically controlled and genetically programmed [5]. These calcareous shell formed by extrapallial fluid, is enclosed between the inner surface of the shell and the mantle, and it is similar to the extracellular fluid of vertebrate bone, which forms the skeletal of all kinds of shells. Some researchers widely used XRF method for major oxide and elemental analysis in bivalve shells [6-13]. Fewer studies have done on biominerals identification in bivalve shells with the help of XRD method [14-23]. In this paper, the chemical characteristics and biomineralization processes in *Meretrix casta* of Yadayanthittu estuary (Marakkanam estuary), Southeast Coast of India are studied in detail.

Materials and Methods

Study area

The study area Yadayanthittu estuary (Marakkanam estuary) falls in the toposheets no. 57P/16 and 66D/4 of 1:50,000 scale, and lies between the Latitudes 12˚ 12' to 12˚ 15'N and the Longitudes 79˚ 56' to 80˚ 00'E. The Estuary extending 3 km from a little northeast of Marakkanam Road Bridge is directly connected to the Bay of Bengal at Alamparai port and develops a lagoon ecosystem. The estuary has a large area of intertidal mudflat that supports local flora and fauna. The site around Marakkanam exposes Cuddalore sandstone of Mio-Pliocene age, resting over the charnockites and in turn is overlain by the Quaternary sediments [24, 25]. The location map of the study area is shown in Figure 1.

Sample collection

Meretrix casta shells were collected along the estuarine shoreline about 1 km distance from the mouth. Representative shell samples were collected in ten locations from the study area. The shell specimens collected within 1×1m squares in the sampling stretch, the distance between sampling squares was 100 m. In the demarcated square, available *Meretrix casta* shells were collected by hand digging and picking. The collected shells were thoroughly washed with backwater at the collection point and placed into clean plastic bags and packed with sample numbers.

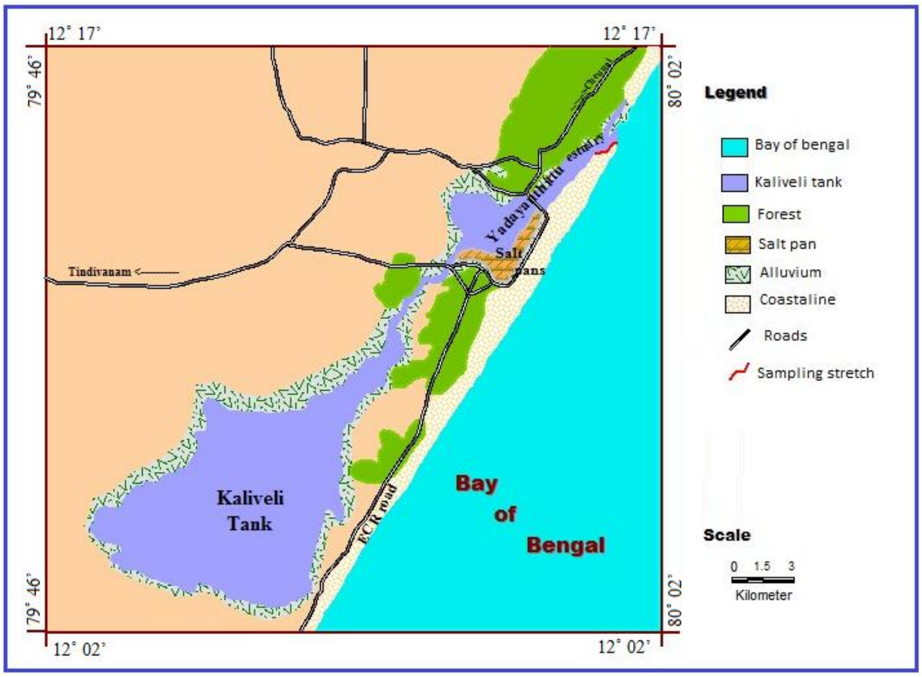

Figure 1: The location map of the study area

Sample preparation

The packed samples dried well, then crushed and pulverized into powder form with the help of agate mortar and pestle. The powered sample labeled separately according to the location numbers. All locations, sample powder was mixed together and stringed well to make a representative sample of the whole. From the representative sample powder required quantity of powder has been taken for chemical and biomineralization analysis.

