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Alkali, Alkaline Earth Metal and Iron Oxides in the inner Continental Shelf Surface Sediments off Besant Nagar To Kovalam Sector, Southeast Coast of India: Inferences on Source and Deposition.

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ABSTRACT

The inner continental shelf surficial sediments of the Bay of Bengal between Besant Nagar and Kovalam, along the Tamilnadu coast, have been analysed to determine the geochemical characteristics of these sediments. The inner shelf floor is carpeted by sandy sediments, with its variants namely, coarse, medium, and fine to very fine sand. The mineral component of the sediments includes minerals such as quartz, feldspars, ilmenite, magnetite, amphiboles, pyroxenes, garnet, sillimanite and epidote, zircon, monazite, kyanite, staurolite, sphene, tourmaline and corundum. The concentration of major oxides such as Na₂O, K₂O, (alkali metals); MgO, CaO (alkaline earth metals) and Fe₂O₃ have been determined for selected fourteen seabed surface sediments collected between 10 m and 30 m water depths in the Bay of Bengal off Chennai – Kovalam sector of the east coast of India. The major oxides MgO and CaO, exhibit higher concentrations than their UCC values in the surface sediments. High CaO content (15.10%) occurs in the sandy sediments. The calcareous skeletal debris such as shells and shell fragments have contributed to the content of CaO and MgO. The minerals occurring in the studied sediments viz., ilmenite, magnetite, pyroxenes, amphiboles, and garnet contribute Fe, Mn, and Mg content to the sediments. Besides being influenced by pore space solutions, feldspars, and clay minerals have contributed to Na and K. These elements enter into the marine environment in the study area through particulate-minerogenic, biogenic and dispersed iron and manganese oxide/hydroxide phases from the source through the Adyar and Palar Rivers.

KEYWORDS: Alkali metal, alkaline earth oxides, inner continental shelf, Kovalam

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INTRODUCTION

In the continental shelf sediments, variations in chemical compositions are controlled by changes in terrigenous supply as well as distance from the source area. The geochemistry of the major, trace and rare earth elements of the siliciclastic sediments provide some information on the types of source rocks and tectonic setting of the sedimentary basin^{1,21}. In marine sediments, the origin of alkali metals (Na, K, Li, and Rb) is considered mostly detrital or hydrothermal. Their enrichments reflect the source rocks, their weathering and maturity (detrital origin) and hot extraction or basalt precipitation (hydrothermal origin). On the other hand, the alkaline earth metals (Ca, Mg, Ba, Sr, and Be) are influenced by the biological enrichment mechanism. An inventory of these elements and other trace elements can illuminate the relative importance and interplay of various natural processes. Of these, Na, K, Mg and Ca being major, have received considerable attention in the world oceans^{7,26}; including the coastal and offshore sediments off the Indian coasts^{22,26}.²⁵ studied the source and distribution of alkali, alkaline earth metals of the surface sediments of Bay of Bengal off the Andhra Pradesh coast.

The study area of the inner continental shelf off the Chennai-Kovalam sector, southeastern coast of India, falls under a wave-dominated zone.¹² examined the trace metal concentration in the seabed sediments between Chennai and Pondicherry to distinguish the areas with pollution due to anthropogenic activity. ²⁴ investigated the geochemical evolution of the continental shelf sediments of the southeast coast of India. ³⁰ studied the texture and depositional environment of the inner shelf sediments off Kalpakkam. ³⁷ studied the Geochemistry and distribution of sediments in the East Indian shelf, SW Bay of Bengal. ²⁸ studied the distribution pattern of trace metals in the coastal waters of Chennai. ²⁹ have investigated the nature of variation of heavy metals in the marine sediments off Kalpakkam. ²⁴ observed that the contamination of heavy metals is negligible in the continental shelf sediments of the southeast coast of India. ³² inferred environmental changes from the study of multi-element concentration in sediments of the Cauvery Delta. ³⁵ have studied the distribution pattern of heavy minerals and chemical elements of the coastal sediments along Besant Nagar and Marakkanam, Tamil Nadu. ¹¹ assessed the accumulation of trace elements off the Chennai coast after a major flood. Then examined the source and enrichment of heavy metals in the Cuddalore estuary sediments¹⁶ carried out a geospatial approach for the radioactive minerals and radionuclides of the Besant Nagar – Kovalam coastal sediments.

