

## **Pore-water sulfate concentration profiles of sediment cores from Krishna-Godavari and Goa basins, India**

A. Mazumdar<sup>\*</sup>, A. L. Paropkari, D.V. Borole, B. R. Rao, N. H. Khadge, S. M. Karisiddaiah, M. Kocherla, Hilda M. João

*Geological Oceanography,  
National Institute of Oceanography,  
Dona Paula, Goa-403 004  
maninda@nio.org  
\* for correspondence*

### Abstract

Several cores from Krishna-Godavari (Western Bay of Bengal) and Goa (Eastern Arabian Sea) basins have been studied for pore water sulfate concentrations in order to understand and contrast diagenetic processes. K-G sediments differ markedly from Goa sediments in pore water sulfate gradients and depth-integrated sulfate reduction rates. Significantly higher sulfate reduction rates in K-G sediments ( $3.6$  to  $15.8$   $\text{nmol cm}^{-2}\text{day}^{-1}$ ), compared to that in Goa sediments ( $0.011$  to  $0.65$   $\text{nmol cm}^{-2}\text{day}^{-1}$ ), can be attributed to higher sedimentation rates. Lower exposure time to oxygen for the organic matter in K-G sediments has preserved reactive organic compounds required for sulfate reducers and possibly methanogens. Authigenic carbonates with depleted carbon isotopic composition ( $\delta^{13}\text{C} = -48$  to  $-50$ ) at the base of the sulfate reduction zone in a core from K-G suggests anaerobic methane oxidation (AMO) process. The possibility, that the underlying methane gas hydrate zone is acting as a methane source for sulfate reduction can not be negated specially in light of the existing geophysical studies. Both methane and the fermentation products of organic matter degradation served as a substrate for sulfate reduction. However, a clear understanding of there relative importance needs further investigation.

### Keywords

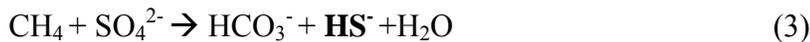
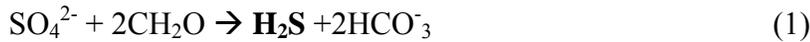
Sulfate reduction, methane oxidation, Krishna-Godavari, Goa, Bay of Bengal, and Arabian Sea.

## 1. Introduction

Biological sulfate reduction (Harrison and Thode, 1958; Sweeney and Kaplan, 1980; Bak and Cypionka, 1987; Jørgensen, 1990; Canfield, 2001; Goldhaber, 2003; Megonigal et al. 2003; Shen and Buick, 2004, Canfield et al., 2005 and Canfield et al., 2006) is a bacterially-mediated metabolic process which results in the breakdown of S-O bonds of dissolved sulfate and subsequent production of H<sub>2</sub>S gas. In case of assimilatory sulfate reduction, which is an energy requiring process, sulfur is incorporated into the cells as organo-sulfur compounds (Dinur et al., 1980; Madigan et al., 2000 and Canfield, 2001), whereas dissimilatory sulfate reduction (Canfield, 2001 and Madigan et al., 2000) is an energy yielding process with  $\Delta G = -48$  kJ and  $-128$ kJ for acetate and lactate oxidation respectively (Megonigal et al., 2003) and is carried out by sulfate reducing bacteria and archaea in anoxic water column or sediment pore waters. Dissimilatory sulfate reduction plays an extremely important role in diagenesis of marine sediments and accounts for half or more of total organic carbon mineralization within sediments (Jørgensen, 1982 and Canfield et al., 1993). Rate of sulfate reduction in marine sediments depends on the availability of labile organic compounds which serve as substrate for sulfate-reducing bacteria (Madigan et al., 2000), on temperature (Westrich and Berner, 1988; Madigan et al., 2000, Canfield et al., 2006) and bacterial species (Canfield, 2001, Detmers et al., 2001). Sulfate reducers predominantly use simple fermentation products (lactate, acetate and alcohol) or H<sub>2</sub> as energy source. Bacterial degradation of organic molecules in the presence of molecular oxygen to less reactive compounds significantly affects the rate of sulfate reduction (Canfield 1994). Rate of sedimentation is an important factor controlling organic matter delivery and preservation and it's availability to sulfate reducers (Reeburgh, 1976, Berner, 1978; Stein, 1990; Canfield, 1991; 1994; Tyson, 1995). On the other hand anaerobic methane oxidation (AMO) (Martens and Berner, 1977 and Martens et al., 1999) is another important process responsible for sulfate reduction in marine sediments. AMO is believed to be performed by a consortium of CH<sub>4</sub>-oxidizing archaea and sulfate-reducing bacteria (SRB) in

marine environments (Hoehler and Alperin, 1996, Boetius et al, 2000 and Orphan et al., 2001).

Dissimilatory sulfate reduction can be represented by equations 1 to 3.



where  $\text{CH}_2\text{O}$  represents a generic form of organic matter as carbohydrate. Equation-3 represents the anaerobic methane oxidation process (AMO).

Concentration of sulfate ion in sediment pore waters is an important parameter in biogeochemical studies. In the present paper, pore-water sulfate profiles from Krishna-Godavari (K-G: east coast of India) and Goa (west coast of India) basins are presented. An attempt has been made to understand the physico-chemical factors which might have influenced the sulfate reduction processes in these areas. This project is a part of National Gas Hydrate Program. These initial studies are expected to throw light on otherwise much less explored areas in Indian Ocean.

## **2. Geology of the study areas**

### *2.1 Krishna- Godavari (Western Bay of Bengal)*

The K-G basin extends from onshore to (Western Bay of Bengal) and formed during the break-up of Gondwanaland. It is a peri-cratonic rift basin located in the middle of the eastern continental margin of India (Rao, 2001). The basin trends NE-SW parallel to the Pre-Cambrian Eastern Ghat trend. It is one of the promising petroliferous basins of India. The maximum sediment thickness of the K-G reaches as much as 8000 m (Prabhakar and Zutshi, 1993). Smectite bearing Godavari clay constitutes the Holocene-Pleistocene stratigraphy of K-G. The study area lies within the continental slope region of eastern India (Fig.1A). Two major rivers, the Godavari and Krishna supply the clastic sediments to the K-G basin. Based on Pb-210 and Th-230 dating, a sedimentation rate approximately 20cm/ky was suggested by Sarin et al.(1979) as a minimum estimate at water depths of 2845-3145m. Rao et al.

(1994) suggested an approximate sedimentation rate of 20-25 cm/ky for the Quaternary period from the multi-channel seismic reflection studies.

## *2.2 Goa (Eastern Arabian Basin)*

The western continental margin of India is a passive margin and characterized by (i) NW-SE trending, continental shelf more than 200 km wide in the north to about 50 km wide in the south near Cape Comorin, (ii) a straight outer edge limited by 200m isobath, (iii) a narrow continental slope bounded by the 200 and 2000m isobaths, (iv) deep sedimentary basins viz., Western Arabian Basin, Eastern Arabian Basin, Kori-Comorin Basin and Kerala-Konkan Basin and (v) several structural features viz., Chagos-Laccadive Ridge, Laxmi Ridge, Pratap Ridge (east of Chagos Laccadive Ridge). Geographically, Goa (Fig.1 B; Eastern Arabian Basin) lies between the eastern end of the Laxmi-Laccadive Ridge and the adjacent western continental slope of India (Biswas, 1982, Kolla and Coumes, 1987, NIO, 2005a). The bathymetry in this basin ranges from 1800 to 3600 m. An approximately 2.9km thickness sediment overlies the basement. The Indus River is the primary source of detrital sediment to this region. Average sedimentation rate here varied from 2 to 6 cm/ ky over the last 100 ky (Banakar et al., 2005).