Analytical methods

The study area *Meretrix casta* shells, chemical and biomineralogical measurements were done with an integrated XRF and XRD instrument (Model: Thermo Scientific- ARL 9900 X-ray Workstation). The specified parameters of ARL 9900 X-ray Workstation are given in Table 1. The samples were dried in an oven at 100˚C for 24 hours, after initial surface free moisture removal at 40˚C for 4 hours. The dried samples were ground in an Insmart® ring mill with Tungsten Carbide elements to a fine powder in order to minimize particle size effect on the analysis. Approximately 9.0g of each resulting powder was mixed with 1ml of Cellulose, which acts as a binding agent [26] and then pressed into 25mm diameter disks. The separate disks were made from a sample material. The disks were analyzed on an XRF spectrometer using an Rh target X-ray tube operating at 60 KV and LiF 200 in a vacuum path for major oxides and elemental analysis. The X-ray diffraction (XRD) method provides an easy way to distinguish two polymorphs of $CaCO_3$, aragonite and calcite. Biominerals identification of *M. casta* shell was studied with the aid of XRD and the results are interpreted with the help of *Visual CRYSTAL 6* Analysis and the peak values are interpreted with scintillation and flow counters technique for biomineral identification.

Table 1: Details of analytical parameters and used Properties for *M. casta* shell determination

Parameter	Value used properties
Method	X_UQ.
Calculated as	Oxides
Matrix (Shape & Imp Fc)	1|Teflon
X-ray path	Vacuum
Film type	No supporting film
Case number	0 All known
Eff. Diam.	25.0 mm
Eff. Area	490.6 mm2
Known Conc.	44.00 % LOI
Rest	0 %
Viewed Mass	18000.00 mg
Dil./Sample	0.100 Cellulose
Sample Height	5.00 mm

Results and Discussion

Major oxide

The result of the major oxides (Table 2) indicates that the loss on ignition (LOI) is about 44.00% which is common in organic shells. The calcium oxide (CaO) concentration is 54.47% of the total chemical compound. The sodium oxide (Na_2O) content in the shells is about 0.697%. Apart from CaO, all other oxides are reported in very small amounts.

Table 2: Major oxides and element concentrations in *Meretrix casta* shells of the study area

S. No.	Compound	Formula	m/m %	Std. Err	Element	Weight %	Std. Err
1	Calcium oxide	CaO	54.47	0.25	Ca	38.95	0.18
2	Sodium oxide	Na_2O	0.697	0.035	Na	0.517	0.026
3	Silicon oxide	SiO_2	0.241	0.012	Si	0.113	0.006
4	Strontium oxide	SrO	0.184	0.009	Sr	0.156	0.008
5	Iron oxide	Fe_2O_3	0.116	0.006	Fe	0.0813	0.0041
6	Sulphur trioxide	SO_3	0.0664	0.0033	Sx	0.0266	0.0013
7	Magnesium oxide	MgO	0.0661	0.0034	Mg	0.0399	0.0021
8	Aluminium oxide	Al_2O_3	0.0587	0.0029	Al	0.0311	0.0016
9	Chlorine	Cl	0.0504	0.0025	Cl	0.0504	0.0025
10	Cadmium oxide	CdO	0.0135	0.0044	Cd	0.0118	0.0038
11	Phosphorus pentoxide	P_2O_5	0.0104	0.0007	Pox	0.0045	0.0003
12	Scandium oxide	**Sc_2O_3**	0.0050	0.0012	Sc	0.0033	0.0008
13	Zirconium oxide	ZrO_2	0.0041	0.0012	Or	0.0030	0.0009
14	Titanium oxide	TiO_2	0.0038	0.0011	Ti	0.0023	0.0007
15	Potassium oxide	K_2O	0.0037	0.0007	K	0.0031	0.0006
16	Rhenium oxide	**Re_2O_7**	0.0031	0.0013	Re	0.0024	0.0010
17	Nickel oxide	NiO	0.0025	0.0009	Ni	0.0020	0.0007
18	Zinc oxide	ZnO	0.0018	0.0009	Zn	0.0014	0.0007
19	Bromine	Br	0.0012	0.0004	Br	0.0012	0.0004

The silicon dioxide (SiO_2) concentration is 0.241%, strontium oxide (SrO) is reported in 0.184% and the total iron has been estimated in the form of Fe_2O_3. The Fe_2O_3 concentration is 0.116%, sulphur (SO_3), magnesium (MgO) and aluminium oxide (Al_2O_3) contents are very less amount and the reported percentages are 0.0664, 0.0661 and 0.0587 respectively. Other oxides like chlorine (Cl), cadmium oxide (CdO), phosphorus pentoxide (P_2O_5), scandium oxide (Sc_2O_3), zirconium oxide (ZrO_2), titanium oxide (TiO_2), potassium oxide (K_2O), rhenium oxide (Re_2O_7), nickel oxide (NiO), zinc oxide (ZnO) and bromine (Br) are also not showing significant values, they are just as a reported value. High level of CaO is common in marine shells, however low value of MgO (0.0661%) indicates that dolomitization process is completely absent in this shell.