These works broadly contribute to the knowledge of contamination and pollution aspects of estuaries and nearshore parts of the shelf. However, little information is available on the systematic

geochemical characterization of the alkali, alkaline metals, manganese and iron oxides of the inner continental shelf sediments of the Tamil Nadu coast. The objective of this paper is to investigate in detail the source and characteristics of alkali metal oxides ($\text{Na}_2\text{O}, \text{K}_2\text{O}$), alkaline earth metal oxides (CaO, MgO), iron oxide of the surface sediment and their distribution pattern in the inner continental shelf, off Besant Nagar-Kovalam sector of the southeastern coast of India.

Climate and Oceanographic Parameters

The average atmospheric temperature ranges from 37 deg C in summer months and 25 deg C in cooler months (December-January). The study area experiences northeast monsoon from October to February and the southwest monsoon from May to September. Generally, northerly current is dominant and net longshore transport for the east coast of India is northerly. The direction of longshore transport is northerly from March to October and Southerly from November to February³. The average significant wave height ranges from 0.39m to 1.66m whereas tidal height ranges from 0.10m to 1.50m.

Geological Setting

The area receives sediments from the rivers viz., the Arniyar, the Koratallaiyar, the Coovum and the Adyar in the northern part and from the Cheyyar and the Palar in the southern part. The Palar is the major non-perennial river in the northern part of Tamilnadu. The drainage basins of the area consist of schistose to amphibolite grade metamorphic rocks, charnockite, garnet-sillimanite gneisses, quartzite with minor sillimanite, calc-granulite, and pink garnet-bearing garnetiferous leptynite and augite bearing norite, granites, migmatites, garnetiferous sillimanite-gneiss and rocks such as Peninsular gneiss, epidote-hornblende gneiss, biotite-hornblende gneiss of Archaen age, basic (dolerite) dykes, syenite, carbonatite and ultramafics of proterozoic age and lower Gondwana (Guduvancheri formation) and the upper Gondwana rocks (Sriperumpattur formation) and the Quaternary fluvial, fluvio-marine and the marine formations³⁴.

STUDY AREA

The area of study of the inner continental shelf zone between Besant Nagar and Kovalam segment of the Bay of Bengal (Fig.1) falls in the NHO chart no.357 (Scale 1:300000 scale) bounded by 13° 01' 0.86" N, 80° 17' 13.07" E; 13° 01' 33.23" N, 80° 23' 41.15" E; 12° 45' 37.86" N, 80° 20' 07.85" E (Fig.1). The continental shelf off Chennai is wide (50 km) with a gentle gradient and it becomes narrow (25 km) between Pondicherry and Cuddalore¹⁸. The inner shelf has an average gradient of 1:400. Chennai – Mahabalipuram coast shows a fining textural gradient from near shore to the inner shelf

which represents recent sediments postdating the stabilisation of sea level. The intermediate clayey sand facies (a mixture of recent terrigenous silty clay with relict sand) are inferred to be palimpsest. The terrigenous sand further offshore is considered a 'relict' due to seaward coarsening texture¹⁸.

