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Research Article

Geochemical Analysis and Beryllium-Dating Studies of Marine Core Sediment Belong to the Central Western Bay of Bengal

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Abstract

A gravity core having size of 4.12 cm was collected from the marginal coastal waters of central western Bay of Bengal, which covered the continental shelf off Krishna Delta (Nizampatnam Bay) during the 157 cruises of O. R.V. Sagar Kanya. It was sub-sampled with every 2 cm interval resulting a total of 212 samples. Half part of each sample was dried at 60 ^{0}C, grinded and sieved through 230 mesh size and studied for organic carbon (OC), calcium and magnesium carbonates ($CaCo_3$ & $MgCo_3$) by titration methods. By following $^{10}Be/^{9}Be$ dating study method; investigations pertaining to rate of sedimentation were also carried out and all the results interpreted based on the existing phenomenon.

Keywords: Marine sediment, calcium and magnesium carbonates, Geochemical, Dating, Organic Carbon

1. Introduction

Research pertaining to ocean environment has been taking place at significant levels during recent years to explore variety of resources belong to a sea [1]. Investigations about geochemistry of marine sediments facilitate to understand or for getting information related to geological and oceanographic systems namely weathering, climatic, biological and diagenetic processes etc. The abundance of elements and their relative distribution in sediments are used to reconstruct the paleoenvironmental and climatic conditions [2]. The objective of the present study is to investigate about possible resources namely carbon and carbonates contained in a marine sediment. In this study, geochemistry and dating of a marine sediment belonging to central western Bay of Bengal that cover the continental shelf off Krishna Delta (Nizampatnam Bay) was undertaken to probe the concentrations of its organic carbon (OC), calcium and magnesium carbonates ($CaCO_3$, $MgCO_3$). Further the sediment core was used to study the 'Be' dating by using Accelerator Mass Spectrometry (AMS) for finding age of the core. This provides to interpret the variability of the surface water primary production and sediment depositional conditions during the last 60 kyr in the coastal margins of the central western Bay of Bengal.

2. Samples Preparation

Fig 1 shows the location of the present study that related to the 15^0 25' 226" N latitude and 81^0 09' 735" E longitudes.

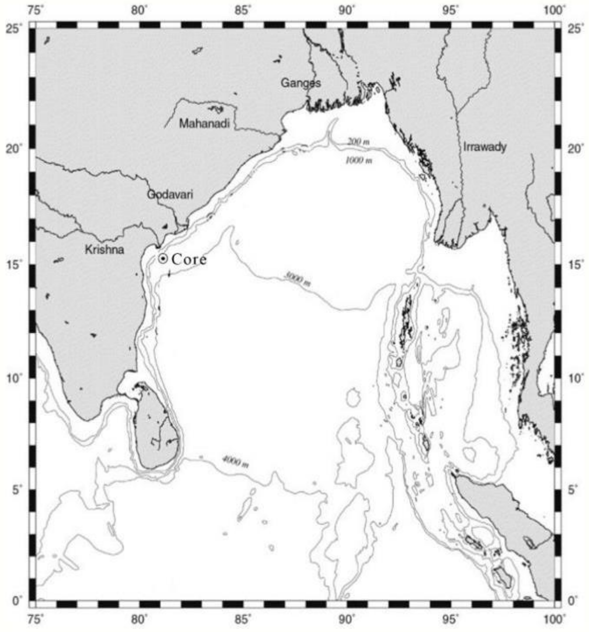

Fig. 1. Location map of the Nizampatnam Bay

The core sediment was sub-sampled for every 2 cm of its length. These samples were dried at 60 ^{0}C, further grinded by using agate mortar to obtain fine powder and sieved through 230 mesh size. Half part of each sample was used for the studies of organic carbon (OC), calcium and magnesium carbonates ($CaCO_3$ & $MgCO_3$) by titration methods. By following $^{10}Be/^{9}Be$ dating study method, accumulation of layers related to the sediment has been evaluated.