The major oxides of *M. casta* shells of the study area are described in a pie diagram is shown in Figure 2. The diagram represents more than half of the area (54%) is covered by calcium oxide, the other oxides, such as Na_2O, SiO_2, SrO, Fe_2O_3, SO_3, MgO, Al_2O_3, and a few more to add all together gives 2% of the total. Except CaO the other major oxides have insignificant values. The loss on ignition (LOI) included gases, impurities like inorganic matter, and water, etc. The carbon dioxide was calculated to satisfy the base, and the amount thus determined, subtracted from the total loss on ignition, gave a fair but rough estimate of organic matter plus water. CaO and Ca values are compared with a column chart and the differences expressed in Figure 3.

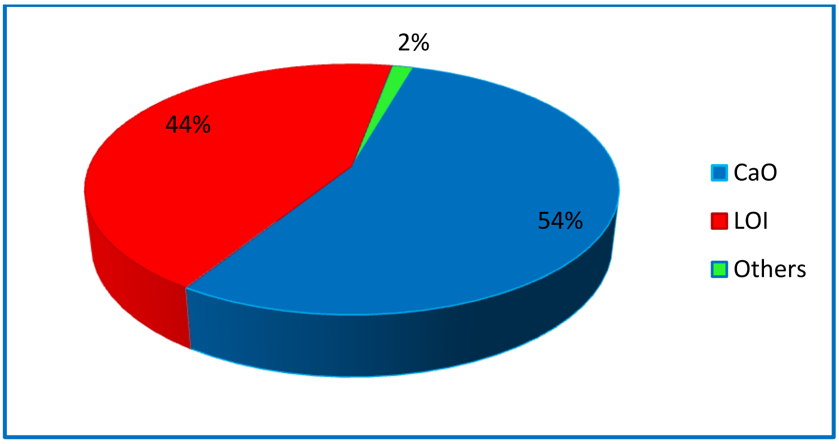

Figure 2: A pie diagram representing oxide values of M. casta shell.

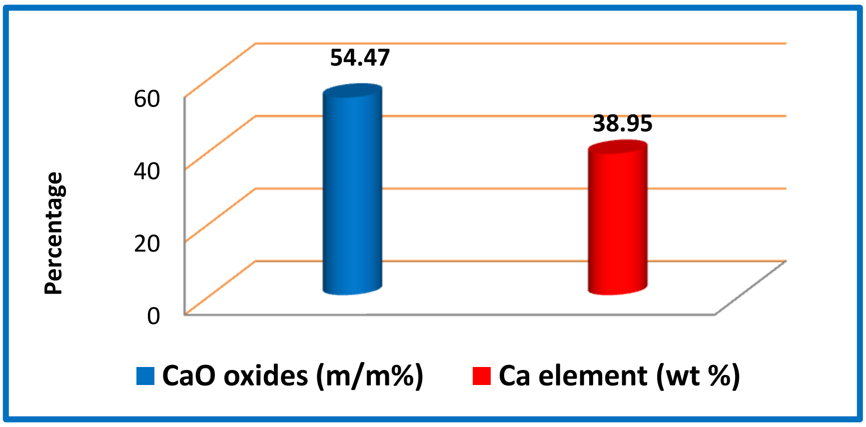

Figure 3: CaO (m/m %) vs. Ca (W %) values compared.

Major elements

In inorganic carbonates, trace element incorporation is a function of both the carbonate mineralogy and the solution chemistry. However, in biogenic carbonates, where the carbonate shell is secreted from the extra pallial fluid produced by the organism, the relationships governing inorganic carbonate chemical compositions do not necessarily exert greater control over the trace element concentrations in the carbonate [27]. The XRF result demonstrates that the elemental concentration in *Meretrix casta* shells of the Yadayanthittu estuary has several elements within it (see table 2). Among the elements, Ca reported in high level as a weight percentage of 38.95. All other elements are just on a reported level not showing any significance, perhaps reflecting the low absorption capacity in shells, bivalve shells from time to time may contain small inclusions of foreign matter [28].

Biomineralization

The Figure 4 exhibits XRD *Visual CRYSTAL 6* image. The instrument 29 peaks among the detected 27 peaks from the scan results, 2 phases (major and minor) index were identified. The major phase is predominantly Aragonite (98%), XRD has also detected a minor phase (2%) of Selwynite, which is hydroxide of Na, K, Al & PO_4, chemical formula [Na K (Be, Al) Zr_2 $(PO_4)_4 \cdot 2\ H_2O$].

