

Anaerobic carbon mineralization through sulphate reduction in the inner shelf sediments of eastern Arabian Sea

Richita Naik*, S. W. A. Naqvi, J. Araujo
CSIR- National Institute of Oceanography, Dona Paula, Goa- 403004, India
Email address: naik.ruchi8@gmail.com

Abstract

Monsoon-induced coastal upwelling, land run-off, benthic and atmospheric inputs make the western Indian shelf waters biologically productive that is expected to lead to high rates of mineralization of organic matter (OM) in the sediments. Dissimilatory sulphate reduction (SR) is a major pathway of OM mineralization in near-shore marine sediments owing to depletion of other energetically more profitable electron acceptors (O_2 , NO_3^- , Mn and Fe oxides) within few millimetres of the sediment-water interface. We carried out first ever study to quantify SR rates in the inner shelf sediments off Goa (central west coast of India) using the ^{35}S radiotracer technique. The highest rates were recorded in the upper 10 cm of the sediment cores and decreased gradually thereafter below detection. Despite significant SR activity in the upper ~ 12 to 21 cm at most of the sites, pore water sulphate concentrations generally did not show much variation with depth. The depth integrated SR rate ($0.066 - 0.46 \text{ mol m}^{-2} \text{ y}^{-1}$) decreased with increasing water depth. Free sulphide was present in low concentrations ($0-3 \mu\text{M}$) in pore waters at shallow stations (depth < 30 m). However, high build-up of sulphide ($100-600 \mu\text{M}$) in pore waters was observed at two deeper stations (depths 39m and 48 m), 7-11 cm below the sediment-water interface. The total iron content of the sediment decreased from ~7% to 5% from the shallowest to the deepest station. The high pyrite content indicates that the shelf sediments act as a sink for sulphide accounting for the low free sulphide levels in pore water. In the moderately organic rich (2-3.5%) sediments off Goa, the measured SR rates are much lower than those reported from other upwelling areas, especially off Namibia and Peru. The amount of organic carbon remineralised via sulphate reduction was $\sim 0.52 \text{ mol m}^{-2} \text{ y}^{-1}$. With an estimated average organic carbon accumulation rate of $\sim 5.6 (\pm 0.5) \text{ mol m}^{-2} \text{ y}^{-1}$, it appears that the bulk of organic matter gets preserved in sediments in the study region.

Key words: Carbon mineralization; sulphate reduction; continental shelf; reactive iron; organic matter; west coast of India

Introduction

Anaerobic processes involving reduction of nitrate, manganese and iron oxides, and sulphate play a major role in organic matter degradation in sediments underlying coastal upwelling zones (Jørgensen 1982; Canfield et al., 1993; Hartnett and Devol, 2003). Organic matter is degraded in sediments by microbes that sequentially utilize electron acceptors in order of decreasing energy yields i.e. $O_2 > NO_3^- > Mn^{4+} > Fe^{3+} > SO_4^{2-} > CO_2$ (Kristensen, 2000). Among these, sulphate reduction (SR) is believed to play a major role in mineralisation of organic matter in sediments in the absence of oxygen (Canfield 1989). An important factor controlling bacterial SR is the quality of organic matter present in the sediments. The labile fractions of organic matter supports higher SRR (Westrich and Berner, 1984). Also, degradation of planktonic marine organic matter is faster than that of the terrestrial organic matter (Schubert et al., 2000). Organic rich upwelling areas have been known to be important sites of C_{org} cycling (degradation and burial) (Hedges and Keil, 1995). Other factors such as sedimentation rate and the presence of anaerobic electron acceptors as nitrate, Fe and Mn oxyhydroxides also affect sedimentary C_{org} mineralization rates. Under anoxic conditions, reductive dissolution of Fe oxyhydroxides produces Fe^{2+} which will react with reduced sulphur species in the pore water to form iron sulphide minerals i.e. pyrite and polysulphides (Rickard and Luther, 1997; Morse, 1999). Pyrite and other polysulphides are stable minerals and act as the main long-term sink of reactive Fe in marine sediments (Raiswell and Canfield, 1998). In sediments which are iron limited, sulphate reduction leads to excess sulphide production which cannot be fixed as iron sulphide (Jørgensen, 1982).

There are as yet no data on SR rates in sediments of the western continental shelf of India based on direct measurements. However, over the adjoining Pakistan margin Lawet al. (2009) reported low SR rates (maximum $0.45 \text{ mmol m}^{-2} \text{ d}^{-1}$) that were attributed to the abundance of Fe oxyhydroxides which suppressed SR. Sulphate reduction rates have also been computed by Mazumdar et al. (2009) in the inner shelf sediments ($\sim 15 \text{ m}$ water depth) off Goa from porewater profiles; these indirect estimates were in the range $\sim 0.05 - 0.345 \text{ mmol m}^{-2} \text{ d}^{-1}$. Based on the first direct measurements of SR rates over the Indian shelf by the $^{35}SO_4^{2-}$ radiotracer technique, the present study aims to evaluate the role of SR in inorganic carbon remineralization over the western continental shelf of India.

Methods

Study area

As other parts of the northern Indian Ocean, the eastern Arabian Sea also experiences large changes in hydrography and circulation associated with the seasonally reversing monsoon winds (summer or southwest monsoon and winter or northeast monsoon (Naqvi et al., 2006)). During the southwest monsoon (June-September), moderate coastal upwelling brings hypoxic, nutrient rich water to the Indian shelf, promoting primary production ($> 500 \text{ mg C m}^{-3} \text{ d}^{-1}$; Naqvi et al., 2000). This in conjunction with very strong near-surface (5-10m) thermohaline stratification that results in development of anoxic conditions in near bottom waters (Naqvi et al., 2000, 2006, 2009). The seasonal oxygen deficient zone over the western continental

shelf of India is the world's largest naturally formed shallow low-oxygen system that at its peak covers an area of ~ 180,000 km² (Naqvi et al., 2000). Off Goa, this system begins to develop with the onset of upwelling in June. It intensifies with time and culminates in complete anoxia ($O_2 = 0 \mu\text{M}$, $H_2S > 0 \mu\text{M}$) in near bottom waters over the inner shelf and sometimes mid-shelf in late September and October (Naqvi et al., 2006). Sulphidic conditions in bottom waters have been found to recur in most years with the highest observed H_2S concentration being $19 \mu\text{M}$ (Naqvi et al., 2000). The sites selected for the present study – from station G3 (12m) to station G7 (45 m) – are located at the inner and mid-shelf (Fig.1). Bottom waters at these sites experience at least suboxic conditions (as indicated by denitrification) during the southwest monsoon. Sediments at the study sites are soft and silt-clay dominated with high porosity (Pratihary et al., 2014) with moderate organic carbon content (Paropkari et al., 1992; Kurian et al., 2009). Supply of labile organic carbon leads to anoxic mineralization and consequent depletion of preferred oxidants such as O_2 , NO_3^- , and oxidized Mn and Fe within few centimetres of surficial sediments.

Sample collection

Sediment samples were collected during the SSK-56 cruise of *RV Sindhu Sankalp* in October 2013 from five stations (G3 to G7) along the CaTS (Candolim Time Series) transect off Goa (Fig.1). The stations were selected to cover the entire inner shelf area off the Goa coast where sediments are seasonally exposed to anoxic bottom waters; as expected during the sampling cruise the near bottom waters at all stations except the shallowest one contained little or no oxygen (Table. 1).

Water samples were collected using Niskin samplers. Sub-samples for dissolved oxygen (DO) were taken immediately and analysed on board ship following the Winkler method having a precision of $<1 \mu\text{M}$ (Grasshoff et al., 1983). A box corer was used to retrieve undisturbed sediments. Two sediment cores were carefully sub-sampled from each site in acrylic core liners (25mm ID and ~30cm length) for SR measurements. The tubes were immediately closed by rubber stoppers, covered by aluminium foil and stored at 4°C until further processing. Separate cores were taken for analyses of porosity, organic carbon, redox sensitive metals and pyrite sulphur. The cores were sectioned at 1cm interval and frozen till further analysis. For pore water extraction, a separate core was collected in a specially designed core liner (ID: 10cm, thickness: 0.5cm) with holes drilled at every 1 cm interval. The holes were blocked by an opaque plastic tape until the extraction of pore water.