## **3. Methodology**

### *3.1 Analytical*

Several chemical and physical parameters of sediment samples obtained from 6 m long gravity cores and water samples have been measured as part of the present work. Sediment cores were collected at water depths ranging from 300 to 1500 m in the K-G basin and from 2600-3200 m in the Goa basin (Figure 1A and B).

Gravity cores were sub-sampled at variable intervals within 15-20 minutes after opening the core and were transferred to on-board laboratory for pore water extraction using a temperature controlled

centrifuge (Heraeus-Biofuge). Sub sampling was carried out from predrilled liners using 60cc plastic cut-syringes with 3cm diameter. Pore waters were collected in 25 ml airtight bottles and stored in refrigerators at -18°C for onshore measurement of SO<sub>4</sub><sup>2-</sup> concentrations using Dionex Ion-chromatograph (DX-600I). Dissolved oxygen concentrations were recorded with dissolved oxygen sensor SBE-43 mounted on a CTD. Total organic carbon (TOC) content in sediments was measured by chromic acid oxidation method (Wakeel and Riley, 1957).

Sampling resolution varied from core to core. Weight percentages of sand, silt and clay particles in each sample were determined by pipette analysis method which uses Stoke's law to calculate particle settling time. Porosity of sediment samples was estimated using the formula:

$$\text{Porosity} = 100 \times \frac{1}{1 + (W \times G / 100)} (\%),$$

where W = water content and G = specific gravity of dry sediment, which were measured using American Standard Test and Method (ASTM, 1995)

### 3.2 Computational

In case of quasi-linear concentration profiles, the following formulation can be used for the calculation of depth integrated sulfate reduction rates (Canfield, 1989, 1991).

$$\mathbf{J} = \phi \mathbf{D}_s \left( \frac{d\mathbf{C}}{d\mathbf{X}} \right) + (\phi_0 \omega \mathbf{C}_0 - \phi_b \omega \mathbf{C}_b) \quad (\text{i})$$

where, J (nmol cm<sup>-2</sup>day<sup>-1</sup>) is equivalent to the depth-integrated sulfate reduction rate and C<sub>0</sub> and C<sub>b</sub> are the sulfate concentrations (nmol cm<sup>-3</sup>) per volume of pore water at the top and bottom of the core. dC/dX is the sulfate concentration gradient in nmol cm<sup>-1</sup>. Sulfate concentration in mM are converted to the unit of nmol cm<sup>-3</sup> for the 'J' calculation.. 'X' is the depth (cm) from sediment surface, D<sub>s</sub> (cm<sup>2</sup> sec<sup>-1</sup>) is the molecular diffusivity corrected for tortuosity, φ is the average porosity and φ<sub>0</sub> and φ<sub>b</sub> are the porosities at the top and bottom of the core. The average porosity (φ) for K-G sediments varies from 56.5 to 57.4%, whereas it varies from 55.1 to 57.1 in Goa sediments. D<sub>s</sub> is calculated by the formula

$$D_s = D_0 / (1 + n(1 - \phi)) \quad (ii)$$

where  $n = 3$  for clays and silt (Iversen and Jørgensen, 1993).  $D_0$  = sulfate diffusivity in the absence of particles ( $0.56 \times 10^{-5} \text{ cm}^2/\text{sec}$  at  $4^\circ\text{C}$ ). The <63 micron fraction (silt + clay) comprises >99% of K-G sediments whereas, it varies from 84 to 90% in Goa sediments.  $\omega$  is the average sedimentation rate. Since  $D_0$  varies with temperature (water depth), we have calculated  $D_0$  for each site in KG basin using an empirical relation based on data set from Li and Gregory (1974). For the shallowest core (at 316m water depth)  $D_0$  is  $7.448 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$  and for deepest core (1450m)  $D_0$  is  $6.0932 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$ . In this study, advective pore water transport (eg. Bioirrigation) or reoxidation of sulfide within the sediment have been neglected. Assessing the error in calculation due to this limitation is beyond the scope of the present work. In case of parabolic profiles GH4/GC-2R, one-dimensional modeling software PROFILE (Berg et al., 1998) is used for depth integrated sulfate reduction rate calculation. The numerical procedure of Berg (1998) assumes that the concentration-depth profile represents a steady state and calculates the rate of net production or consumption as function of depth together with flux across the sediment-water interface. The program needs as input some basic chemical and physical parameters of the sediment column. It first divides the sediment into arbitrary number of equidistant zones with a constant process rate and through iterative process tries to reproduce the measured concentration profile. The base of the sulfate reduction zone or the zone of sulfate-methane interface ( $Z_{\text{sulf}}$ ) has been calculated (by extrapolation) using the regression line equations. The zone of maximum sulfate penetration ( $Z_{\text{sulf}}$ , Jørgensen et al., 2004) has been used to calculate the time (t) required for adjustment of the sulfate profile in response to changes in key parameters like organic matter flux, change in bottom water sulfate concentration or methane flux. Time (t) is calculated using the relation:

$$t = \pi (Z_{\text{sulf}})^2 / 4D_s \quad (iii)$$

(Sten-Knudsen, 1995 *cf.* Jørgensen et al., 2004)

All the calculated flux values reported in this study have taken into consideration the range of published sedimentation rates from K-G and Goa sediments referred in the present paper.

#### **4. Results**

The dissolved oxygen (D.O.) profile of the water column in the K-G basin shows a concentration of  $9 \mu\text{mole kg}^{-1}$  between 50 to 450m (Fig. 2A). Oxygen concentration then increases steadily from 9 to  $85 \mu\text{mole kg}^{-1}$  down to 1500 m water depth. In the Goa basin, oxygen concentration is also approximately  $0.9 \mu\text{mole kg}^{-1}$  from 100 to 700m and steadily increases from 9 to  $142 \mu\text{mole kg}^{-1}$  down to a depth of 3200m (Fig. 2B). Average TOC concentrations (Table-2A and 2B) range from 0.8 to 1.3% for K-G sediments and from 0.54 to 0.66% for Goa sediments (Figure-3A and 3B). Pore-water sulfate concentrations profiles (Table 1A and B) show marked contrast between the two basins. In K-G sediments, sulfate concentrations (Fig. 4A) decrease significantly with depth linearly except for GH4/GC-2R which show parabolic curve, whereas Goa sediments show very gentle linear sulfate gradients.

Sulfate reduction rate (J) in K-G sediments with linear concentration profile varies from 3.6 to  $10.8 \text{ nmol cm}^{-2} \text{ day}^{-1}$ , whereas for the parabolic profile, J is  $15.78 \text{ nmol cm}^{-2} \text{ day}^{-1}$ . In case of Goa sediments, it varies from 0.011 to  $0.94 \text{ nmol cm}^{-2} \text{ day}^{-1}$ . The estimated diffusion time (t) for sulfate to the base of the sulfate reduction zone is 783-16140 years for the linear profiles of KG sediments.