3. Experimental Details

Experimental procedures followed in the present studies for dating and geochemical properties have been described below.

3.1. ^{10}Be/^{9}Be dating

Approximately 1-gram quantity of each sample was taken to perform leaching process for extracting the maximum possibility of beryllium (Be) isotopes. The leachate was processed to divide the beryllium isotopes. Collected ‘Be’ was placed on hot plate at 120 ^{0}C temperature and dried till it reaches a quantity equal to 1 ml. ‘Be’ samples were transferred into separate centrifuge tubes and equivalent amount of ammonia (NH_3) was added to get precipitation. After getting precipitation, these centrifuge tubes were put into centrifuge machine at 4500 RPM to remove liquid from the precipitation. The precipitated one was beryllium hydroxide [Be $(OH)_2$]. The liquid part was separated from the precipitation and put into a furnace taking in quartz vials and maintained the temperature at 90 ^{0}C for 4 hours, 400 ^{0}C for 6 hours and finally at 900 ^{0}C for 8 hours. Hydroxides of ‘Be’ were converted into oxides form; the powdered ‘BeO’ that loaded into the cathode tube with niobium (Nb) powder [3] and analyzed for ^{10}Be/^{9}Be by using Accelerator Mass Spectrometer (AMS). Beryllium-10 was measured on the Tandem Accelerator Mass Spectrometer at the Inter University Accelerator Centre (IUAC), New Delhi. Stable ‘^{9}Be’ concentration was determined by using Inductively Coupled Plasma Mass Spectrometry (ICPMS) at Centre for studies on Bay of Bengal, Andhra University, Visakhapatnam; India.

3.2. Geochemical analysis

Organic carbon (OC) was studied by using Walkey Black method while $CaCO_3$, $MgCO_3$ determined by using Barnes method [4] at marine chemistry laboratory, Andhra University, Visakhapatnam.

4. Results and Discussion

Some of the physical properties of the present sediment are described below.

4.1. Colour

Iron and manganese play a vital role in variation of the sediment colour. Lyle [5] reported that iron and manganese oxy-hydroxides were observed to form under oxic conditions where they fully oxidized resulting brownish tinge to the sediments. Therefore, sediment colour is an important parameter that indicates about the paleo redox conditions of the sediment(s). Hence, brown or pale brown colour sediment can be regarded as representative of the oxic facies in a sedimentary basin. Organic matter also plays significant role in the modification of sediment colour. If organic matter present, it shows a darker colour resulting in dark grey to the olive-coloured sediment. The poor oxygen replenishment arises in anoxic condition at the bottom surface of sea. Thus, darker colour formation of sediment believed to be as it formed under anoxic conditions of deposition. Besides the colour of the sediment, trace metals profile(s) have also been utilized to deduce the paleo redox conditions.

The colour of the present core has brownish oxidized layer up to 0 – 30 cm and from 31 cm onwards till the end of the core it found to be in dark black colour. Dark black colour that appears after 30 cm may indicate presence of higher organic matter. The supply of organic matter was abundant due to enough quantity of oxygen availability at bottom of sea water to oxidize most of it resulting by deposition of sediment upper sections in the present interglacial period. The sedimentation of the core lower portion related to the Nizampatnam Bay assumed to took place during the last glacial period under anoxic conditions.

4.2. ^{10}Be/^{9}Be dating and rate of sedimentation

Dating studies of the core sediment are useful to delineate possible boundary of Holocene/Pleistocene period. The details of the dating, rate of sedimentation, organic carbon besides calcium and magnesium carbonates with their data are given in Table 1. Seven sections of core samples i.e., from 50 to 350 cm by having 50 cm gap or space between each successive specimen (7 samples) were used for dating studies that carried out by using cosmogenic ^{10}Be/^{9}Be radio isotopes.

Table 1:
Age, sedimentation rates and correlation between rate of sedimentation, OC, $CaCO_3$, and $MgCO_3$ of the sediment core (Bay of Bengal).