Chemical analysis

Solid phase analysis

Porosity was determined at every 1cm interval for all cores. Samples were oven dried at 60°C, ground and homogenised using mortar and pestle. The wet and dry weights of the sediment samples were noted before and after drying the samples in order to determine the water content of the sediment. Known quantity of the sediment (2g) was taken in pre-weighed (calibrated) specific gravity bottles (25ml). The bottle containing sediment was completely filled with water and kept standing for 24 hours. Weight of the bottle containing

sediment and water was then noted. Porosity of the sediments was determined following the protocol described by Pratihary et al. (2014). Samples for organic carbon (C_{org}), pyrite sulphur, trace metals and grain size analysis were freeze dried. Total carbon (TC) and total nitrogen (TN) contents of sediment samples were measured using an elemental analyser (Thermo Flash EA 1112 series) with precision of $\leq 0.8\%$ and $\leq 6\%$ for TC and TN respectively. Inorganic carbon (TIC) content of the sediments was determined using a UIC Carbon Coulometer (CM 5015) with a precision better than 3%. The C_{org} content was then calculated by subtracting the TIC values from TC. The C/N ratios were also calculated in order to trace the source and nature of organic matter. The C_{org} accumulation rates were also calculated for the inner shelf following Thang et al., 2013. We used the average sedimentation rates at two stations, assuming the sedimentation rates to be similar at all the stations due to the close proximity of the stations from each other.

$$J_{C_{org}} = C_{org}/100 \times 1/12 \times \omega \times \rho \text{ (mol m}^{-2} \text{ year}^{-1}\text{)}$$

Where $J_{C_{org}}$ is the organic carbon accumulation rate, C_{org} is the average organic carbon (%), ω is the sedimentation rate (cm y^{-1}) and ρ is the density of dry bulk sediment (g cm^{-3}). Pyrite sulphur content was determined by single step cold chromium distillation method (Kallemeyer et al., 2004) with a precision of $\leq 4\%$. The chromium reducible sulphur pool comprises mostly pyrite, elemental sulphur, and other reduced sulphur compounds that are not dissolved during cold acid distillation, e.g. greigite (Howarth and Jørgensen, 1984; Fossing, 1990). The distillation product (Zinc sulphide) was dissolved in HCl at a ratio of 1:1 and the released H_2S was fixed by addition of mixed diamine reagent (N,N-dimethyl-p-phenylenediamine sulphate and ferric chloride) (Cline, 1969) followed by colorimetric measurement at 670 nm using a Shimadzu UV 1700 Spectrophotometer. For the analysis of major elements (Al, Mg, Fe, Ti, Ca), the powdered sediment samples were digested by adding a mixture of suprapure acids ($\text{HF} + \text{HNO}_3 + \text{HClO}_4$) in 7:3:1 ratio at 190°C on a hot plate. The digested samples were dissolved in 4ml of 50% HNO_3 (suprapure) and the volume was made up to 100 ml with nano-pure water. Digested samples were analysed by an ICP- OES (Agilent Technologies, 700 series). The standard reference material MAG-1 was digested simultaneously along with the samples. Precisions of the measurements based on duplicate analysis were $\pm 0.88\text{ppm}$ for Al, $\pm 0.07\text{ppm}$ for Mg, $\pm 0.53\text{ppm}$ for Fe, $\pm 0.05\text{ppm}$ for Ti, and $\pm 0.11\text{ppm}$ for Ca. Fe/Al ratios were calculated so as to estimate the sedimentary reactive iron pool (Law et al, 2009). Grain size analysis was carried out at every 1cm interval in all cores. Around 1g of sediment was weighed and the sand fraction ($<2000\ \mu\text{m}$ to $>63\ \mu\text{m}$) was separated by sieving the sediment through $63\ \mu\text{m}$ sieve. The silt ($<63\ \mu\text{m}$ to $>4\ \mu\text{m}$) and clay ($<4\ \mu\text{m}$) fractions were analysed using Malvern Laser Particle size analyser (Master size 2000). The percentage of sand, silt and clay were determined following Folk (1968).

Pore water extraction and measurements

After sampling the cores were transported to the laboratory and the pore water extraction was done within 2-3hr. Pore water samples were taken at 1cm interval through Rhizon tubings (Rhizosphere Research Products, Wageningen, Netherlands) following Seeberg-Elverfeldt et al. (2005). Rhizon tubing consists of an inert

porous polymer tube with a length of 10 cm and a pore size of 0.1 μm . The tubings were soaked in deionized water for 30 minutes prior to pore water collection. The pore water was extracted by vacuum created with disposable 10 mL plastic syringes (B-Braun) connected to the Rhizon tubings. The first 0.5 mL of extracted pore water was discarded and the rest was used for the analyses of nutrients and sulphate. For H_2S measurements, 5ml of pore water was extracted in He flushed (for 4-5 minutes) gastight Hamilton glass syringes (to avoid re-oxidation of H_2S) and immediately fixed by adding 0.4ml of mixed diamine reagent. The absorbance at 670 nm was measured using a Shimadzu, UV 1700 Spectrophotometer after 20 minutes (Cline, 1969). The precision of this method was determined by duplicate analysis of the standards and was better than $\pm 0.14 \mu\text{M}$. Sulphate was analysed by anion exchange chromatography with suppressed conductivity detection using an Ion Chromatograph (Dionex, ICS 5000). Prior to sample injection, the samples were diluted by a factor of 100 in order to reduce the interference of other ions and then injected by passing through 0.2 μm syringe filter. The anions present in the sample were separated on an anion exchange column (ion pack AS9-HC). Calibration was performed using a Dionex combined five anions standard (composition: fluoride, chloride, nitrate, potassium and sulphate) procured from Thermo Scientific. The precision of analysis was better than $\pm 0.05 \text{mM}$. Nutrient samples were first analysed without dilution for NO_3^- and NO_2^- , the concentrations of which were expected to be low. Later, the samples were diluted by a factor of 10-20 and analysed for NH_4^+ , PO_4^{3-} and SiO_4^{4-} using a Skalar segmented flow autoanalyser following Grasshoff et al. (1999). The precisions of the measurements for NO_3^- , NO_2^- , NH_4^+ , PO_4^{3-} and SiO_4^{4-} were ± 0.06 , ± 0.006 , ± 0.01 , ± 0.003 and $\pm 0.06 \mu\text{M}$, respectively.

Sulphate reduction rates

Sulphate reduction rates were quantified using the whole core incubation method (Jørgensen, 1978). The acrylic core liners used for incubations had predrilled holes sealed with translucent silicone sealant in order to prevent loss of porewater and ease the injection of $^{35}\text{SO}_4^{2-}$ tracer into the sediment core. The water overlying the sub-cores was carefully siphoned off without disturbing the surficial sediments, leaving a thin (2-3 mm) layer of water on top. The overhead was flushed with N_2 and the core liner was plugged with a rubber stopper. ^{35}S labelled sulphate solution (10 μL of $\sim 60 \text{kBq ml}^{-1}$ $^{35}\text{SO}_4^{2-}$ in deionized water) was injected through each hole into the sediment at 1 cm interval. The holes were blocked with an opaque plastic tape and the core liner was kept upright for incubation for 12-16 hours in the dark at near in-situ temperature. Later these cores were sectioned at 1 cm interval and transferred to 50 ml centrifuge tubes containing 10 ml of 20% zinc acetate solution (w/v) to halt bacterial activity. After mixing well, these samples were stored at -20°C until further analysis. During incubation, some of the ^{35}S labelled sulphate is taken up by the bacteria and reduced to sulphide. The total reducible inorganic sulphur was determined by single step cold chromium distillation method (Kallmeyer et al., 2004). The final activity was counted on a Wallace liquid scintillation counter using Ultima gold XR scintillation cocktail (Perkin Elmer).

Sulphate reduction rates were calculated using the following equation (Jørgensen, 1978):

$$\text{SRR} = (\text{SO}_4)^{2-} \times P_{\text{sed}} \times [a_{\text{tris}} / (a_{\text{tris}} + a_{\text{tot}})] \times (1/t) \times 1.06 \quad (\text{nmol cm}^{-3} \text{ d}^{-1})$$

Where $(\text{SO}_4)^{2-}$ is the pore water sulphate concentration (mmol L^{-1}); P_{sed} is the porosity; a_{tris} is the activity of total reducible inorganic sulphur (counts per minute, CPM/ decays per minute, DPM); a_{tot} is the total activity injected (CPM/DPM); and t is the incubation time (days). The factor 1.06 is the estimated fractionation factor between ^{35}S and the natural isotope ^{32}S (Jørgensen and Fenchel, 1974). The precision of the measurements for duplicate samples was better than 10%. Corrections were made for blanks by subtracting the background and blank sample values from those incubated with the radiotracer (Kallmeyer et al., 2004).