#### **5. Discussion**

Comparison of pore-water sulfate concentration profiles from K-G and Goa sediments show sharp contrast and reflect differences in chemical and physical parameters controlling diagenetic sulfate reduction processes in the sediment. The rate of sulfate reduction (sulfate consumption) is dependent on the availability of labile organic biomass or upward diffusive flux of  $\text{CH}_4$  (Eq.3). Sedimentation rate (Bernier, 1978; Canfield, 1991, 1994), bottom water oxygen concentration, and productivity

(Heinrich and Reeburgh, 1987; Pederson and Calvert, 1990; Calvert and Pederson, 1992; Paropkari et al., 1992 and Hartnett et al., 1998) are important factors which control the availability of labile organic matter. The labile components primarily include hydrolyzable carbohydrates and amino acids (Lee, 1988, Cowie et al., 1995, Grémare et al., 2005). Under oxic bottom water conditions, sedimentation rate plays an important role in determining the preservation and pathway of organic matter decomposition (Canfield, 1991, 1994). Hedges and Keil (1995), Hartnett et al. (1998), Hedges et al. (1999) and Gélinas et al. (2001) suggested “oxygen exposure time (OET)” of organic matter as an important factor affecting preservation of labile components. Suthhof et al. (2000) suggested duration of exposure to molecular oxygen as an important factor controlling preservation of amino acid and organic matter degradation. As sediment accumulation rate becomes slower, in situ O<sub>2</sub> exposure time increases. On the contrary, rapid sedimentation would cut-off the oxygen supply below sediment water interface. Rapid sedimentation delivers lots of organic matter to the sediments so that oxygen is consumed by decomposition of organic matter, hence oxygen consumption rate > oxygen diffusion rate. Either pathway results in preservation of a part of labile organic compounds available for anaerobic oxidation. Consortia of microorganisms are involved in anaerobic carbon decomposition (Canfield, 1994). The decomposition pathway involves hydrolysis and fermentation of complex organic structures to smaller moieties including low molecular weight organic acids, eg., formate, acetate, lactate etc. and H<sub>2</sub> (Biagini et al., 1998 and Megonigal et al., 2003). Being a terminal electron acceptor, sulfate (SO<sub>4</sub><sup>2-</sup>) oxidizes simple organic compounds (primarily acetate) under anoxic conditions. Canfield (1994) estimated that at a sedimentation rate >30cm ky<sup>-1</sup>, bottom-water O<sub>2</sub> concentrations has little effect on organic matter preservation. In contrast, at slow sedimentation rates, labile organic matter has sufficient time to be aerobically oxidized which results in creating refractory organic matter. Owing to lack of reactive organic compounds and enrichment of refractive compounds, sulfate reduction rates are significantly lowered.

From CTD profiles (Figure 2A and 2B) it is evident that the sedimentation in our sampling sites took place under oxygenated bottom water conditions, except for sampling sites GH4/GC2R where deposition took place in the oxygen minimum zone. Significantly, low sedimentation rates (2-6cm/ky: Banakar, 2005) in Goa sediments compared to that of K-G sediments (20-25cm ky<sup>-1</sup>: Sarin et al., 1979; Rao et al., 1994) seems to be responsible for very limited sulfate reduction in the former owing to rapid remineralization of organic compounds to refractory components not amenable to sulfate reducers and methanogens. Depth integrated sulfate reduction rate (J) in Goa varies from 0.011 to 0.942 nmol cm<sup>-2</sup> day<sup>-1</sup>. Böttcher et al. (2000) also recorded very limited sulfate reduction from the Arabian Sea sediments at 3186-4426 m water depth. Average TOC% (0.54 to 0.66%) recorded in the present study is comparable with that recorded by Böttcher et al.(2000). Although Arabian Sea has much higher primary productivity than the Bay of Bengal, the organic carbon (C<sub>org</sub>) flux is marginally higher in the latter (Ramaswamy and Nair, 1994 and Gauns et al, 2005). Higher C<sub>org</sub> flux in K-G may be attributed to very high fluvial/ clastic flux (Subramanian, 1993 and Rao, 1985) and subsequent rapid removal of OM by coagulated particles (ballast effect: Ittekkot, 1993) compared to that in Eastern Arabian Sea. Unger et al.(2005) reported presence of 2.3-3.7% hydrolyzable carbohydrates and 8.3-10.6% amino acids of the TOC in the surface sediments of Bay of Bengal. Bhosle and Dhople (1988) reported total amino acids 1.5-1.70 % of TOC from shallow sediments (~200m water depth) of K-G. These labile components in Bay of Bengal sediments are the possible sources of acetate via fermentation by anaerobic microbes. However Takii et al.(2003) showed that amino acid itself can act as an important substrate for sulfate reducing bacteria in sediments.

The sulfate reduction rates recorded from K-G and Goa sediments are plotted (Fig. 5) on the sulfate reduction rate vs. sediment burial rates cross plot of Canfield (1989), which is a compilation of data from different sedimentary basins and ranging from oxic to euxinic depositional milieus. The fluxes have been converted to the units of mmolcm<sup>-2</sup>y<sup>-1</sup> to compare with Canfield (1989). Data points fall

well within the normal oxic marine realm. Canfield (1989) assumed that at sediment porosity of 60%, sedimentation rate expressed in unit of  $\text{g cm}^{-2} \text{y}^{-1}$  (sediment accumulation rate) is identical to units of  $\text{cm y}^{-1}$ . Since our measured porosities are close to 60%, approximate sediment burial rates in K-G and Goa may be expressed as  $0.020\text{-}0.025 \text{ g cm}^{-2} \text{y}^{-1}$  and  $0.002\text{-}0.006 \text{ g cm}^{-2} \text{y}^{-1}$  respectively. This would mean an organic carbon burial flux of  $1.61 \times 10^{-4}$  to  $3.33 \times 10^{-4} \text{ gC cm}^{-2} \text{y}^{-1}$  for K-G sediments and  $1.08 \times 10^{-5}$  to  $4.19 \times 10^{-5} \text{ gC cm}^{-2} \text{y}^{-1}$  for Goa sediments. The range of organic carbon burial flux calculated for Goa is comparable with that reported by Banakar (2005). Assuming a 2:1 molar ratio between  $\text{CH}_2\text{O}$  and  $\text{SO}_4$  consumption (equation 1), approximate carbon oxidation rate by sulfate reduction may be estimated as  $7.2$  to  $31.48 \text{ nmolC cm}^{-2} \text{day}^{-1}$  and  $0.02$  to  $1.88 \text{ nmolC cm}^{-2} \text{day}^{-1}$  for K-G and Goa sediments respectively. The organic carbon fluxes to sediment in Central Bay of Bengal and Eastern Arabian Basin and are approx.  $3.1 \times 10^{-4}$  and  $1.9 \times 10^{-4} \text{ gC cm}^{-2} \text{y}^{-1}$  respectively (Ramaswamy and Nair, 1994). Consequently, the approximate percentages of the organic flux that is oxidized by sulfate reduction alone can be estimated to be around 10.2 to 44 % for K-G and 0.046 to 4.3% for Goa. However, owing to variation in primary productivity, the  $\text{C}_{\text{org}}$  flux is expected to have varied through time.

No noticeable correlation could be observed between TOC% (Figure-3A and B) and sulfate profiles for either of the depositional sites owing to the fact that it is the amount of metabolizable organic matter and not the total organic content which controls sulfate reduction. This may be particularly true with increasing sediment depth as the metabolizable fraction diminishes and TOC becomes dominated by refractory organic compounds (Tyson, 1995).

The sulfate profiles in K-G are mostly defined by straight lines. Borowski et al. (1996) suggested that linear sulfate profiles instead of convex-up curvature suggest significant sulfate reduction through anaerobic methane oxidation, fueled by upward diffusion of methane to the base of the sulfate reduction zone. The upward methane flux has been linked to the presence of methane gas hydrate below sediment surface (Borowski et al., 1996). In our study, the convex up curvature has been

recorded in shallow water site GH4/GC2R at a water depth of 316m. Whereas, linear sulfate profiles are recorded over water depth of 950-1450m. Based on geophysical studies, presence of methane hydrate stability zone (~230m below sediment surface; Ramana et al.(2006)) have been predicted under the deeper waters (600 to 2000m) of KG basin by Rastogi et al. (1999). Record of authigenic carbonate crystals like high magnesium calcite and aragonite with highly depleted carbon isotopic composition ( $\delta^{13}\text{C} = -48$  to  $-50\%$ ; Kocherla et al., 2006) from the base of sulfate concentration profile of a core in K-G supports possible role of anaerobic methane oxidation in these sediments. Initial report on methane concentrations from the K-G sediments is 1 to 2 nmole  $\text{g}^{-1}$  or less (NIO, 2005b) up to a depth of 4-6 m from sediment surface. Such low concentrations may be attributed to methane consumption by anaerobic methane oxidation (AMO: Eq.3). Much higher concentration of methane is expected below the zone of sulfate reduction. Data on additional parameters viz., carbonate alkalinity and stable isotopic composition of methane/  $\text{CO}_2$  is required to assess the extent to which AMO is fueled the sulfate reduction process here. A detailed investigation in these directions is in progress as part of National Gas Hydrate Program (NGHP).