According to the XRD results the *Meretrix casta* shell of the study area is mainly composed of Aragonite biomineral with 98%. This indicates that *Meretrix casta* shell gets calcined by aragonite rich $CaCO_3$ biomineral process under the marine conditions. The minor phase biomineral Selwynite is uncommon mineral present in this study area *Meretrix casta* shell. The Selwynite mineral (Gainesite group) is a very rare variety of minerals; it occurs as a cavity filling in veins, formed under reducing conditions during late-stage cooling in granite pegmatite. It was discovered 1995 from the Wycheproof granite quarry, Wycheproof, Buloke Shire, Victoria, Australia. It was named to honour Alfred Richard Cecil Selwyn (1824–1902), founding Director of the Geological Survey of Victoria, Australia, and later, the Geological Survey of Canada [29]. According to Brich et al. 1995 the occurrence of Selwynite found in cavity filling veins, granite pegmatite and this mineral also a very rare variety. Whereas in Yadayanthittu estuary, *Meretrix casta* shell comprise a little amount of Selwynite mineral (2%) of total mineral constituent. The estuary receives water from Kaliveli Tank, which lies about 3km to the northeast of the tank. The tank is semi-permanent fresh to brackish water lagoon. During the monsoon the tank receives runoff water from neighboring farmland and drainage channels.

Charnockite and biotite-hornbelende gneiss of Eastern Ghat Complex occurred to the western side of the lake. Many dolerite dyke quarries are operating towards west of Kaliveli tank. During heavy rainfall the runoff water from quarry flows towards eastern slope and joins in the tank, subsequently the overflow tank water inflow to Sea through the estuary. This can be one of the sources for Selwynite mineral leached out from the source rock and it mixed with backwater.

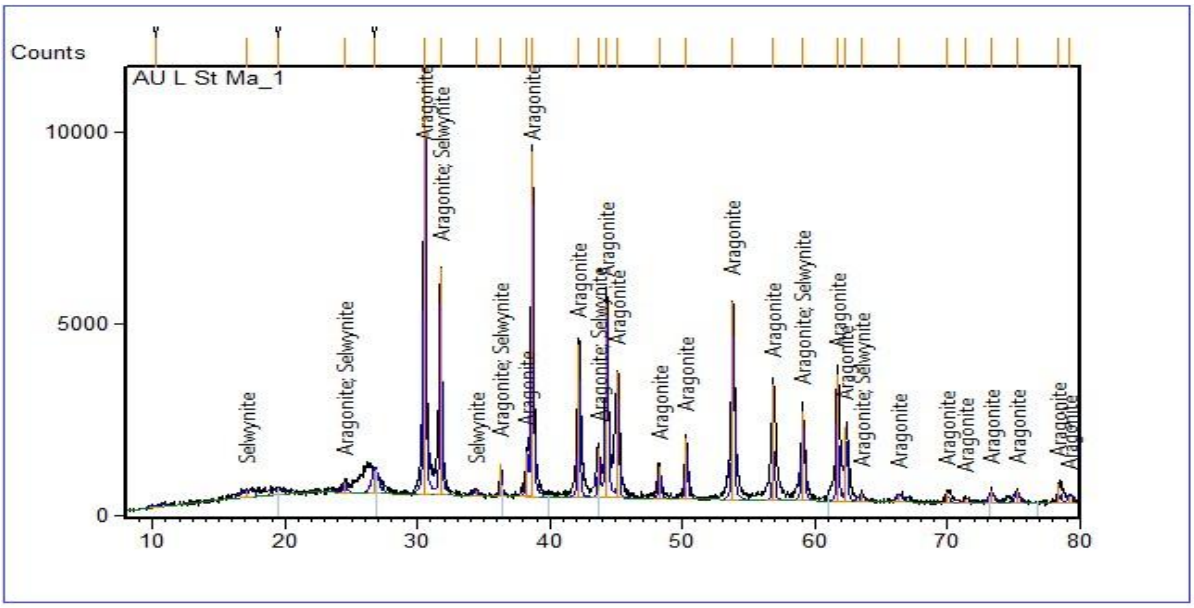

Figure 4: Visual CRYSTAL 6 images indicate the Aragonite and Selwynite minerals peaks.

Conclusion

The results revealed that the *Meretrix casta* shells of Yadayanthittu estuary having the high calcium carbonate (54.47%). This high CaO content will be useful for many lime based industries as well as other chemical industries, The remaining all other oxides constituents below 2% of total oxides constituents. The rare oxides of scandium (Sc_2O_3) and rhenium oxide (Re_2O_7) also presented in the shell. The XRD detected the aragonite biomineral (98%) phase indicates that predominates to form the hard shell of *Meretrix casta* shells of the study area.

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