Results

The bottom water oxygen concentration decreased from G3 (37.9 μM) to G5 (0 μM) and then increased to 3.8 μM subsequently at G6. However, as the measurements were made with the Winkler procedure all but one (G3) bottom water oxygen levels were indistinguishable from zero. Sulphidic conditions prevailed at station G5 (~ 3.2 μM of H_2S in near bottom water) few days prior to our sampling cruise, but at the time of sediment core sampling H_2S was not detected. Relatively high concentrations of NH_4^+ (5.06 μM) were also recorded in the bottom waters at G5 as compared to other stations (Table 1). Nitrate and nitrite were absent in bottom waters at G3-G5 due to complete denitrification, but these were detected at G6 and G7 (maximum 10.9 μM and 4.3 μM , respectively) indicating partial N-loss (Table 1). The sediment porosity decreased from the surface to the bottom in all cores, ranging from 0.87 to 0.6 and showing slight variability from one station to another (Fig. 2). No major downcore variations in sediment grain size were seen, while a slight variation was observed between the sites (Fig. 3). Sediments were mostly composed of silt (~75 weight%) and clay (~24 weight%). The percentage of sand was higher at G3 (2.4 weight%) than at other stations (Fig. 3). In general, the C_{org} content of the sediments decreased gradually with depth and ranged from 2 to 3% of dry weight (Fig. 2). At stations G4 and G6, the C_{org} content decreased from 2.6 % to less than 2% from 17 to 20 cm depth. The C/N ratios exhibited values ranging between 8 and 12.5 at all the stations (Fig. 2). There was a decrease in total iron content of the sediments from station G3 to G7, but no appreciable down-core variation was observed at any of the stations (Fig. 4). The sedimentary reactive iron as estimated by the Fe/Al ratio showed a decreasing trend from G3 to G7 (Fig. 4). The chromium reducible sulphur (Pyrite) content of the sediments were low (~4 mg g^{-1}) in surface sediments and increased gradually to ~16 mg g^{-1} with depth at all the stations (Fig. 4). While higher pyrite content was observed in surface sediments of G3 and G4 (~6-7 mg g^{-1}), comparatively lower values (~4-5 mg g^{-1}) were found at rest of the stations (Fig. 4).

Dissolved pore water sulphide (H_2S) ranged from non-detectable levels to a maximum of ~ 1-2 μM at stations G3, G4 and G5 (Fig. 5). However, at stations G6 and G7, we observed gradual increase in H_2S levels below a depth of 10-15 cm, reaching a maximum of ~100 μM and ~580 μM at G6 and G7, respectively (Fig. 5). Nitrate (NO_3^-) and nitrite (NO_2^-) concentrations were significantly low in pore waters, indicating their consumption through denitrification. In contrast, high concentrations of ammonium (NH_4^+) and phosphate (PO_4^{3-}) were

observed at all the study sites (Fig.7). The NH_4^+ concentration reached a maximum of $\sim 1600 \mu\text{M}$ at G5 (Fig.7), substantially higher than at other stations. The concentrations increased almost linearly with depth at stations G3 to G5; at the other two stations (G6 and G7) NH_4^+ concentrations remained fairly constant. Accumulation of PO_4^{3-} in porewaters was observed at G3, G4 and G5, ranging from ~ 40 to $120 \mu\text{M}$ and exhibiting little or no variation with depth (Fig.7). At stations G6 and G7, PO_4^{3-} concentrations were appreciably higher in upper $\sim 10\text{cm}$ (Fig.7). Overall the concentrations of SiO_4 in pore water ranged from 142 to $5199 \mu\text{M}$ at all the stations with maximum concentration of around $\sim 5200 \mu\text{M}$ at station G6. However, SiO_4 did not exhibit any particular trend down the core. It has been reported earlier that the depth profiles of both $\delta^{13}\text{C}_{\text{org}}$ and C/N weight ratio of sediments suggest that the organic matter is of planktonic origin (Agnihotri et al, 2009). The ratio of $\text{NH}_4^+ : \text{SiO}_4^{2-}$ varied from 0.04 to 0.7 signifying the abundance of diatoms in our study area. The observed high concentration of NH_4^+ , PO_4^{3-} and SiO_4^{4-} in the pore waters illustrates their regeneration through mineralisation of organic matter. Pore waters sulphate concentrations did not show appreciable variation with depth at all sites (Fig.5). The sulphate concentrations in surface sediments ranged from ~ 29 to 31 mM . At station G5, sulphate concentration at the surface (25.5 mM) was lower than at other stations (Fig.5).

The measured SR rates followed similar pattern at all the sites (Fig.5). Overall, the rates were higher in the upper $0\text{-}15\text{cm}$ falling below detection at greater depths at all the stations. However, at station G5 SR rate was measurable throughout the core. The highest SR rate at G3 was observed at sediment surface ($16 \text{ nmol cm}^{-3} \text{ d}^{-1}$) with a sudden decrease to below detection levels at 4cm depth followed by an increase. The SRR peaked at subsurface depths ($\sim 2\text{-}5 \text{ cm}$) at G4, G5, G6 and G7 with values as high as 13.8 , 12.2 , 4.5 , and $4.8 \text{ nmol cm}^{-3} \text{ d}^{-1}$, respectively (Fig.5). The depth integrated SR rates were calculated for all the stations within the depth range where measurable sulphate reducing activity was detected, i.e. up to 17.5 cm at G3, 27.5 cm for G4 and G5, 13.5 cm at G6, and 11.5 cm at G7. Maximum depth integrated SR rate was observed at G4 ($\sim 0.464 \text{ mol m}^{-2} \text{ y}^{-1}$) while it was the lowest at G7 ($\sim 0.066 \text{ mol m}^{-2} \text{ y}^{-1}$) (Fig. 6).

Discussion

Sulphate reduction and organic carbon reactivity

In the present study, the highest rates of SR occurred in the top $10\text{-}25\text{cm}$ and then decreased thereafter at all the sites (Fig.5). Similar trends in the SR rate peaking close to the sediment-water interface have been previously reported from other coastal upwelling areas such as the Chilean shelf (Ferdelman et al., 1997) and Peruvian shelf (Fossing, 1990) in the eastern Pacific Ocean, and the Namibian shelf (Ferdelman et al., 1999; Brüchert et al., 2003) in the eastern Atlantic Ocean.

Over the western Indian shelf, upwelling of nutrient rich waters sustains moderately high primary productivity (PP) ($>500 \text{ mg C m}^{-3} \text{ d}^{-1}$) as compared to other seasons when Arabian Sea becomes oligotrophic ($6.7 \text{ mg C m}^{-3} \text{ d}^{-1}$) during spring intermonsoon, Laluraj et al., 2012). The high PP supplies copious amount of reactive organic matter to the sediments (Naqvi et al., 2006). The C_{org} content of the inner shelf sediments off Goaranges from ~ 2 to 3.5% (weight %) (Fig.2) which is consistent with earlier measurements by Agnihotri et al. (2008) and

Kurian et al. (2009). A part of this reactive organic matter gets degraded in the water column. However, due to the shallow water depth most of the degradation should occur at or within the seafloor, especially during periods when anoxic conditions prevail in bottom waters. Most of this organic matter is expected to be degraded through anaerobic respiration processes. The high SR rates in the upper sediments are presumably due to availability of labile organic matter (Fig.5). In general, the low C/N values (5-7) are indicative of marine origin of organic matter (Redfield et al., 1963) while higher values are characteristic of organic matter from the terrestrial source. As the organic matter is degraded it loses protein-rich material and the C/N values increase up to 10 (Schubert, 2000). In this study, the C/N values ranged from 8.5 to 12 (Fig.2). Previous studies have also suggested that, in spite of large riverine runoff, the organic matter in our study area (inner shelf) is predominantly of marine origin as indicated by stable isotopic data (Maya et al. 2011, Cowie et al., 2014). The relatively higher C/N values at deeper depths of the core suggest an increase of refractory material with depth. The depth integrated SR rates were lower at G3, peaked at G4 and decreased thereafter with increasing water depth (Fig.6). The high depth integrated SR rates at G4 and G5 were probably related to very low levels of dissolved oxygen in the bottom waters at these stations (Table 1). A marked decrease in the integrated rates occurred at G6 and G7, as compared to G4 and G5. This may also be due to lesser availability of labile organic matter. The high productivity along the west coast of India during the southwest monsoon is restricted to a narrow band close to the coast as the upwelled water is generally unable to break through the strong near-surface pycnocline. Thus, there exists a sharp cross shelf gradient in the downward flux of labile organic matter, which also decreases as the water depth increases (Jahnke, 1996).

The amount of C_{org} remineralised through SR can be calculated from the stoichiometry of oxidation of organic matter by sulphate ($SO_4^{2-} + 2CH_2O \rightarrow 2HCO_3^- + H_2S$), according to which two moles of organic carbon are consumed for one mole of sulphate respired (Luckge, 1999). Obviously, the carbon remineralisation rates follow the same variability as the SR rates are highest at G4 ($0.928 \text{ mol m}^{-2} \text{ y}^{-1}$) and the lowest at G7 ($0.132 \text{ mol m}^{-2} \text{ y}^{-1}$) (Fig.6). The sedimentation rates in the inner shelf off Goa at G6 and G7 are 2.07 and 2.17 mm y^{-1} , respectively (Kurian et al., 2009; unpublished data). Assuming the sedimentation rates to be similar all along the transect, we used an average sedimentation rate of 2.12 mm y^{-1} to compute the organic carbon accumulation rate at each site. The computed rates are slightly higher at the shallow stations G3 ($5.635 \text{ mol m}^{-2} \text{ y}^{-1}$), G4 ($6.15 \text{ mol m}^{-2} \text{ y}^{-1}$) and G5 ($5.92 \text{ mol m}^{-2} \text{ y}^{-1}$) than at G6 ($5.19 \text{ mol m}^{-2} \text{ y}^{-1}$) and G7 ($5.03 \text{ mol m}^{-2} \text{ y}^{-1}$). As stated above, the organic matter flux to the seafloor is expected to be higher at stations located closer to the coast. Thus, from the accumulation and degradation rates we can infer that only 9% of organic matter is getting degraded via SRR and the bulk (91%) gets buried in the sediments making the shelf sediments of eastern Arabian Sea a net sink for organic carbon.