## **6. Conclusion**

Contrasting pore water sulfate concentration profiles in K-G and Goa sediments and significantly higher sulfate reduction rates in the K-G sediments cores reflect the importance of both sedimentation rate and methane oxidation on the efficiency of sulfate reduction. In spite of higher primary productivity in the Eastern Arabian Sea compared to that of K-G basin, the latter has marginally higher organic carbon flux owing to very high fluvial/ lithogenic input and rapid transfer to sediment by coagulated particle ballast. Higher sedimentation rate leads to lower oxygen exposure time for the sedimented organic matter, thus making labile components like amino acids and carbohydrates amenable to anaerobic microbes. Sulfate reduction is promoted by simple organic molecules like acetate, lactate etc. which are fermentation products of amino acids and carbohydrates. We have so far

limited but definite evidence of sulfate reduction by anaerobic methane oxidation from K-G sediments. In view of the available geophysical data suggesting existence methane gas hydrate below the KG basin sediment, the possibility of methane flux from gas hydrate zone to the base of sulfate reduction zone can not be negated. However, the extent to which this process is responsible for the observed sulfate reduction rates needs to be studied in details. Both methane and the fermentation products of organic matter degradation served as a substrate for sulfate reduction. A clear understanding of there relative importance needs further investigation.

### **Acknowledgements**

We thank the Director of NIO Dr. Satish Shetye for providing facilities to publish this work. This research was funded by National Gas Hydrate Program (NGHP). Senior author is thankful to Dr. M.V. Ramana for his valuable scientific comments.

### **Reference:**

ASTM, 1995. Annual book of ASTM standards, 04:08 Soil and Rocks (I) D420-D4914, ASTM, Philadelphia, USA, 981 pp.

Bak, F. and Cypionka, H., 1987. A novel type of energy metabolism involving fermentation of inorganic sulphur compounds. *Nature* 326, 891-892.

Banakar, V. K. , Oba, T., Chodankar A. R., Kuramoto, T., Yamamoto, M. and Minagawa, M., 2005. Monsoon related changes in sea surface productivity and water column denitrification in the Eastern Arabian Sea during the last glacial cycle. *Marine Geology* 219, 99-108.

- Berg, P., Risgaard-Petersen, N., Rysgaard, S, 1998. Interpretation of measured concentration profiles in sediment pore water. *Limnology Oceanography* 43, 1500-1510..
- Berner, R. A., 1978. Sulfate reduction and the rate of deposition of marine sediments. *Earth Planet. Sci. Lett.* 37, 492-498.
- Berner, R. A., 1980. *Early Diagenesis: A Theoretical Approach*. Princeton University Press, New Jersey pp 241.
- Bhosle, N. B. and Dhope, V. M., 1988. Distribution of some biochemical compounds in the sediments of Bay of Bengal. *Chemical Geology*, 67, 341-352.
- Biagini, G. A., McIntyre, P. S., Finlay, B. J and Lloyd, D., 1998. Carbohydrate and amino acid fermentation in the free-living primitive protozoon *Hexamita* sp. *Applied and Environmental Microbiology*. 203-207.
- Biswas, S. K., 1982, Rift basins in the western margin of India and their hydrocarbon prospects. *Bull. Am. Assoc. Pet. Geol.* 66, 1497-1513.
- Boetius, A., Ravenschlag, K., Schubert, C. J., Rickert, D., Widdel, F., Giesecke, A., Amann, R., Jørgensen, B. B., Witte, U. and Pfannkuche, O., 2000. A marine microbial consortium apparently mediating anaerobic oxidation of methane. *Nature* 407, 623– 626.
- Borole, D.V., Karisiddaiah, S. M. and Rao, B. R., 2003a, Priliminary investigations to understand the process of Anaerobic Methane Oxidation (AMO), from the sediments of Krishna-Godavari . International symposium on recent trends in surface geochemical prospecting and risk reduction for hydrocarbon exploration and development, Hyderabad (Abstract).

- Borole, D.V., Karisiddaiah, S. M. and Rao, B. R., 2003b, Evaluating the significance of geochemical distribution pattern of methane (CH<sub>4</sub>), sulphate (SO<sub>4</sub><sup>2-</sup>) and Chloride (Cl<sup>1-</sup>) from the Arabian Sea (off Goa) sediments International symposium on recent trends in surface geochemical prospecting and risk reduction for hydrocarbon exploration and development, Hyderabad (Abstract).
- Borowski, W. S., Paull, C. K. and Ussler, W. III., 1996. Marine pore-water sulfate profiles indicate in situ methane flux from underlying gas hydrate. *Geology* 24 655-658.
- Bötcher, M., Schale, H., Schetger, B., Wallmann, K. and Brumsack, H-J., 2000. Stable sulfur isotopes indicate net sulfate reduction in near-surface sediments of the deep Arabian Sea. *Deep-Sea Research II* 47, 2769-2783.
- Calvert, S. E. and Pederson, T. F., 1992. Organic carbon accumulation and preservation in marine sediments: how important is anoxia. In: Whelan, J. K. and Farrington, J. W. (Eds.), *Productivity, Accumulation and Preservation of Organic matter in Recent and Ancient Sediments*, Columbia University Press, New York, N.Y. pp 231-263.
- Canfield, D. E., 1989. Sulfate reduction and oxic respiration in marine sediments: implications from organic carbon preservation in euxinic environments. *Deep Sea Research*, 36, 121-138.
- Canfield, D. E., 1991. Sulfate reduction in deep sea sediments: *American Journal of Science* 291, 177-188.
- Canfield, D. E., 1994. Factors influencing organic carbon preservation in marine sediments. *Chem. Geol.* 114, 315-329.
- Canfield, D. E., 2001. Biogeochemistry of sulfur isotopes. *Reviews in Mineralogy and Geochemistry*, 43, 607-636.

- Canfield, D. E., Jørgensen, B. B., Fossing, H., Glud, R., Gundersen, J., Ramsung, N. B., Thamdrup, B., Hansen, J. W., Nielsen, L. P. and Hall, P. O. J., 1993. Pathways of organic carbon oxidation in three continental margin sediments. *Marine Geology* 113, 27-40.
- Canfield, D.E., Kristensen, E. and Thamdrup, Bo., 2005. The Sulfur Cycle. *Advances in Marine Biology*, 48, 2005, 313-381.
- Canfield, D. E., Olesen, C. A. and Cox, R. P. 2006. Temperature and its control of isotope fractionation by a sulfate-reducing bacterium. *Geochimica Cosmochimica Acta*, 70, 548-561
- Cowie, G. L., Hedges, J. I., Prahl, F. G. and de lange, G. J., 1995. Elemental and major biochemical changes across an oxidation front in a relict turbidite: an oxygen effect. *Geochimica et Cosmochimica Acta*, 59, 33-46,
- Detmers, J., Bruchert, V. Habicht, K and Kuever, J. 2001. Diversity of sulfur isotope fractionations by sulfate-reducing prokaryotes. *Applied Environmental Microbiology*. 67, 888-894.
- Dinur, D., Spiro, B. and Aizhenshtat, A., 1980. The distribution and isotopic composition of sulfur in organic-rich sedimentary rocks. *Chem. Geol.* 31, 37-51.
- Gauns, M., Madhupratap, M., Ramaiah, N., Jyothibabu, R., Fernandes, V., Paula, J. T. and Kumar, S. P., 2005. Comparative accounts of biological productivity characteristics and estimates of carbon fluxes in the Arabian Sea and the Bay of Bengal. *Deep Sea Research II* 52,1-15.
- Gélinas, Y., Baldock, J. A. and Hedges, J. I., 2001. Organic carbon composition of marine sediments: effects of oxygen exposure on oil generation potential. *Nature*, 294, 145-148.