Core depth (cm)	**Age (year)**	**Rate of sedimentation {cm/yr)**	**Organic carbon (OC)**	**Calcium carbonate ($CaCO_3$)**	**Magnesium carbonate ($MgCO_3$)**
50	1300 ± 169	0.013	1.787	4.0	1.26
100	4902 ± 637	0.008	2.529	2.5	1.34
150	11120 ± 1446	0.006	3.131	2.5	1.26
200	19879 ± 2584	0.004	3.216	1.5	1.68
250	31212 ± 4958	0.004	3.168	1.5	1.09
300	45161 ± 5871	0.003	3.968	2.1	1.05
350	61786 ± 8032	0.006	3.578	2.05	0.88
		Correlation	-0.91019	0.92538	0.07037

The rate of sedimentation in the upper part (0 – 150 cm) of the undertaken present core is 0.009 cm/yr (or) 9 cm/kyr, while in the range 150 – 350 cm of the core found to be 0.0042 cm/yr or 4.2 cm/kyr. The rate of sedimentation on the entire core up to 350 cm is 0.0062 cm/yr or 6.2 cm/kyr. In the core, obtained low sedimentation rate at a depth 300 cm is 0.003cm/yr or 3cm/kyr that belong to the Pleistocene period while high rate of sedimentation at a depth 50 cm is 0.013 cm/yr or 13 cm/kyr observed, which belongs to Holocene period. Based on the ages and rate of sedimentation of the present core, its range 0 to 150 cm assumed to belong to the Holocene period and below 150 cm it considered to be the middle Pleistocene period. This is also corroborated by the results of $CaCO_3$ shown in the Fig. 2. Similar age and sedimentation rates of the core from the continental margin of the south western Bay of Bengal was reported by Sri Rama Krishna [6], about the Nizampatnam Bay by Venkateswara Rao [7].

4.3. Organic carbon

Organic carbon (OC) is an important constituent of marine sediments that used for deciphering the history of the depositional environment. It plays a key role in controlling the redox potential of the sediment and thereby the behaviour of other chemical processes. The transported sediment in situ major input sources of organic carbon is (i) allochthonous: the humus rich organic matter transported by the rivers [8], and (ii) autochthonous: The planktonic organic matter produced in the surface water as well as the benthos that contributed to organic matter on the shallow sea bottom. A number of biological, physical, chemical and geological factors controlling the organic carbon inputs at bottom of the sediments, such as primary productivity of overlying waters, dissolved oxygen concentration in bottom waters, texture of sediments and rate of sedimentation [9-11].

The vertical variation of the OC, $CaCO_3$ and $MgCO_3$ in the present studies has been evaluated based on the core spectrum shown in Fig. 2. The OC content in the present results is observed to vary from 1.09% to 4.19% with an average of 3.05%. Higher amount of organic carbon is observed at the depth range of 282 – 364 cm (av. 3.732%); while the lower OC content av. 2.55% occurred at 0 –70cm. Higher concentrations of OC is attributed to upwelling associated productivity in the overlying waters, reducing conditions in bottom waters and due to deposition of sediments through slumps and slides down the continental slope. The low OC content from 0 – 70cm is observed primarily due to the low supply of OC from primary productivity of the overlying waters, terrestrial and reworked sediments and dilution by constituents, as observed in the eastern Arabian sea by earlier investigators [12]. Normally, OC is showing an increasing trend with increasing clay percentage, coarse fraction weight percentage, decreasing grain size and increasing standard deviation.

Similar variations of organic carbon in the sediments of continental shelf of Bay of Bengal was observed by Rao [13]; Rao and Sarma [14] and they reported that the sediment texture plays a minor role as the sediments contain mostly carbonate-rich silty clay. The concentration of organic matter in sediments depends on the absolute quantities of organic matter injected to the bottom notably by (upwelling aided) high primary production [15,16]. This is the so called "productivity hypothesis" in which productive input of OC far exceeds its oxic removal [17]. High biogenic productivity on surface water does not always ensure high sediment organic carbon. Thus, the regions of high biogenic productivity (< 0.75g $C/m^2/day$) of the eastern Arabian Sea, namely north of Gulf of Kutch and south of Kochi have about the same organic carbon in their sediments as those present in between the Gulf and Kochi [18]. After a protracted controversy, OC of the eastern Arabian Sea sediments was believed to be conforming to the productivity theory [19].