Hydrogen sulphide and pyrite formation

The shelf sediments off Goa are rich in total iron (Fe_T) and also in pyrite sulphur (Fig.4). During bacterial SR, hydrogen sulphide is produced as the end product, which may react with reactive iron eventually forming pyrite (Jørgensen, 1982). The presence of chromium reducible sulphur (pyrite) at all the study sites explains the

insignificant levels of free sulphide in pore waters at stations G3, G4 and G5, reflecting the presence of substantial quantity of reactive iron in the sediments. In sediments of the Bay of Concepcion in Chile, Ferdelman et al. (1997) reported high SR rates similar to those observed in shelf sediments off Namibia. Although the rates were comparable, the sulphide fluxes over the Chilean shelf were negligible as compared to those encountered off Namibia. Brüchert et al. (2003) attributed this to higher reactive iron content of sediments of the Chilean shelf. Although the SR rates in the eastern Arabian Sea are much lower than those off Namibia, there are copious amounts of pyrite sulphur present in the sediments. Pyrite contents in sediments off Namibia (4 to 6 mg g⁻¹) and off central Peru (2 to 5 mg g⁻¹) are also lower than that in shelf sediments off Goa (4 to 16 mg g⁻¹) (Fossing, 1990; 2000). Pyrite formation seems to serve as sink for hydrogen sulphide formed during sulphate reduction. It is possible that other anaerobic processes such as denitrification, and iron and manganese reduction may play an important role in organic matter degradation in the shelf sediments off Goa (Kurian et al., 2009; Pratihary et al., 2014). Reactive iron was not measured in the present study, but we have used the Fe/Al ratios (Fig. 4) and pore water PO₄³⁻ as indicator of reactive iron in sediments (Rozan et al., 2002, Kraal et al., 2012). In oxic surface sediments, Fe oxyhydroxides scavenge the PO₄³⁻ regenerated through organic matter degradation. As the sediments turn anoxic, reductive dissolution of these Fe oxyhydroxides takes place releasing the associated phosphate to the pore water (Rozan, 2002; Pratihary et al., 2014). However, degradation of organic matter also releases PO₄³⁻ and NH₄⁺ to the system. McManus et al. (1997) showed that PO₄³⁻ released to overlying waters was related to Fe oxyhydroxides bound PO₄³⁻. Hence high concentrations of pore water PO₄³⁻ in these sediments may also be considered as an indicator of the presence of reactive iron (Fig. 7). Accumulation of free sulphide in the porewaters was observed below 15cm and 12cm at stations G6 and G7, respectively (Fig. 5). One of the major pathways by which dissolved sulphide is removed from porewaters is by binding with Fe forming iron sulphides. However, when the reactive iron is fully consumed, the residual Fe minerals will react slowly with sulphides, leading to slow accumulation of dissolved sulphides in porewaters (Raiswell & Canfield, 1998). Another important factor for accumulation of free sulphide is the oxidation of methane by sulphate that may lead to upward diffusion of H₂S to shallower depths (Brüchert et al., 2003). Similar build-up of free sulphide at deeper levels was also reported by Fossing et al. (2000) in continental margin sediments off Namibia which they attributed to oxidation of methane by sulphate. Gas charged sediments containing pockets of methane gas were observed at a site located in the inner shelf off Goa (Mazumdar et al., 2009). Hence, the oxidation of methane by sulphate could also contribute to accumulation of H₂S at deeper depths of stations G6 and G7.

Low SRR in the eastern Arabian Sea compared to other upwelling and non-upwelling areas

The most intense upwelling in the oceans occurs along their eastern boundaries. The Indian Ocean is an exception – it houses the world's only major western boundary upwelling system (off Somalia, Yemen and Oman). In comparison, upwelling along the Indian west coast – a mini eastern boundary upwelling zone – is far less intense (Naqvi et al., 2010). Sulphate reduction rates are apparently dependent on organic carbon loading and reactive iron availability in the sediments. In the other major upwelling zones, especially off Peru-

Chile and Namibia, upwelling is far more intense with primary productivity as high as $\sim 10 \text{ g C m}^{-2} \text{ d}^{-1}$ and $1.8 \text{ g C m}^{-2} \text{ d}^{-1}$, respectively (Fossing, 1990, 1995; Bruchert et al., 2003). As a result, a lot more organic matter reaches the seafloor and the organic carbon contents of sediments is much higher (e.g. 20 to 40% off Peru (Fossing, 1990); 10% off Namibia (Bruchert et al., 2003)). The massive organic loading is not only primarily responsible for the development of intense oxygen deficiency in the water column, but it also sustains high benthic respiration including SR as evident from the high SR rates (Ferdelman et al., 1997, 1999). The SR rates measured by us in the eastern Arabian Sea are much lower (Table 2) than those reported from the Namibian shelf sediments (Benguella upwelling system) and in Concepcion Bay (Humboldt upwelling system). The SR rates reported in these areas are $8.5\text{--}22.4 \text{ mmol m}^{-2} \text{ d}^{-1}$ and $64.2 \text{ mmol m}^{-2} \text{ d}^{-1}$, respectively (Table 2). Similarly high SR rates have also been reported from several other coastal areas such as the Baltic Sea, Skagerrak and Kattegat Bay (Denmark). Sediments in these shallow regions are rich in organic carbon, ranging from 2 to 3.7% in the Baltic Sea and even higher (7.5–12.3%) in Skagerrak and Kattegat Bay (Thang et al., 2013.; Iversen and Jorgensen., 1985). It must, however, be noted that more than the quantity, the quality of organic matter is an important factor controlling the SR rates. Lückge (1999) and Law et al. (2009) found little or no sign of sulphate reduction at any site in Pakistan margin sediments. The low rates of SR were attributed either to the availability of other post-oxic metabolic pathways (Fe cycling) or to an absence of reactive organic matter. Similarly, Cowie (2005) also observed that sulphate reduction was suppressed in sediments of the Pakistan margin. The presence of reactive Fe may check SR rates in our study region as well. Moreover, the rates are also low because the sediments do not receive as much organic matter as the other eastern boundary upwelling systems so that the effect of reactive iron is not overwhelmed. Thus, the difference between the Indian margin and the Peruvian and Namibian margin sediments with regard to SR is in part due to the difference in the geology of the adjoining landmasses, which results in larger iron supply off India, and in part due to difference in hydrography, which results in lower primary production and consequently lower organic loading to sediments. Unlike the other eastern boundary areas, shelf anoxia off India is more of a physical origin (low oxygen content of upwelling waters and a very strong thermohaline stratification). The combined effect of the lower SR rates and removal of sulphide as pyrite is the conspicuous lack of free sulphide build-up in porewaters in the near-surface sediments. This has an important biogeochemical implication: the Indian margin does not support the growth of sulphur bacteria such as *Thiomargarita*, *Thioploca* and *Beggiatoa* that are commonly found off Peru-Chile and Namibia (Fossing et al., 1995; Schulz et al., 1999).

Conclusions

The SR rates over the inner shelf off Goa are much lower ($0.066\text{--}0.46 \text{ mol m}^{-2} \text{ y}^{-1}$) than those reported previously from coastal sediments in other eastern boundary upwelling areas. The rates generally decrease away from the coast. Significant build-up of hydrogen sulphide was only observed at the two deepest stations, but it occurred well below ($>12 \text{ cm}$) the sediment-water interface. The low SR rates may in part be because of the availability of reactive iron, which also causes sulphide removal into the solid phase, as evident from high concentrations of chromium reducible sulphur (pyrite) in the sediments. The other important factor controlling

SR rates in these sediments seems to be below availability of labile organic matter in the sediments. As compared to the other eastern boundary upwelling systems, upwelling is far less intense over the western Indian shelf that seems to limit deposition of labile organic matter to the seafloor. The amount of organic matter mineralized through SR is an order of magnitude smaller than the amount of carbon buried in the sediments. Low SR rates coupled with sulphide removal do not seem to provide favourable conditions for the growth of bacteria that oxidize sulphide with nitrate. This study clearly shows the relatively minor role of SR in organic carbon mineralization over the Indian shelf. However, the importance of other anaerobic electron acceptors, and in fact of oxygen itself still remains to be quantified in this region.