- Grémare, A., Gutiérrez, S., Anschutz, P., Amouroux, J. M, DeXandre, B. and Vétion, G., 2005. Spatio-temporal changes in totally and enzymatically hydrolyzable amino acids of superWcial sediments from three contrasted areas. *Progress in Oceanography*, 65, 89–111.
- Goldhaber, M. B., 2003. Sulfur-rich sediments. In: Mackenzie, F. T., (Eds.) *Treatise on Geochemistry*. Elsevier Vol. 7, Pp 257-288.
- Harrison, A. G. and Thode, H.G., 1958. Mechanism of the bacterial reduction of sulphate from isotopic fractionation studies. *Faraday Society Transaction* 54, 84-92.
- Hartnett, H. E., Keil, R. G., Hedges, J. L. and Devol, A. H., 1998. Influence of oxygen exposure time on organic carbon preservation in continental margin sediments. *Nature*, 391, 572-574.
- Hedges, J. I. and Keil, R.G., 1995. Sedimentary organic matter preservation: an assessment and speculative synthesis. *Marine Chemistry* 49, 81-115
- Hedges, J. I., Hu, F. S, Devol, A. H., Hartnett, H. E., Tsamakis, E and Keil, R. G., 1999. Sedimentary organic matter preservation: a test for selective degradation under oxic conditions. *American Journal of Science*, 299, 529–555
- Heinrich, S. M. and Reeburgh, W. S., 1987. Anaerobic mineralization of marine sediment organic matter: rates and the role of anaerobic processes in the oceanic carbon economy. *Geomicrobiology Jour.* 5, 191-237.
- Hoehler, T. M. and Alperin, M. J. 1996. Anaerobic methane oxidation by methanogen-sulfate reducer consortium: Geochemical evidence and biochemical considerations. In: Lindstrom, M. E. and Tabita, F. R. (Eds.) *Microbial Growth on C<sub>1</sub> compounds*, Elsevier 3, pp 53–75.

- Ittekkot, V., 1993. The abiotically driven biological pump in the ocean and short term fluctuations in the atmospheric CO<sub>2</sub> contents. *Global and Planetary Change*, 8, 17-25.
- Iversen, N. and Jørgensen, B. B. 1993. Diffusion coefficients of sulfate and methane in marine sediments: Influence of porosity. *Geochim. Cosmochim. Acta* 57, 571–578
- Jørgensen, B. B., 1982. Mineralisation of organic matter in the sea bed: the role of sulfate reduction. *Nature* 296, 643-645.
- Jørgensen, B. B., 1990. The sulfur cycle of freshwater sediments: role of thiosulfate. *Limnology and Oceanography* 35, 1329-1342.
- Jørgensen, B. B., Böttcher, M. E., Lüschen, H., Neretin, L. N. and Volkov, I. I., 2004. Anaerobic methane oxidation and a deep H<sub>2</sub>S sink generate isotopically heavy sulfides in Black Sea sediments. *Geochim Cosmochim Acta*. 68, 2095-2118.
- Muralidhar, K., Mazumdar, A., Karisiddaiah, S.M., Borole, D.V. and Rao, B. R., 2006. Evidences of methane-derived authigenic carbonates from the sediments of the Krishna-Godavari (K-G) Basin, eastern continental margin of India. *Current Science*, 91, 318-323
- Kolla, V and Coumes, F., 1987. Morphology, internal structure, seismic stratigraphy and sedimentation of Indus Fan. *Bulletin AAPG*. 71, 650-677.
- Lee, C., 1988. Amino Acid and Amine Biogeochemistry in Marine Particulate Material and Sediments. In: T. H. Blackburn, T. H. and Sørensen, J. (Eds.) *Nitrogen Cycling in Coastal Marine Environments*. 125-141.

- Li, Yuan-Hui and Gregory, S. 1974. Diffusion of ions in sea water and in deep sea sediments. *Geochim Cosmochim Acta.* 38, 703-714
- Madigan, M., Martinko, J. and Parker, J., 2000. *Biology of Microorganisms*, Prentice-Hall, New Jersey, pp.
- Martens, C. S., Albert, D. B., and Alperin, M. J., 1999. Stable isotope tracing of anaerobic methane oxidation in the gassy sediments of Eckernforde Bay, German Baltic Sea. *American Journal of Science* 299, 589-610.
- Martens, C. S. and Berner, R. A., 1977. Interstitial water chemistry of anoxic Long island Sound sediment. I- Dissolved gases; *Limnology and Oceanography* 22, 10-35.
- Megonigal, J. P., Hines, M. E. and Visscher, P. T., 2003. Anaerobic Metabolism: Linkages to Trace Gases and Aerobic Processes. In: Holland, H. D. and Turekian, K. K. (Eds.), *Treatise on Geochemistry, Vol. 8, Biogeochemistry*. Elsevier Pergamon. pp. 317-424.
- NIO, 2005a. Geoscientific Investigations of Shallow Sediments in Goa , West Coast. National Gas Hydrate Research Program report (NIO/TR-12-2003). *Unpublished* pp. 81.
- NIO, 2005b. Geoscientific Investigations of Shallow Sediments in KG , East Coast. National Gas Hydrate Research Program report (NIO/TR-12-2003), *Unpublished*, pp. 84.
- Orphan, V. J., House, C. H., Hinrichs, K-U., McKeegan, K. D. and DeLong, E. F., 2001 Methane-consuming archaea revealed by directly coupled isotopic and phylogenetic analysis. *Science* 293, 484– 487.

- Paropkari, A. L., Babu, C. P. and Mascarenhas, A., 1992. A critical evaluation of depositional parameters controlling the variability of organic carbon in the Arabian Sea sediments. *Mar. Geol.* 107, 213-220.
- Pederson, T. F. and Calvert. S. E., 1990. Anoxia vs. productivity: what controls the formation of organic-carbon rich sediments and sedimentary rocks? *AAPG Bull.* 74, 454-466.
- Prabhakar, K. N. and Zutshi, P. L., 1993. Evolution of southern part of Indian East Coast Basin, *Jour. Geol. Soc.India* 41, 215-230.
- Ramana, M.V., Ramprasad, T., Desa, M., Sathe, A.V., Sethi, A.K., 2006. Gas hydrate-related proxies inferred from multidisciplinary investigations in the India offshore areas. *Current Science*, 91, 183-189.
- Ramaswamy, V. and Nair, R. R., 1994. Fluxes of material in the Arabian Sea and Bay of Bengal— sediment trap studies. *Proceedings of the Indian Academy of Sciences (Earth Planetary Sciences)* 103, 189–210.
- Rao, Ch. M., 1985. Distribution of suspended particulate matter in the waters of eastern continental margin of India. *Indian Journal of Marine Science*, 14, 14-19.
- Rao, D. G., 2001. Sedimentation, Stratigraphy, and Petroleum Potential of Krishna-Godavari Basin, East Coast of India. *AAPG Bull.* 85, 623-1643.
- Rao, D. P., Bhattacharya, G. C., Ramana, M. V., Subramanyam, V., Ramprasad, T., Krishna, K. S., Chaubey, A. K., Murty, G. P. S., Srinivas, K. and Desa, M., 1994. Analysis of multi-channel seismic reflection and magnetic data along 13° N latitude across the Bay of Bengal. *Marine Geophysical Researches* 16, 225-236.