As per the "preservation hypothesis", the presence of oxygen depleted waters at the intermediate depths in some parts of open ocean environments or in enclosed marginal basins has been held responsible for the sedimentary organic carbon of eastern Arabian Sea sediments [10,18,20]. Such conditions are usually met optimally in the continental slope regions. Here the shelf width and the slope gradient play an important role. In the Black Sea, where oxygen-rich waters are restricted by the presence of a shallow sill and a strong pycnocline regarded as most extreme and member of such a scenario [21]. Such basins turn truly anoxic and H_2S is present even in the water column [22,23]. More recently, it has been shown that the accumulation rate of OC in anoxic Black Sea sediments has no different from that of sediments forming at similar water depths under fully oxygenated conditions [24]. In view of these contrasting conditions of OC enrichment mechanism, it would be interest to explore the enrichment mechanism in the present core sediments.

A general Holocene enrichment and Pleistocene depletion seems to be directly related to primary productivity changes in surface water as shown by $CaCO_3$ variations in Fig.2. This can be authenticated as observed in the eastern Arabian sea in the earlier study [12]. The brief peak at and prior to the Last Glacial Maximum (LGM) indicates the productivity pulse also as indicated by $CaCO_3$. The Holocene maximum indicates that in addition to contribution from enhanced primary production, the terrestrially derived clay (due to intensified SW monsoons caused continental erosion) rich of adsorbed OC also plays a significant role in these sediments.

In the marine environment, greater depth provides favourable conditions/environment for the preservation of organic carbon consequently the rate of decomposition decreases with depth. It is believed that under successively lower temperatures, the organic decay brings down the metabolic activity by bacteria resulting in the high organic carbon content in the marine sediments. The results obtained in the present study suggest that the organic carbon is derived from biogenic and terrigenous sources.

With the obtained elements of the present core published elsewhere [25], organic carbon present in the core showed positive correlation in relation to Co ($r = 0.33$), K ($r = 0.31$), Zn ($r = 0.15$), Fe ($r = 0.13$), Cr ($r = 0.12$), Ni ($r = 0.11$), Rb ($r = 0.05$), Cu ($r = 0.003$), and negative correlation with $CaCO_3$ (-0.56), $MgCO_3$ (-0.11), Ti ($r = -0.001$), V ($r = -0.038$), Ca ($r = -0.201$), Mn ($r = -0.238$), Sr ($r = -0.238$), Sc ($r = -0.336$) indicating their origin from terrigenous and association with clay. Similar relationships were reported in eastern Arabian Sea margin also by Thamban et al. [26] in the sediments of Bay of Bengal by Rao and Sarma, [14] and Venkateswara Rao [13]. The statistical variations of the organic carbon, calcium and magnesium carbonates are presented in the Table 1 and their mean values are presented in the table 2.

Table 2
The average concentrations of the Organic carbon (OC), calcium and magnesium carbonates (%) present in the core.

Location	Core depth (m)	Organic Carbon		$CaCO_3$		$MgCO_3$	
		Range (%)	Total core Av. (%)	Range (%)	Total core Av. (%)	Range (%)	Total core Av. (%)
Nizampatnam Bay	4.12	4.19 to 1.09	3.07	6.00 to 1.30	2.51	2.10 to 0.08	1.25

4.4 Calcium and magnesium carbonates

Variation in calcium carbonate content is one of the more unique characteristics of deep-sea sediment cores. Biogenic contribution is the major source of calcium carbonate ($CaCO_3$) in the deep-sea sediments. Preservation of $CaCO_3$ is influenced by numerous parameters such as sea surface productivity, transportation time through the water column, seawater and pour water chemistry, sedimentation rate, bio turbidity, sediment mineralogy, climate and deep-sea environment. Kolla et al., [27] postulated that calcium carbonate can be used as a climatic control parameter, this can be controlled by biological productivity in the overlying water, its depth, pressure, chemistry, turbulence and dilution by non-carbonate components could be considered as the main factors influencing the carbonate distribution. The enrichment of $CaCO_3$ can be affected by dissolution and dilution from non-biogenic components.