Acknowledgements

We are grateful to the Captain, Chief Scientist Dr. D.M. Shenoy and the crew of RV Sindhu Sankalp (cruise SSK 56) for the sample collection. Mr. B.R.Thorat is thanked for his help in sampling. We are grateful to Dr. Timothy Ferdelman from Max Planck Institute, Bremen, Germany for training R. Naik in SRR measurements. Dr. Amit Sarkar helped in designing the experimental set up. We thank Dr. S. Kurian for providing sedimentation rate data and ICP analysis, and Dr. D.M Shenoy for physico-chemical data. Mrs. S. Karapurkar and Dr. P. Kessarkar are thanked for their help in organic carbon and grain size analyses. We are grateful to Dr. A. K. Pratihary and Dr. S. Kurian for their help in manuscript preparation. R. Naik and J. Araujo thank CSIR and UGC respectively for providing research fellowship. This work was funded through SIBER India project (GAP 2425, funded from MoEs, Delhi), and CSIR funded INDIAS IDEA project (PSC 0108). This is NIO contribution number XXXX.

REFERENCES

- Agnihotri R., S. Kurian, M. Fernandes, K. Reshma, W. D'Souza, and S. W. A Naqvi. 2008. Variability of subsurface denitrification and surface productivity in the coastal eastern Arabian Sea over the past seven centuries. *Holocene* 18, 1–10.
- Aller R.C. 1990. Bioturbation and manganese cycling in hemipelagic sediments. *Philosophical Transactions of the Royal Society of London Series A—Mathematical Physical and Engineering Sciences* 331 (1616), 51–68.
- Brüchert V., B. B. Jørgensen, K. Neumann, D. Riechmann, M.Schlösser, and H. Schulz. 2003. Regulation of bacterial Sulphate reduction and hydrogen sulfide fluxes in the central Namibian coastal upwelling zone. *Geochimica Cosmochimica Acta*.67(23), 4505–4518.
- Canfield D. E. 1989. Sulfate reduction and oxic respiration in marine sediments: Implications for organic carbon preservation in euxinic environments. *Deep Sea Research*. 36, 12 I- 138.
- Canfield D.E., B. Thamdrup, J.W. Hansen. 1993a. The anaerobic degradation of organic matter in Danish coastal sediments: iron reduction, manganese reduction, and sulphate reduction. *Geochimica Cosmochimica Acta* 57 (16), 3867–3883.
- Canfield D.E., B.B. Jørgensen, H. Fossing, R. Glud, , J. Gundersen, N.B. Ramsing, B. Thamdrup, J.W. Hansen, L.P. Nielsen, P.O.J. Hall. 1993b. Pathways of organic-carbon oxidation in three continental-margin sediments. *Marine Geology* 113 (1–2), 27–40.
- Canfield D. E. 2006. Models of oxic respiration, denitrification and Sulphate reduction in zones of coastal upwelling. *Geochimica Cosmochimica Acta*. 70, 5753–5765.

- Canfield D.E., F. J. Stewart, B. Thamdrup, L. D. Brabandere, T. Dalsgaard, E. F. Delong, N. P. Revsbech, and O. Ulloa. 2010. A cryptic sulfur cycle in Oxygen-Minimum-Zone waters off the Chilean coast. *Science*. 330, 1375–1378.
- Cline J. D. 1969. Spectrophotometric determination of hydrogen sulfide in natural waters. *Limnology and Oceanography*. 14:454-458.
- Cowie G. 2005. The biogeochemistry of Arabian Sea surficial sediments: A review of recent studies, *Progress in Oceanography*. 65, 260–289.
- Cowie, G., S. Mowbray, S. Kurian, A. Sarkar, C. White, A. Anderson, H. Kitazato. 2014. Comparative organic geochemistry of Indian margin (Arabian Sea) sediments: estuary to continental slope. *Biogeosciences*. 11(23), 6683–6696.
- Fossing, H. 1990. Sulphate reduction in shelf sediments in the upwelling region off Central Peru, *Continental Shelf Research*. Vol. 10. No. 4, pp. 355-367.
- Fossing, H., V. A. Gallardo, B. B. Jørgensen, M. Hiittel, L. P. Nielsen, H. Schulz & A. Teske. 1995. Concentration and transport of nitrate by the mat-forming sulphur bacterium *Thioploca*. *Nature*, 374, 20.
- Fossing H., T. G. Ferdelman and P. Berg. 2000. Sulphate reduction and methane oxidation in continental margin sediments influenced by irrigation (South-East Atlantic off Namibia). *Geochimica Cosmochimica Acta*. 64, 897–910.
- Ferdelman T. G., C. Lee, S. Pantoia, J. Harder, B. Bebout, and H. Fossing. 1997. Sulphate reduction and methanogenesis in *Thioploca*-dominated sediment off the coast of Chile. *Geochimica Cosmochimica Acta*. 61, 3065–3079.
- Ferdelman T.G., H. Fossing, K. Neumann. 1999. Sulphate reduction in surface sediments of the southeast Atlantic continental margin between 15°38'S and 27°57'S (Angola and Namibia). *Limnology and Oceanography*. 650-661.
- Folk R.L., 1968. Petrology of Sedimentary Rocks. Hemphils, Drawer's M. University Station, Austin, Texas p. 170
- Grasshoff K., M. Ehrhardt, K. Kremling. 1983. Methods of Seawater Analysis. *Verlag Chemie*, pp. 419
- Hartnett, H.E., A.H. Devol. 2003. Role of a strong oxygen-deficient zone in the preservation and degradation of organic matter: a carbon budget for the continental margins of northwest Mexico and Washington State. *Geochimica Cosmochimica Acta*. 67 (2), 247–262.
- Hedges J. I., R. G. Keil. 1995. Sedimentary organic matter preservation: an assessment and speculative synthesis. *Marine Chemistry*. 49, 81-115.
- Henrichs S.M., W.S. Reece. 1987. Anaerobic mineralisation of marine organic matter—rates and the roles of the anaerobic processes in the oceanic carbon economy. *Geomicrobiology Journal*. 5 (3–4), 191–237.
- Hines, M.E., J. Faganeli, R. Planinc. 1997. Sedimentary anaerobic microbial biogeochemistry in the Gulf of Trieste, northern Adriatic Sea: influences of bottom water oxygen depletion. *Biogeochemistry*. 39, (1), 65–86.
- Howarth, R.W. and B.B. Jørgensen. 1984. Formation of ³⁵S labelled elemental sulfur and pyrite in coastal marine sediments (limfjorden and Kysing Fjord, Denmark) during short term ³⁵SO₄²⁻ reduction measurements. *Geochimica Cosmochimica Acta*. 48:1807-1818.
- Iversen N., and B.B. Jørgensen. 1985. Anaerobic methane oxidation rates at the sulfate–methane transition in marine sediments from Kattegat and Skagerrak (Denmark). *Limnology and Oceanography*. 30: 944–955.
- Jahnke R. A. 1996. The global flux of particulate organic carbon: Areal distribution and magnitude. *Global Biogeochemical Cycles*. 10, 71–88.
- Jensen M.M., B. Thamdrup, S. Rysgaard, M. Holmer, H. Fossing. 2003. Rates and regulation of microbial iron reduction in sediments of the Baltic-North Sea transition. *Biogeochemistry*. 65 (3), 295–317.
- Jørgensen B.B., T. Fenchel. 1974. The sulfur cycle of a marine sediment model system. *Marine Biology*. 24:189-201