- Rastogi, A., Deka, B., Budhiraja, I. L. And Agarwal, G. C. (1999) Possibility of large deposits of gas hydrates in deeper waters of India. *Marine Georesources and Geotechnology*, 17, 49-63.
- Reeburgh, W. S. (1976) Methane consumption in Cariaco Trench waters and sediments. *Earth Planet. Sci. Lett.* 28, 337-344
- Sarin, M. M., Borole, D. V. and Krishnaswami, S., 1979. Geochemistry and geochronology of sediments from the Bay of Bengal and the equatorial Indian Ocean, *Proceedings of the Indian Academy of Sciences.* 88, 131-154.
- Shen, Y. and Buick, R., 2004. The antiquity of microbial sulfate reduction. *Earth-Science Reviews* 64, 243-272.
- Sten-Knudsen, O., 1995. Material Transport, Membrane Potential, and Electrical Impulses over Biological Membranes (in Danish) pp. 526 Akademisk Forlag, Copenhagen.
- Stein, R., 1990. Organic carbon content/sedimentation rate relationship and its paleoenvironmental significance for marine sediments. *Geomarine Letters*, 3, 37-44.
- Subramanian, V., 1993. Sediment load of Indian rivers. *Current Science* 64, 928–930.
- Suthhof, A. Jennerjahn, T. C. Schafer and Ittekkot, V., 2000., 2000. Nature of organic matter in surface sediments from the Pakistan continental margin and the deep Arabian Sea: amino acids. *Deep Sea Research II*, 47, 329-351.
- Sweeney, R.E., and Kaplan, I.R., 1980. Diagenetic sulfate reduction in marine sediments. *Marine Chemistry* 21, 165–174.
- Tyson, R. V., 1995. *Sedimentary Organic Matter: Organic facies and palynofacies.* Chapman and Hall, pp. 615.

Unger, D., Ittekkot, V., Schäfer, P. and Tiemann, J., 2005. Biogeochemistry of particulate organic matter from the Bay of Bengal as discernible from hydrolysable neutral carbohydrates and amino acids. *Marine Chemistry*, 96, 155-184.

Westrich, J. T. and Berner, R. A. 1988. The effect of temperature on rates of sulfate reduction in marine sediments, *Geomicrobiology Jour.* 6, 99-117.

Wakeel, E .L., and Riley, J. P., 1957. The determination of organic carbon in marine mud. *Jour. Con. Int. Explo. Mer.* 22, 180–183.

## Figure and Table Captions

**Figure 1. A and B.** Location map of sediment cores from Krishna-Godavari (A) and Goa basins (B). Isobaths in meter. The core numbers marked on 1A are GH4/GC-2R to GH4/GC-73 and core number marked on 1B are GH2/GC-3 to GH2/GC24.

**Figure 2 A and B.** CTD profiles from Krishna-Godavari (A) and Goa basins (B). CTD stations are marked by stars in Figure-1.

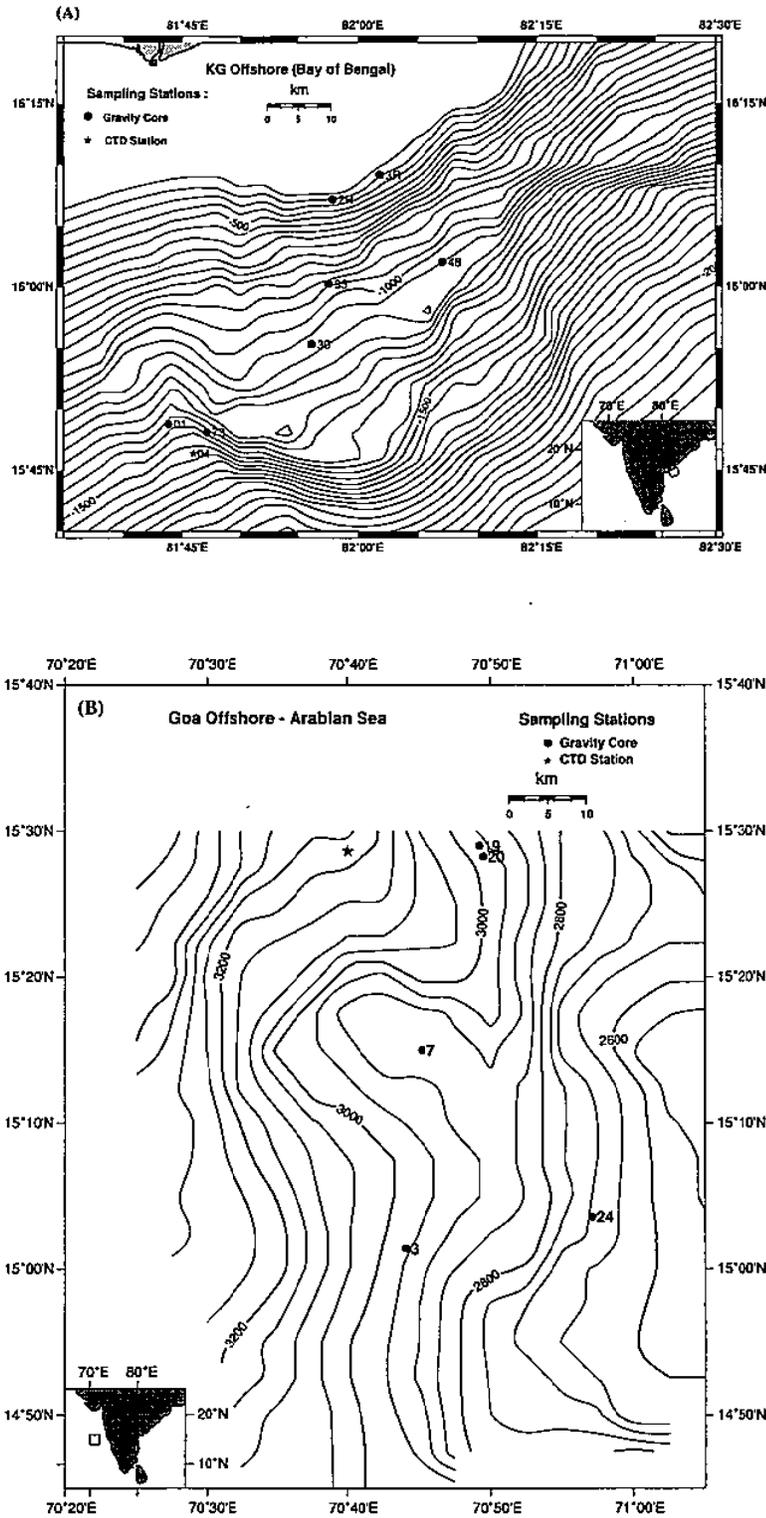
**Figure 3 A and B.** Total organic carbon (TOC) values (%) of sediments from Krishna-Godavari (A) and Goa (B) basins.

**Figure 4 A. and B.** Pore-water sulfate concentration profiles of sediments from Krishna-Godavari (A) and Goa (B) basins. Best fit equations and correlation coefficients ( $R^2$ ) are shown. J is the depth integrated sulfate reduction rate in  $\text{nmol cm}^{-2}\text{day}^{-1}$ .