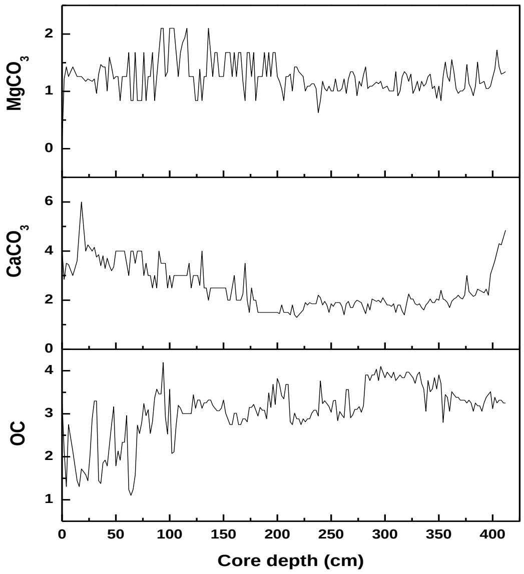

Fig.2. Down core variations of OC, $CaCO_3$ and $MgCO_3$ (%) in core sediment.

In the present study, $CaCO_3$ content varied from 6% to 1.3% with an average of 2.59%, whereas $MgCO_3$ content varied from 2.1% (many down core sections) to 0.084% with an average of 1.239%. $CaCO_3$ is relatively less at 184 – 224 cm (1.52%), while it found to be higher at 0 – 74 cm (av. 3.84%).

The observed increase of $CaCO_3$ content from glacial to interglacial periods may be due to higher primary production aided deposition, i.e., the sea surface primary production [28]. The earlier reports by Divakar Naidu et al., [29], Peterson and Prell [30] and Oba [31] also showed higher $CaCO_3$ concentration in the glacial and / or at glacial/ interglacial transitions in the Indian Ocean. On observing the available dating data, it shows that the upper part (0 to 150 cm) of core sedimentation rate (0.009 cm/year) is higher than lower part (152 – 350 cm) sedimentation rate (0.004 cm/year). Thus, the core $CaCO_3$ shows positive relationship with sedimentation rate.

Literature on calcium carbonate data of full glacial-interglacial cycles is not available from earlier studies on the Bay of Bengal sediments. In the present study, an Atlantic pattern of calcium carbonate enrichment is observed i.e., $CaCO_3$ enriched during interglacial and impoverished during the glacial periods [32-34]. Due to dissolution of carbonate in deep sea, its minima have been observed in the present specimens belong to glacial periods. Holocene $CaCO_3$ deposition indicates an intensification of the SW monsoon that has promoted upwelling in the region. Lower carbonate accumulation rate during the glacial phase indicates the weakening of the SW monsoon.