- Jørgensen B. B., 1978. A comparison of methods for the quantification of bacterial sulphate reduction in coastal marine sediments 1. Measurement with radiotracer techniques. *Geomicrobiology Journal*. 1(1):11-27.
- Jørgensen B.B., 1982. Mineralisation of organic-matter in the sea-bed—the role of sulphate reduction. *Nature*. 296 (5858), 643–645.
- Kallmeyer J., T. G. Ferdelman, A. Weber, H. Fossing, B.B. Jørgensen. 2004. A cold chromium distillation procedure for radiolabeled sulfide applied to sulphate reduction measurements. *Limnology and Oceanography*. 171–180.
- Kristensen E. 2000. Organic matter diagenesis at the oxic/anoxic interface in coastal marine sediments, with emphasis on the role of burrowing animals. *Hydrobiologia*. 426, 1–24.
- Kurian S., R. Agnihotri, D. V. Borole, S. W. A. Naqvi, A. M. Ferreira, and C. Vale. 2009. Possible solar control on primary production along the Indian west coast on decadal to centennial timescale. *Journal of Quaternary Science*. 24, 109–116.
- Laluraj, C. M., K. K. Balachandran, and P. Sabu. 2012. "Enhanced biological production in the southeastern Arabian Sea during spring intermonsoon." *Advances in Oceanography and Limnology* 3.2: 133-145.
- Law G., T. W., T. M. Shimmield, G. B. Shimmield, G. L. Cowie, E. R. Breuer and S. Martyn Harvey. 2009. Manganese, iron, and sulphur cycling on the Pakistan margin. *Deep-Sea Research*. 5 Pt. II, 56, 305–323, doi:10.1016/j.dsr2.2008.06.011.
- Lućkge, A., M. Ercegovac, H. Strauss, R. Littke. 1999. Early diagenetic alteration of organic matter by sulphate reduction in Quaternary sediments from the northeastern Arabian Sea. *Marine Geology*. 158 (1–4) 1–13.
- Maya, M. V., S. G. Karapurkar, H. Naik, R. Roy, D. M. Shenoy, & S. W. A. Naqvi. 2011. Intra-annual variability of carbon and nitrogen stable isotopes in suspended organic matter in waters of the western continental shelf of India. *Biogeosciences*, 8, 3441–3456.
- Mazumdar, A., A. Peketi, P. Dewangan, F. Badesab, T. Ramprasad, M. V. Ramana, D. J. Patil, A. Dayal. 2009. Shallow gas charged sediments off the Indian west coast: Genesis and distribution. *Marine Geology*. 267, 71–85.
- McManus J., W. M. Berelson, K. H. Coale, K. S. Johnson, T. E. Kilgore. 1997. Phosphorus regeneration in continental margin sediments. *Geochimica Cosmochimica Acta*. 61: 2891–2902.
- Naqvi S. W. A., D. A. Jayakumar, R. V. Narvekar, H. Naik, V. V. S. S. Sarma, W. D' Souza, S. Joseph, M. D. George. 2000. Increased marine production of N₂O due to intensifying anoxia on the Indian continental shelf. *Nature*. 408.
- Naqvi S. W. A., P. V. Narvekar, E. Desa. 2006. Coastal biogeochemical processes in the north Indian Ocean (14, S-W). *The Sea: Ideas and observations on progress in the study of the seas*. Vol. 14: Interdisciplinary regional studies and syntheses. Part A. eds. by: Robinson, A. R.; Brink, K. H. Harvard University Press; Cambridge, MA; USA; 2006; 723-781.
- Naqvi S. W. A., H. Naik, A. Jayakumar, A. K. Pratihary, G. Narvekar, S. Kurian, R. Agnihotri, M. S. Shailaja and P. Narvekar. 2009. Seasonal anoxia over the western continental shelf. *Indian Ocean Biogeochemical Processes and Ecological variability. Geophysical Monograph Series*. 185, 333–345.
- Naqvi S. W. A., H. W. Bange, L. Farias, P. M. S. Monteiro, M. I. Scranton and J. Zhang. 2010. Marine hypoxia/anoxia as a source of CH₄ and N₂O. *Biogeosciences*. 7(7), 2159–2190.
- Overnell J., S. M. Harvey, R. J. Parkes. 1996. A biogeochemical comparison of sea loch sediments. Manganese and Iron Contents, Sulphate Reduction and Oxygen Uptake Rates. *Oceanologica Acta*. 19, 41–55.
- Paropkari A. L., C. Prakash Babu, and A. Mascarenhas, 1992a. A critical evaluation of depositional parameters controlling the variability of organic carbon in Arabian Sea sediments. *Marine Geology*. 107, 213–220, doi:10.1016/0025-3227(92)90168-H.
- Paropkari A. L., C. P. Babu, A. Mascarenhas. 1992b. New evidence for enhanced preservation of organic carbon in contact with the oxygen minimum zone on the western slope of India. *Marine Geology*. 111, 7–13.

- Kraal P., C. P. Slomp, D. C. Reed, G.-J. Reichart and S. W. Poulton. 2012. Sedimentary phosphorus and iron cycling in and below the oxygen minimum zone of the northern Arabian Sea. *Biogeosciences Discussion*. 9, 3829–3880.
- Pratihary A.K, S. W. A. Naqvi, H. Naik, B.R. Thorat, G. Narvenkar, B.R. Manjunatha, V.P. Rao. 2009. Benthic fluxes in a tropical Estuary and their role in the ecosystem. *Estuarine, Coastal and Shelf Science*. 85, 387–398.
- Pratihary A.K, S. W. A. Naqvi, G. Narvenkar, S. Kurian, H. Naik, R. Naik, and B. R. Manjunatha. 2014. Benthic mineralization and nutrient exchange over the inner continental shelf of western India. *Biogeosciences*. 11, 2771–2791.
- Qasim S. Z. 1982. Oceanography of the northern Arabian Sea. *Deep Sea research*. 29, 1041–1068.
- Raiswell R. and D. E. Canfield. 1998. Sources of iron for pyrite formation in marine sediments. *American Journal of Science*. <http://doi.org/10.2475/ajs.298.3.219>.
- Redfield A.C., B.H. Ketchum, F.A. Richards. 1963. The influence of organisms on the composition of sea water. In: Hill, M.N. (Ed.). *The Sea*. Wiley, New York. pp. 26±77.
- Rickard, D. and G.W Luther. 1997. Kinetics of pyrite formation by the H₂S oxidation of iron(II) mono-sulfide in aqueous solutions between 25 and 125 degrees C: The mechanism, *Geochimica Cosmochimica Acta*, 61, 135–147.
- Rozan T. F., M. Taillefert, R. E. Trouwborst, B. T. Glazer, S. Ma, J. Herszage, L. M. Valdes, K. S. Price and G. W. Luther. 2002. Iron-sulfur-phosphorus cycling in the sediments of a shallow coastal bay: Implications for sediment nutrient release and benthic macroalgal blooms. *Limnology and Oceanography*. 45, 1346–1354.
- Seeborg-Elverfeldt J., M. Schlüter, T. Feseker and M. Kolling. 2005. Rhizon sampling of porewaters near the sediment-water interface of aquatic systems. *Limnology and Oceanography-Methods*. 3, 361–371. [http://doi.org/Pii S0012-821x\(02\)01064-6](http://doi.org/Pii S0012-821x(02)01064-6) Doi 10.1016/S0012-821x(02)01064-6.
- Schubert C.J., T.G. Ferdelman, B. Strotmann. 2000. Organic matter composition and sulphate reduction rates in sediments off Chile. *Organic Geochemistry*. 31, 351±361.
- Schulz, H. N., T. Brinkhoff, T. G. Ferdelman, M. Hernández Mariné, A. Teske, and B. B. Jørgensen. 1999. "Dense populations of a giant sulfur bacterium in Namibian shelf sediments. *Science*. 284, no. 5413: 493-495.
- Thang N. M., V. Brüchert, M. Formolo, G. Wegener, L. Ginters, B. B. Jørgensen and T. G. Ferdelman. 2013. The Impact of Sediment and Carbon Fluxes on the Biogeochemistry of Methane and Sulfur in Littoral Baltic Sea Sediments (Himmerfjärden, Sweden). *Estuaries and Coasts*. 36(1), 98–115. <http://doi.org/10.1007/s12237-012-9557-0>.
- Thamdrup B., D.E. Canfield. 1996. Pathways of carbon oxidation in continental margin sediments off central Chile. *Limnology and Oceanography*. 41 (8), 1629–1650.
- Thamdrup B. 2000. Bacterial manganese and iron reduction in aquatic sediments. *Advances in Microbial Ecology*. 16, 41–84.
- Westrich, J.T. and R.A. Berner, 1984. The role of sedimentary organic matter in bacterial sulfate reduction: The G model tested. *Limnol. Oceanogr.*, 29: 236-249.

Figures

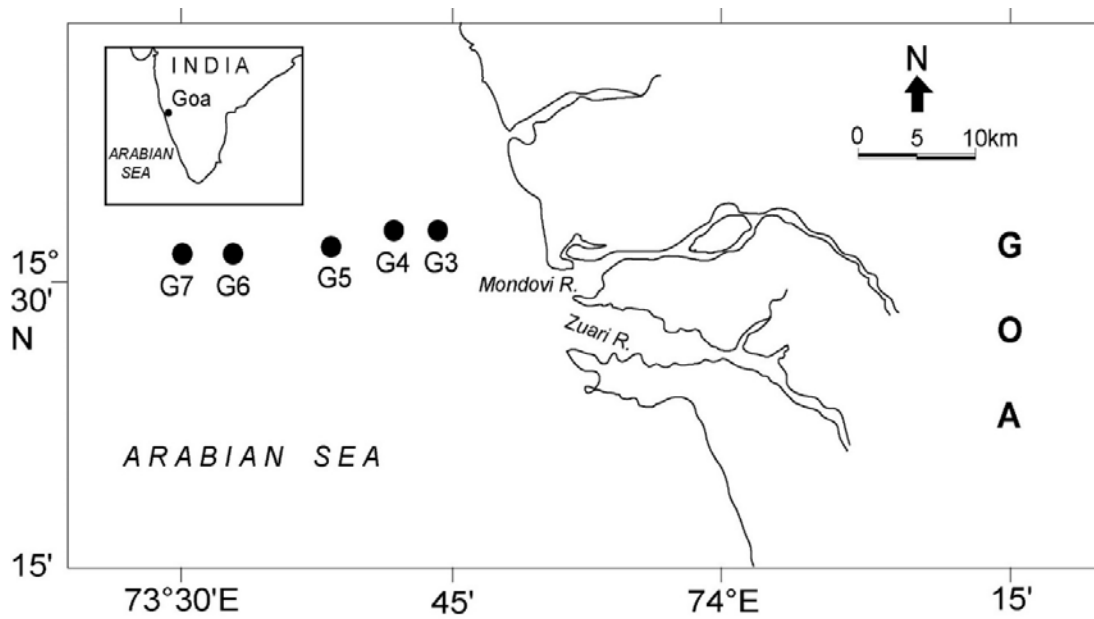


Fig.1. Map showing the geographical location of the study area- the inner shelf off Goa, Eastern Arabian Sea.