MATERIALS AND METHODOLOGY

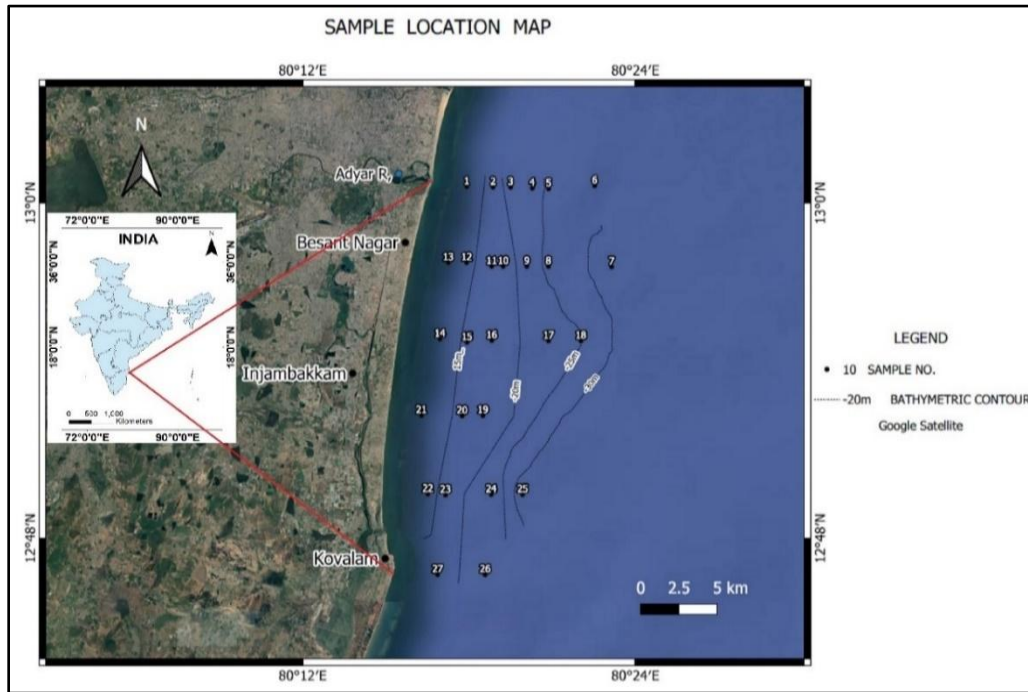


Figure 1. The map of the study area showing the sample location

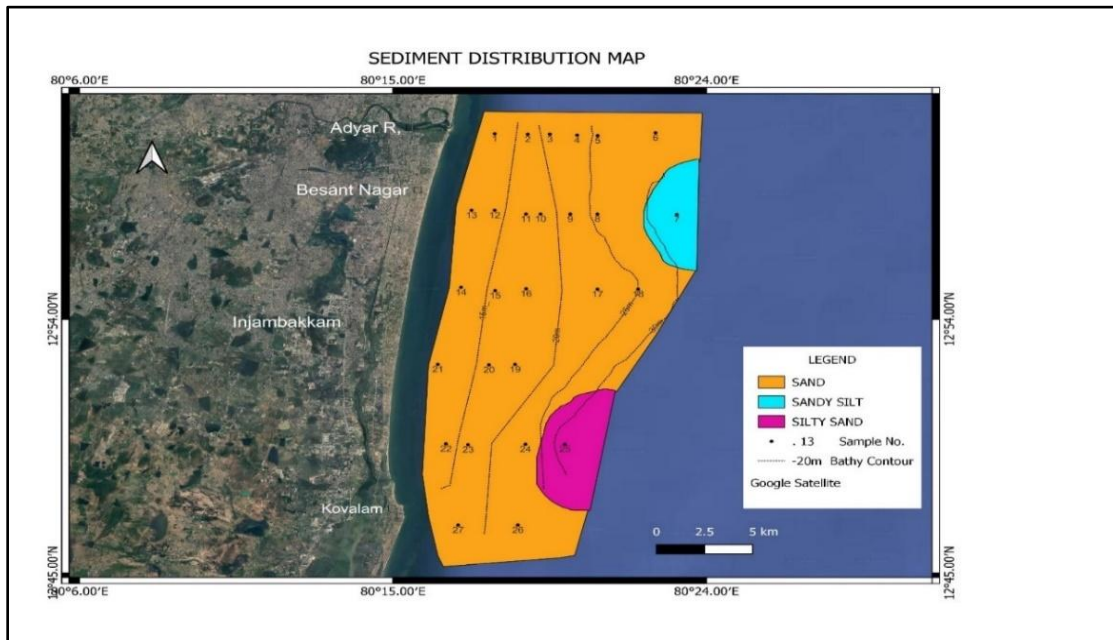


Figure 2. Textural variation of the seafloor sediments in the study area.

Twenty-seven seabed sediments were collected from the study area by Van Veen grab sampler between 10 m and 30 m water depths in the Bay of Bengal off the Besant Nagar – Kovalam sector of the southeast coast of India, using a mechanised commercial fishing boat in March 2019. Position fixing was carried out using GPS and the spot depth was noted from the on-board echo sounder. QGIS 3.24 software was used to prepare spatial maps. The concentration of major oxides such as Na₂O, K₂O, MgO, CaO, and Fe₂O₃ have been determined for fourteen seabed sediment samples.

The samples were air-dried and analysed using an XRF instrument for major oxides such as Na₂O, K₂O, CaO, MgO and Fe₂O₃. The abundance of major oxides (%) in the bulk sediments is tabulated (Table 1). The correlation coefficient matrix of the major oxides was also calculated (Table -2). Spatial distribution maps of the sample location and sediment distribution on the inner continental shelf floor using QGIS 2021 version software (Fig.1 and Fig. 2).

MAJOR ELEMENTS

Na₂O: In the surface sediments the values of Na₂O vary from 1.92 to 4.59% with a mean value of 3.33% (Table 1). The average content of Na₂O is depleted when compared with its UCC value of 3.90%. The higher concentration of Na₂O (4.59%) occurs in the surface sediments (Sample no.15) at 16.30 m water depths off Injambakkam. The Na₂O content is associated with sand. The surface distribution of Na₂O values shows a northward increasing trend and has a significant positive correlation with Fe₂O₃ (0.62) (Table-2).