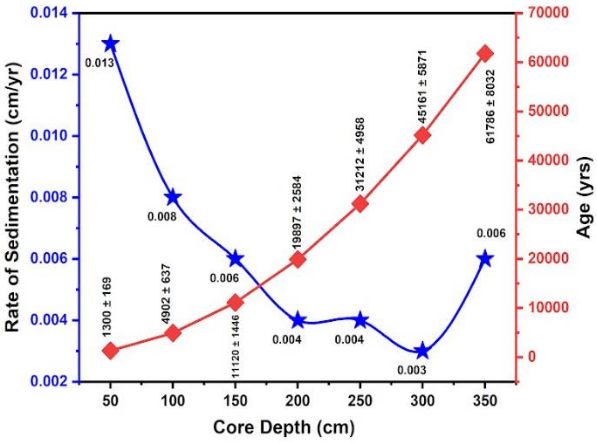

Fig. 3. Variation of sedimentation rate with core depth and age

As shown in the table 1, $MgCO_3$ shows inverse relationship with $CaCO_3$ from surface (0 cm) to 182 cm in the down core, which indicate that the deposition of calcareous organism is higher at these depth range when compare with magnesium deposition. From 182 cm onwards both carbonates varied showing parallel relations up to bottom of the core. Fig.3 indicates opposite trend of sedimentation rate with age of the core as a function of core depth. Lower the age higher is the sedimentation rate and converse is true reflecting for higher the age of core corresponding to lower sedimentation rate.

Based on the elements of the present sediment reported elsewhere [25] by the present group, $CaCO_3$ showed a significant positive correlation with Sc (r = 0.63), Ca (r = 0.43), Mn (r = 0.26), Sr (r = 0.24), V (r = 0.01), Cu (r = 0.01), which indicates that these are biological origin and negative correlation with OC (r = -0.57), Co (r = -0.38), K (r = -0.30), Zn (r = -0.17), Cr (r = -0.15), Fe (r = -0.13), Ni (r = -0.15), Rb (r = -0.12), Ti (r = -0.009), suggesting that it derived mainly from the marine source. $MgCO_3$ showed a significant positive correlation with Rb (r = 0.10), Ca (r = 0.09), V (r = 0.08), Sc (r = 0.07),Ni (r = 0.07), Zn (r = 0.06), Fe (r = 0.04),Co (r = 0.04), Ti (r = 0.03),Cu (r = 0.03), Mn (r = 0.02), K (r = 0.01), which indicates that both are originated from the same source either from biological or marine source and negative correlation with Cr (r = -0.04), Sr (r = -0.013) and OC (r = -0.08) indicating its dominant marine origin.

Most of the accumulated $CaCO_3$ gets deposited on the sea floor in margin sediments. Weathering products of calcium carbonated materials in bottom water; re-suspension and re-deposition could contribute to $CaCO_3$. Calcium carbonate enhancement causes variation both in chemical and biological production processes that show impact on ocean ecosystem. Decrease of $CaCO_3$ may be due to its increased dissolution varying composition of the sediment. Carbonate content is inversely related to organic content in the core samples.

The calcium carbonate distribution in the surficial sediments of the eastern margin of India [35] indicates that the modern sediments are poor in calcium carbonate. This may be due to the dilution effect of the detritus derived from the adjacent landmass. The carbonate content in the nearshore sediments is about 5%. Although the lime deposition has taken place on the entire outer shelf all along the east coast of India at a time of lowered glacial periods [36], the biogenic sediments that now exposed only in some smaller zones have not yet been completely masked by recent deposition of terrigenous sands and muds coming either from the river mouth or from the coastal erosion [37].

5. Conclusions

Colour of the present core from 0 – 30 cm found to be brownish oxidized and from 31 cm onwards till the end of the core exhibited dark black colour due to presence of organic matter in larger quantity. The OC content in the present results is observed to vary from 1.09% to 4.19% having an average of 3.05%. In the present core; obtained low sedimentation rate at a depth 300 cm is 0.003cm/yr or 3cm/kyr that belong to the Pleistocene period while high rate of sedimentation at a depth 50 cm is 0.013 cm/yr or 13 cm/kyr observed, which belongs to Holocene period. Dark black colour that appears after 30 cm may indicate presence of higher amount of the produced $CaCO_3$ gets deposited on the sea floor in marginal sediments. In the present studies obtained $MgCO_3$ found to show inverse relationship with $CaCO_3$ from the surface (0 cm) to 182 cm in the down core indicating that the deposition of calcareous organism is higher at these depth range when compare with magnesium deposition. From 182 cm onwards both carbonates varied showing parallel relations up to bottom of the core. Weathering products of calcium carbonated materials in bottom water, resuspension and their redeposition could contribute to $CaCO_3$.

Conflicts of Interest

The authors declare no conflicts of interest.

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