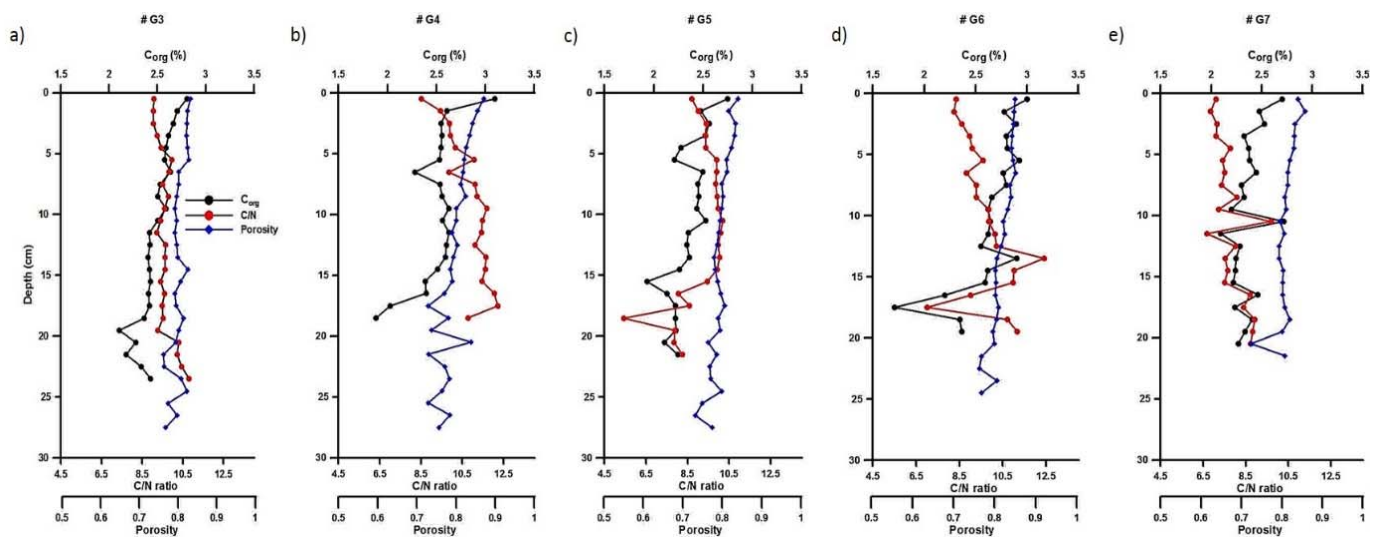


Fig. 2: Vertical profiles of organic carbon content, C/N ratio and porosity of the sediment cores at stations G3 to G7.

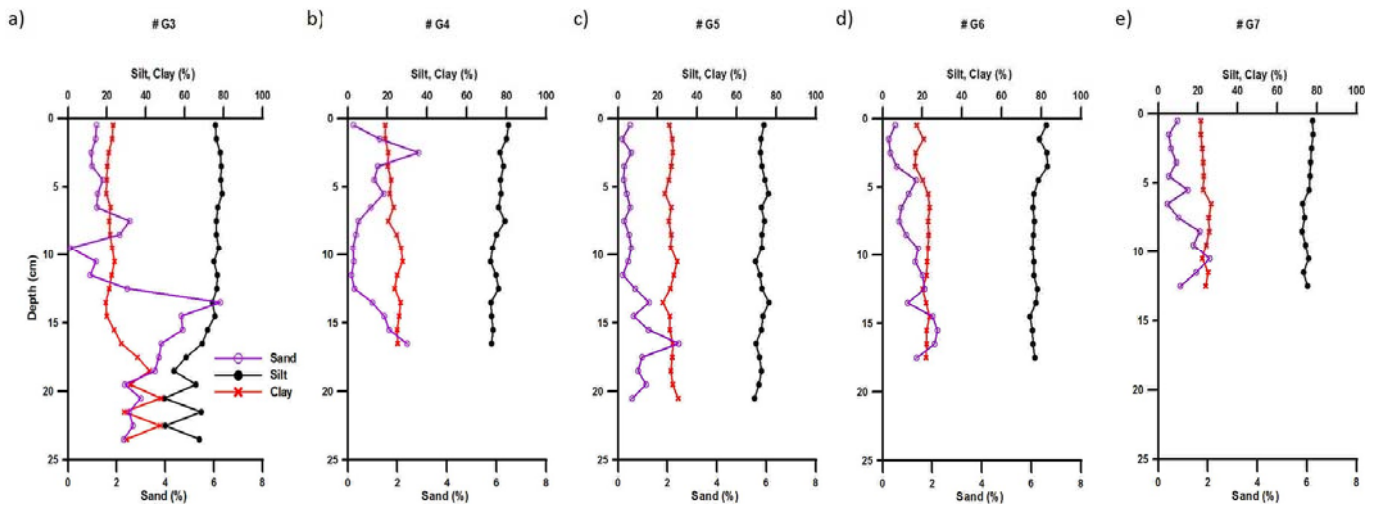


Fig. 3: Plots showing the down-core variation in sediment texture in terms of percentage of sand, silt and clay content of the sediments at all the stations.

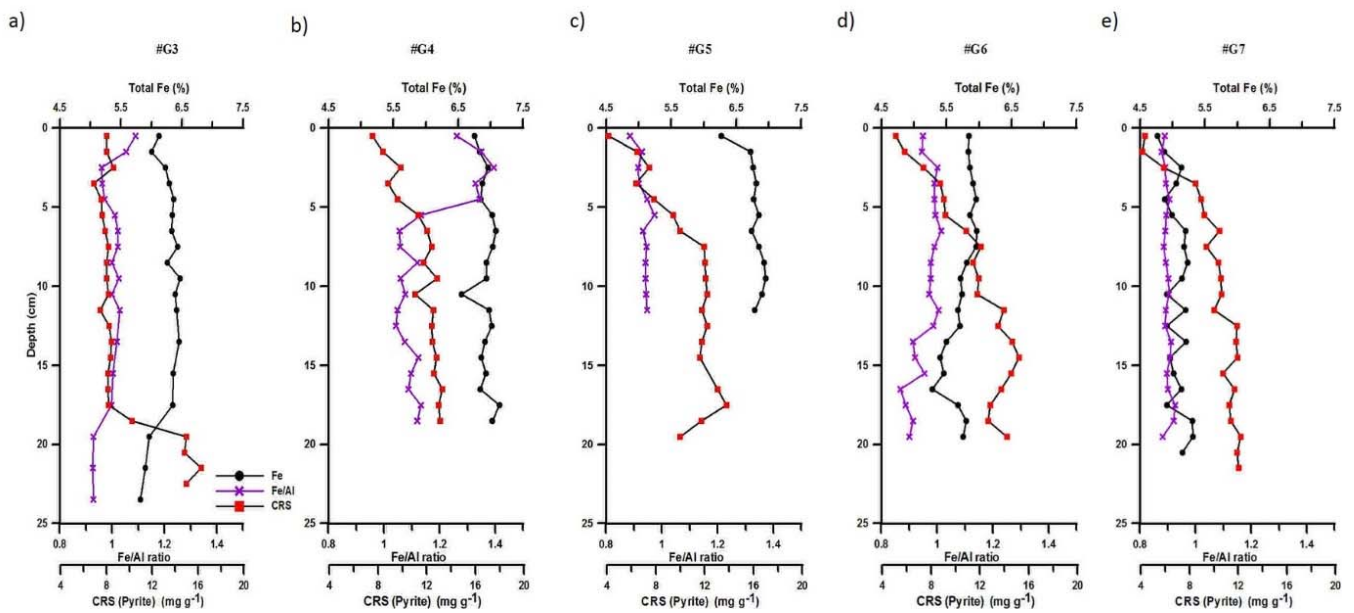


Fig. 4: Variation of total Fe, chromium reducible sulfur (Pyrite) and Fe/Al ratios at all the study sites.