K₂O: In the surface sediments the values of K₂O vary from 0.62 to 1.96% with a mean value of 1.19% exhibiting a depletion concerning its UCC value of 3.40% (Table -1). The higher concentration (1.96%) in the surface sediments occurs (Sample no.7) at 30.70 m water depth off Besant Nagar. In the surface sediments a northward increasing content of K₂O is noticed in the area. The K₂O content is associated with sandy sediments. The K₂O exhibits a significant positive correlation with Fe₂O₃ (+0.81) and MgO (+0.67).

MgO: The MgO values vary from 1.58 to 3.93% with a mean of 2.63% in the surface sediments, showing an enrichment when compared with its UCC value of 2.20% (Table -1). The content of MgO (>3%) in the surface sediments has a seaward-increasing trend around 30m isobath off Besant Nagar. However, a higher MgO (>3%) value occurs around 15 to 20m isobaths off Injambakkam. The MgO content is associated with sandy sediments. The MgO has a positive correlation with CaO (r = +0.59),

and Fe₂O₃ (r = +0.45), in the surface sediments (Table -2).The enrichment of magnesium in the studied sediments, when compared to the crustal value,could be due to the association of shells and shelly materials of marine organisms.

Table: 1. Major oxides in the Bulk Sediments

(UCC = Upper continental crust elemental values after Condie,1993)

SAMPLE	Na2O%	K2O%	MgO%	CaO%	Fe2O3%	DEPTH
2	3.8	0.85	2.13	10.00	1.35	16.20
4	4.54	1.33	2.64	5.10	1.92	22.20
6	4.32	1.58	3.91	15.10	4.71	28.90
7	4.4	1.96	3.93	10.00	5.17	30.70
9	4.24	1.24	2.51	5.00	1.80	21.70
11	2.92	1.24	2.31	5.50	2.05	18.60
13	4.32	1.88	2.51	5.50	4.53	10.20
15	4.59	1.51	3.1	5.80	2.37	16.30
17	2.36	1.13	2.23	7.50	1.96	21.10
19	1.92	0.92	1.58	5.00	3.72	19.10
21	2.01	0.97	3.14	11.50	0.09	12.40
22	2.17	0.62	2.01	5.50	0.60	11.60
24	2.43	0.7	2.14	5.53	0.99	24.60
27	2.55	0.83	2.67	15.00	1.41	17.70
	Na2O%	K2O%	MgO%	CaO%	Fe2O3%	
Minimum	1.92	0.62	1.58	5.00	0.09	
Maximum	4.59	1.96	3.93	15.10	5.17	
Average	3.33	1.20	2.63	8.00	2.33	
UCC	3.90	3.40	2.20	4.20	4.50	

CaO: The CaO content in the surface sediments varies from 5.00 to 15.10% with a mean value of 8.00 %, exhibiting an enrichment when compared with its UCC value of 8.00% (Table -1). The CaO content of the surface sediments in a major part of the study area is less than 8%, while greater than 8% to 12% CaO occurs in patches around 15 to 20m isobaths off Adyar River and between 28m and 30.70m isobaths off Besant Nagar. The concentration of CaO >12% occurs at 30m isobath off Besant Nagar and also between 15m and 25m isobaths off Kovalam. A high CaO concentration of 15.10% occurs (sample no.6) at 28.90m water depth in fine sands. The CaO has a strong positive correlation with MgO (0.59) in the surface sediments (Table 2). The CaO content might be derived from the skeletal remains of gastropods and pelecypods associated with the sandy sediments.

Fe₂O₃: The Fe₂O₃ contents vary from 0.09 to 5.17% with a mean value of 2.33 (Table -1) in the surface sediments. It shows a depletion concerning its UCC value of 3.90. The higher average content (5.17%) of iron occurs (Sample no.7)at 30.70m water depth in fine sand.

Table: 2. Correlation Coefficient matrix of the chemical components in the surface sediments

	Na ₂ O	K ₂ O	MgO	CaO	Fe ₂ O ₃
Na ₂ O	1	0.33	-0.07	-0.25	0.62
K ₂ O		1	0.67	0.04	0.81
MgO			1	0.59	0.45
CaO				1	0.1
Fe ₂ O ₃					1

The surface sediments show a northward increasing iron content with a pocket of >4% Fe₂O₃, occurring between 30m and 30.7m isobaths off Besant Nagar in the fine sand (Fig.6).The strong correlation between Fe₂O₃ and K₂O (r = 0.81), with Na₂O (r = 0.62) and with MgO (r=+0.45) indicate the derivation of iron from ferromagnesian minerals, feldspars, iron oxide coatings and clay minerals. In the continental shelf sediments, the iron content is derived from the weathering of continental rocks. The concentration of Fe₂O₃ is mainly controlled by ilmenite, magnetite, pyroxenes, amphiboles and garnet in the sand size fraction of the sediments and to some extent by aluminosilicates in the clayey sediments.