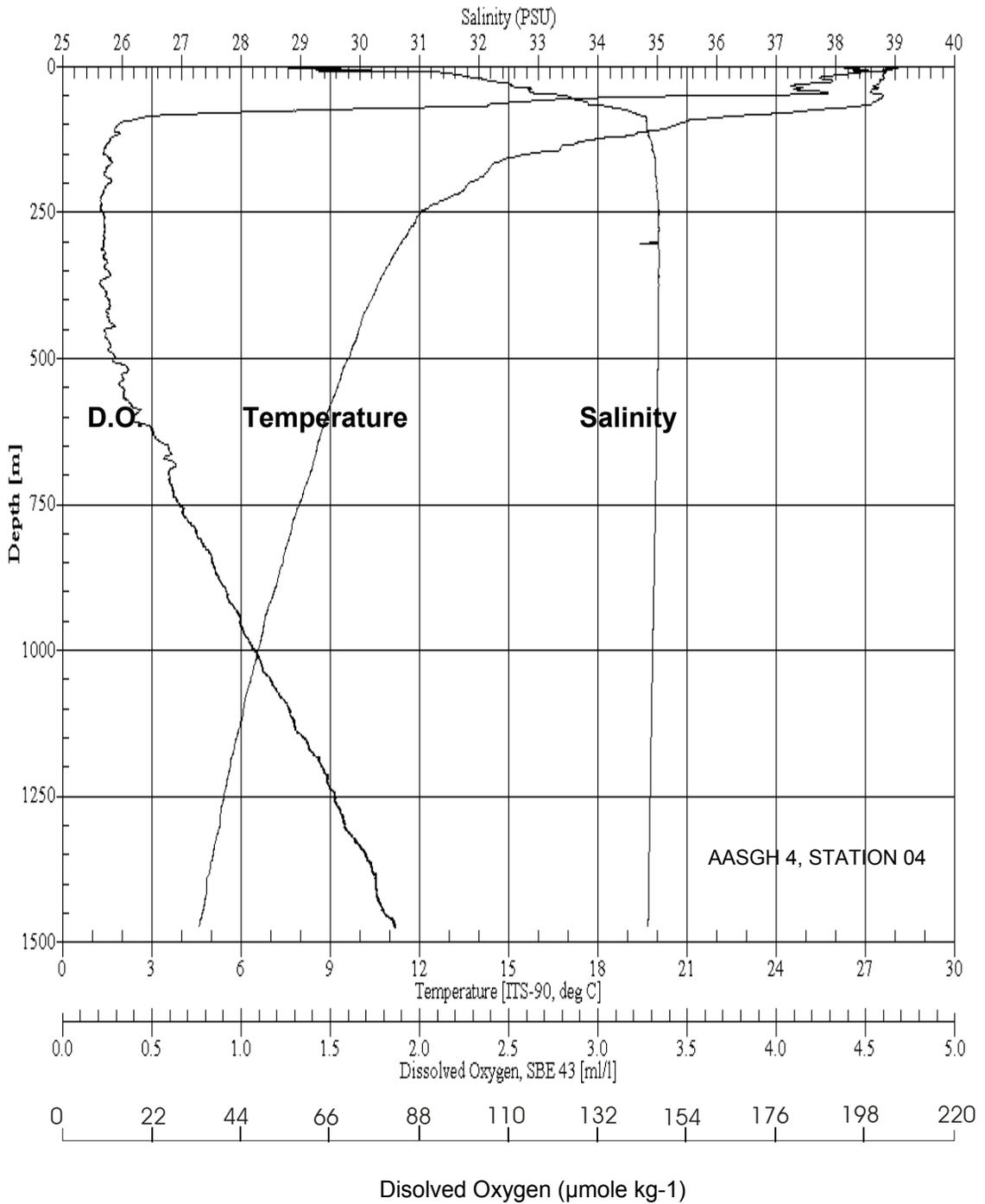
**Figure 5.** Variation in sulfate reduction rate with sediment burial flux. The range of sulfate reduction rate with sediment burial flux data from Krishna-Godavari and Goa are plotted on the graph from Canfield (1989).

**Table-1A and B.** Pore water sulfate concentrations in sediment cores from Krishna-Godavari (A) and Goa (B) basins. Water depths for individual cores are given in bracket.

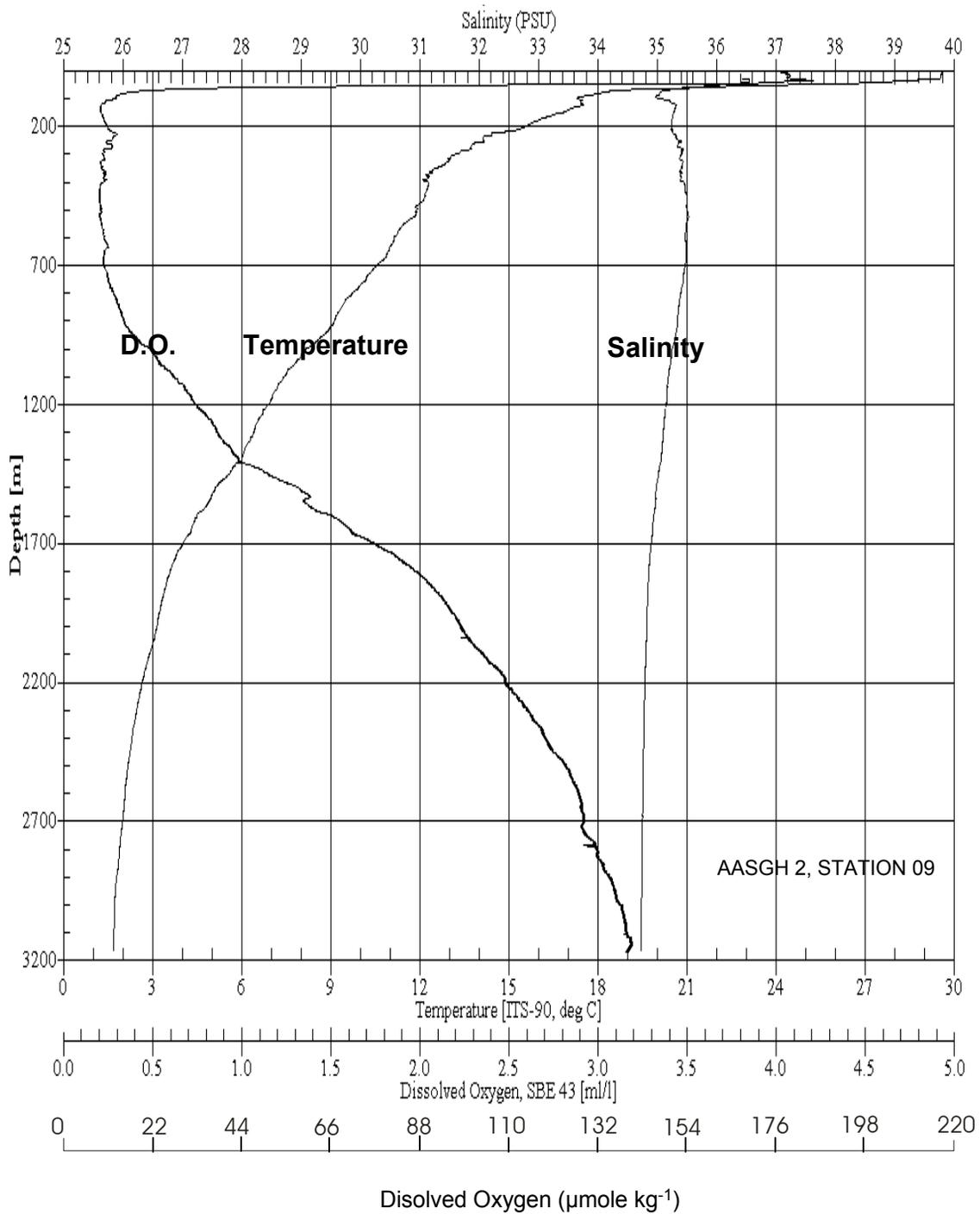
**Table-2A. and B.** Total organic carbon percentages in sediment cores from Krishna-Godavari (A) and Goa (B).