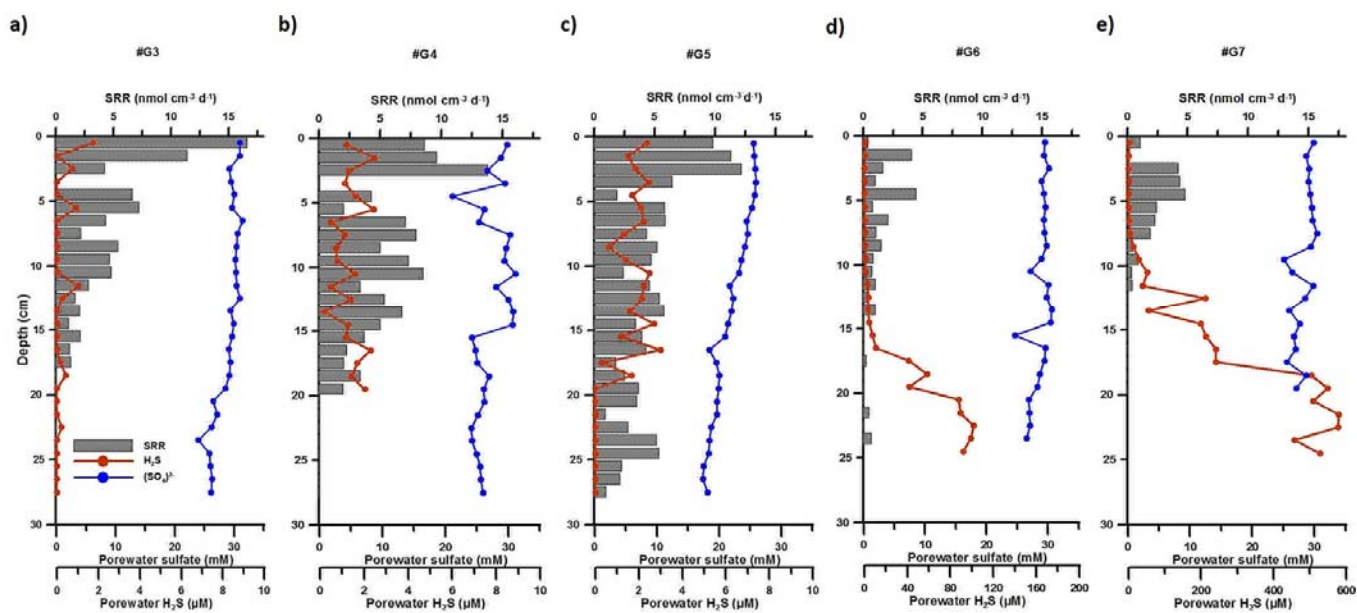


Fig. 5: Variation of sulfate reduction rates in the sedimentary column, pore-water H₂S and sulfate concentrations at all the study sites. Note the change in X axes at stations G6 and G7 for pore-water H₂S concentration.

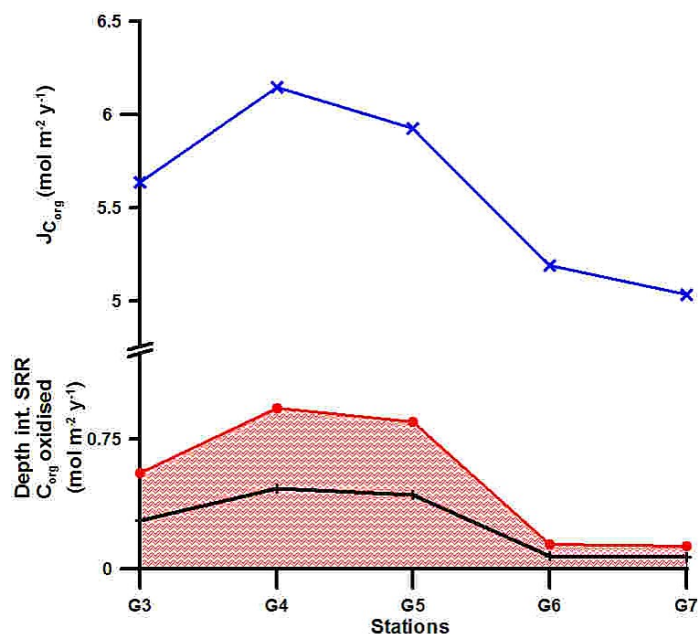


Fig.6: Calculated C_{org} accumulation rates and the depth integrated sulfate reduction rates in the inner shelf region of the eastern Arabian Sea. The shaded portion indicates the amount of organic carbon remineralised by sulfate reduction process in these sediments. Note the break in Y-axis from 1.2 to 4.8.

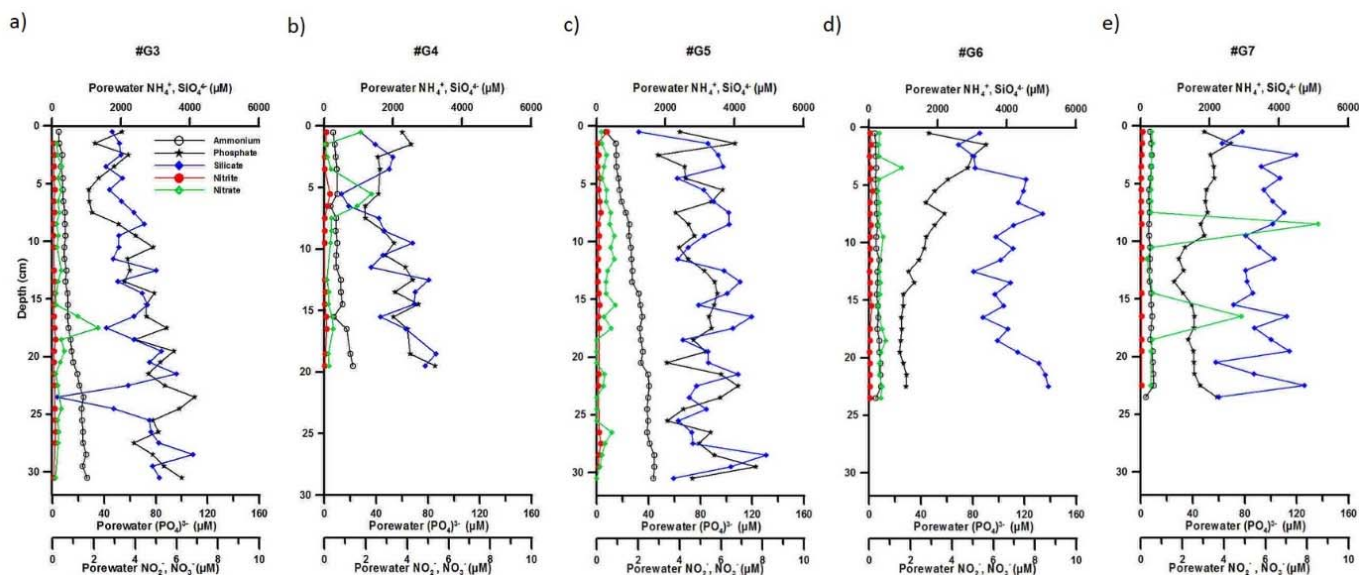


Fig.7: Variation of Nitrate, Nitrite, Ammonium, Phosphate and silicate in the pore-waters of the sediment cores collected from stations G3 to G5.

Table 1 : Location of the study sites, water depth, temperature, oxygen and nutrients in the bottom waters at the sampling sites over the inner shelf of Eastern Arabian Sea.

| Station | Location | | Water depth (m) | Bottom water | | Nutrients | | |
|---------|-----------------|------------------|-----------------|------------------|-------------|--------------|--------------|---------------|
| | latitude | longitude | | Temperature (°C) | oxygen (μM) | Nitrate (μM) | Nitrite (μM) | Ammonium (μM) |
| G3 | 15° 31' 47.0" N | 073° 44' 19.3" E | 14 | 23.06 | 37.89 | 0.00 | 0.01 | 0.09 |
| G4 | 15° 31' 04.8" N | 073° 43' 48.2" E | 16 | 22.74 | 8.00 | 0.00 | 0.00 | 4.78 |
| G5 | 15° 30' 47.0" N | 073° 42' 03.6" E | 20 | 22.33 | 0.00 | 0.00 | 0.00 | 5.06 |
| G6 | 15° 31' 47.0" N | 073° 39' 06.5" E | 39 | 20.85 | 3.82 | 7.70 | 4.30 | 0.29 |
| G7 | 15° 31' 47.0" N | 074° 05' 30.2" E | 48 | 20.50 | 3.54 | 10.94 | 2.51 | 0.00 |

Table 2: Comparison of sulfate reduction rates reported in other upwelling and coastal areas with the present study.

| Area | Water depth | SRR (mmol m ⁻² d ⁻¹) | Reference |
|---------------------------------|-------------|---|---------------------------------------|
| Bay of Concepcion | 37- 85m | 22.4 - 8.5 | Schubert et al., 2000 |
| Himmerfjorden, Baltic Sea | 25-50m | 4-5.3 | Thang et al., 2013 |
| Namibian shelf | 25m | 64.2 | Bruchert et al., 2003 |
| Skagerrak and Kattegat(Denmark) | 43-200 m | 24.1- 33.98 | Iversen and Jorgensen., 1985 |
| Off Goa | 14.7 m | 0.05 - 0.34 | Mazumdar et al., 2009 (modelled data) |
| Inner shelf off Goa | 12- 45m | 0.18-1.27 | Present study |