DISCUSSION

The metal content in the sediments depends on their chemical and mineralogical compositions .The seabed surface sediment texture varies from coarse sand, medium, fine, and very fine sand to coarse silt.The sand mainly comprises angular vitreous quartz grains and sub-rounded quartz grains with ferruginous coatings. The abundance of vitreous grains varies from 1% to 45% while the quartz grains with ferruginous coatings range from 85% to 2%. A high abundance of 85% quartz grains with ferruginous coatings occurs around 25m water depth.The seabed sediments comprise quartz, orthoclase and plagioclase feldspars, hornblende, arfvedsonite, orthopyroxenes and clinopyroxenes, ilmenite, magnetite, sillimanite, garnet, epidote, zircon, monazite, rutile, kyanite, sphene, staurolite, tourmaline, corundum, micaceous minerals – muscovite, biotite, phlogopite and clay minerals which play major role in controlling the chemical composition of the sediments of the study area.The clay minerals could have contributed alkali, alkaline earth metals and iron content to the sediment. The sediments derived from

peninsular India showed a high amount of montmorillonite¹⁰. Clay minerals such as illite, kaolinite, smectite and chlorite are present in the shelf sediments off Chennai³⁷. Minerals such as plagioclase feldspars, sodic amphiboles- arfvedsonite, feldspathoids and clay minerals can contribute Na to the sediments. Sodium may also occur in calcareous shell material through the biological removal of sodium from seawater by certain calcareous organisms⁶. The sodium occurs as dissolved Na^+ in interstitial fluids. Magnesium is found in feldspars and would have been transported to the sea along with other weathered minerals. The higher content of Mg in the marine sediment is attributed to Mg^{2+} by the ionic exchange process with Ca^{2+} . The distribution of Mg in marine sediments can also be controlled by biological processes⁷. The average CaO value (8%) is higher than its UCC value (4.20%). The average UCC values, the MgO and CaO are higher than their crustal values. Calcium in oxide and carbonate forms is mainly contributed by shells and shell debris though oxide form is also derived from minerals such as plagioclase feldspars, clinopyroxene, diopside, and hornblende.

The minerals ilmenite, magnetite, pyroxenes, amphiboles, and garnet present in the sediments of the study area contribute Fe, Mn, and Mg. The Na and K have been derived from feldspars and clay minerals and are influenced by pore space solutions of coarse to medium sands. During weathering, the Mn is dissolved as bi-carbonate and transported in solution as a constituent of sediment debris into the ocean. It can also be transported to the sea as colloidal MnO_2 ⁹. Iron is transported from the continents and is associated with minerals such as feldspars, augite, hornblende, magnetite, and ilmenite. Iron oxide coatings on minerals are geochemically important as they can act as scavengers for trace elements; and subsequently be transported to the sea along with minerals such as feldspars. The coarser particles tend to be deposited adjacent to the continents. The finer-sized clay mineral with discrete grains of iron and manganese hydrous oxides can have a high content of trace elements by adsorption and co-precipitation reactions. Because of their size, these particles may escape deposition on the continental shelf and be transported to the deep-sea areas.

CONCLUSIONS

- The studied marine sediments exhibit enrichment of alkaline earth elements MgO and CaO content compared to the average of upper continental crust (UCC) values.
- Alkali (Na and K) and alkaline earth metals (Mg and Ca) could have derived from feldspars and pyroxenes, amphiboles and clay minerals such as montmorillonite and illite as well as interstitial pore waters since the sediments studied are all sands ranging from coarse, medium and fine-grained.

- Minerals such as ilmenite, magnetite, pyroxenes, amphiboles, garnet and clay minerals could have contributed to iron and manganese content in the sediments. Iron oxide coatings on minerals are geochemically important as they can scavenge for trace elements. Iron and manganese could be transported to the marine environment as a colloidal solution and as an oxide or hydroxide solution from the hinterland source.
- The dispersal of alkali, alkaline earth metals and iron oxides of the surface sediments of the study area was carried out through particulate-minerogenic, biogenic and dispersed iron and manganese oxide/hydroxide phases from the source through the Adyar and Palar Rivers. The variation of elemental concentrations is related to supply due to sea level fluctuation and variations in the weathering of rocks due to climate change in the hinterland.

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