*Fig. 1. Location map of sediment cores from Krishna-Godavari (A) and Goa basins (B). Isobaths in meter. The core numbers marked on (A) are GH4/GC-2R to GH4/GC-73 and core number marked on (B) are GH2/GC-3 to GH2/GC24.*



**Figure 2A**



**Figure 2B**

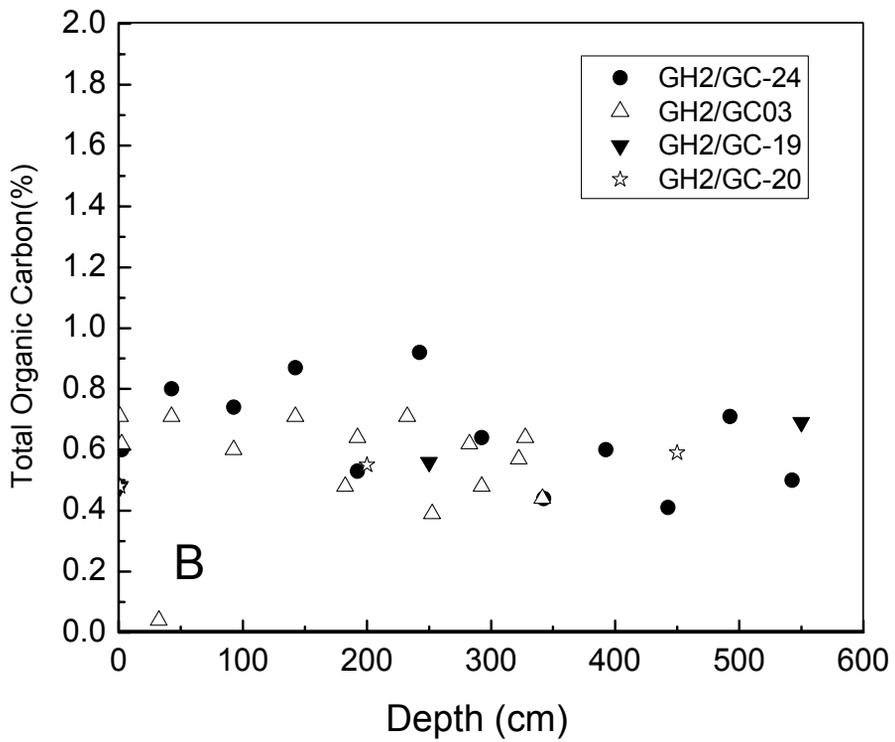
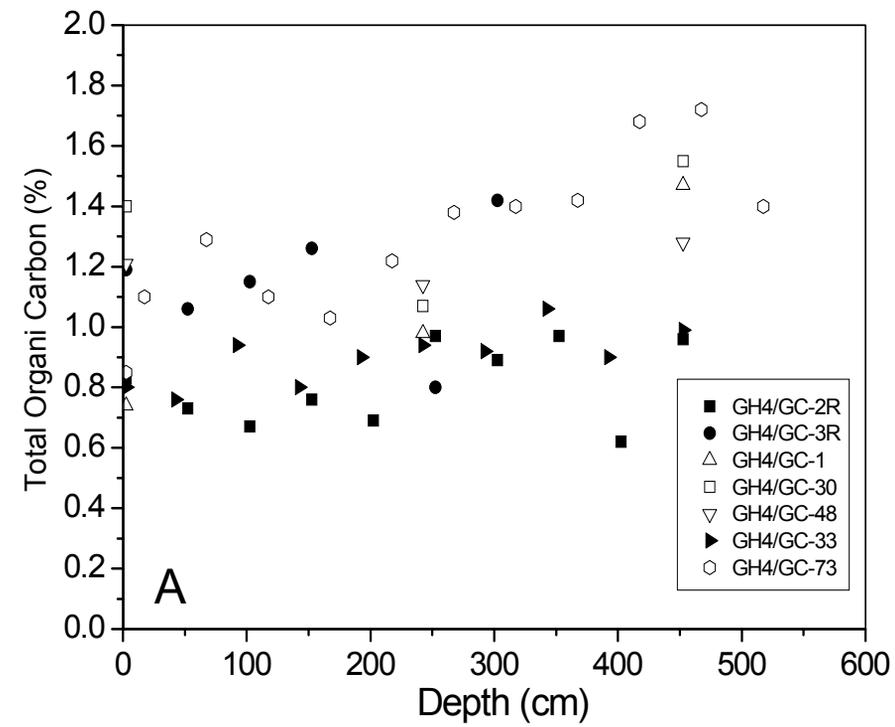


Figure 3

Sulfate Concentration (mM)

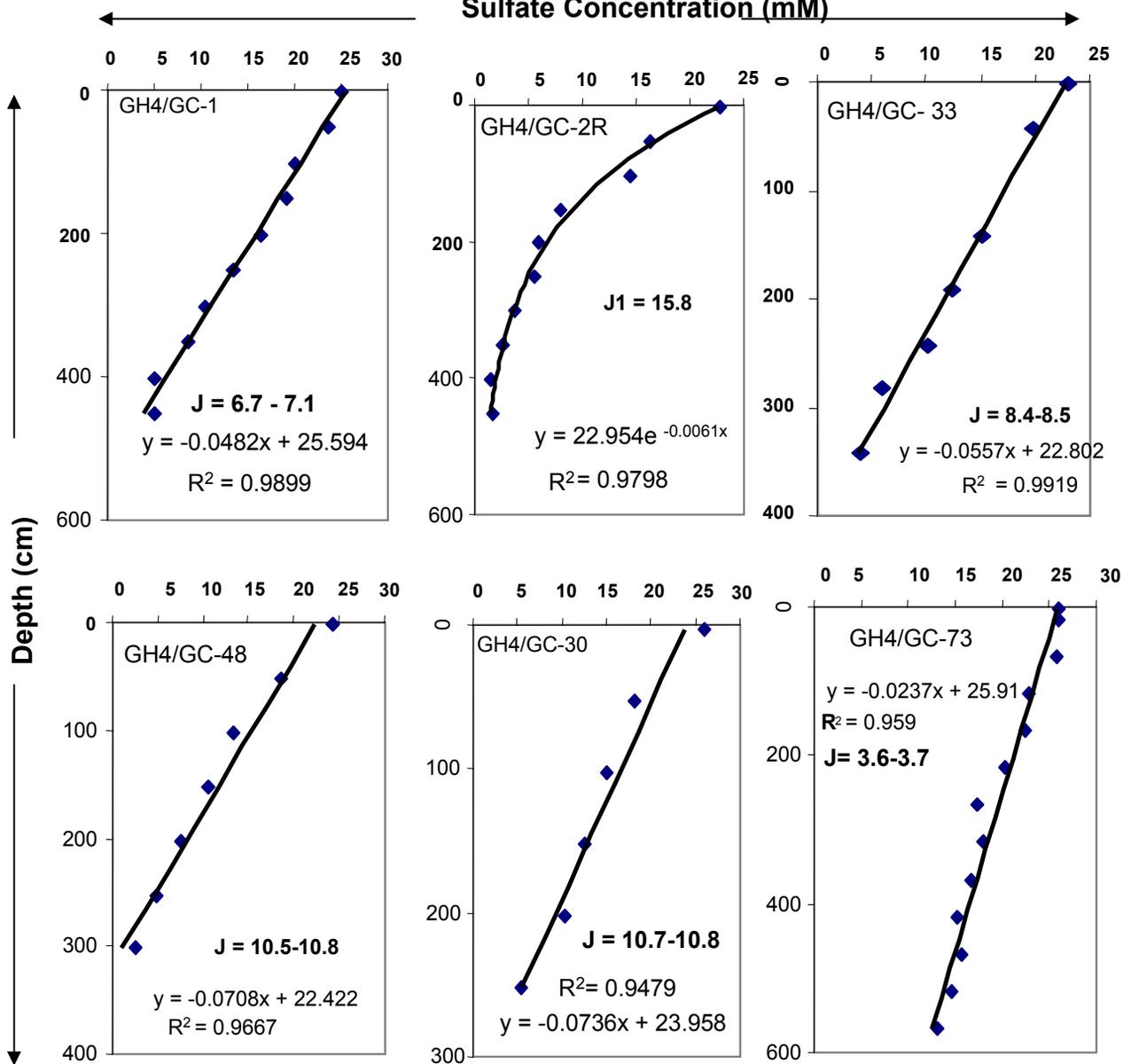


Figure 4A

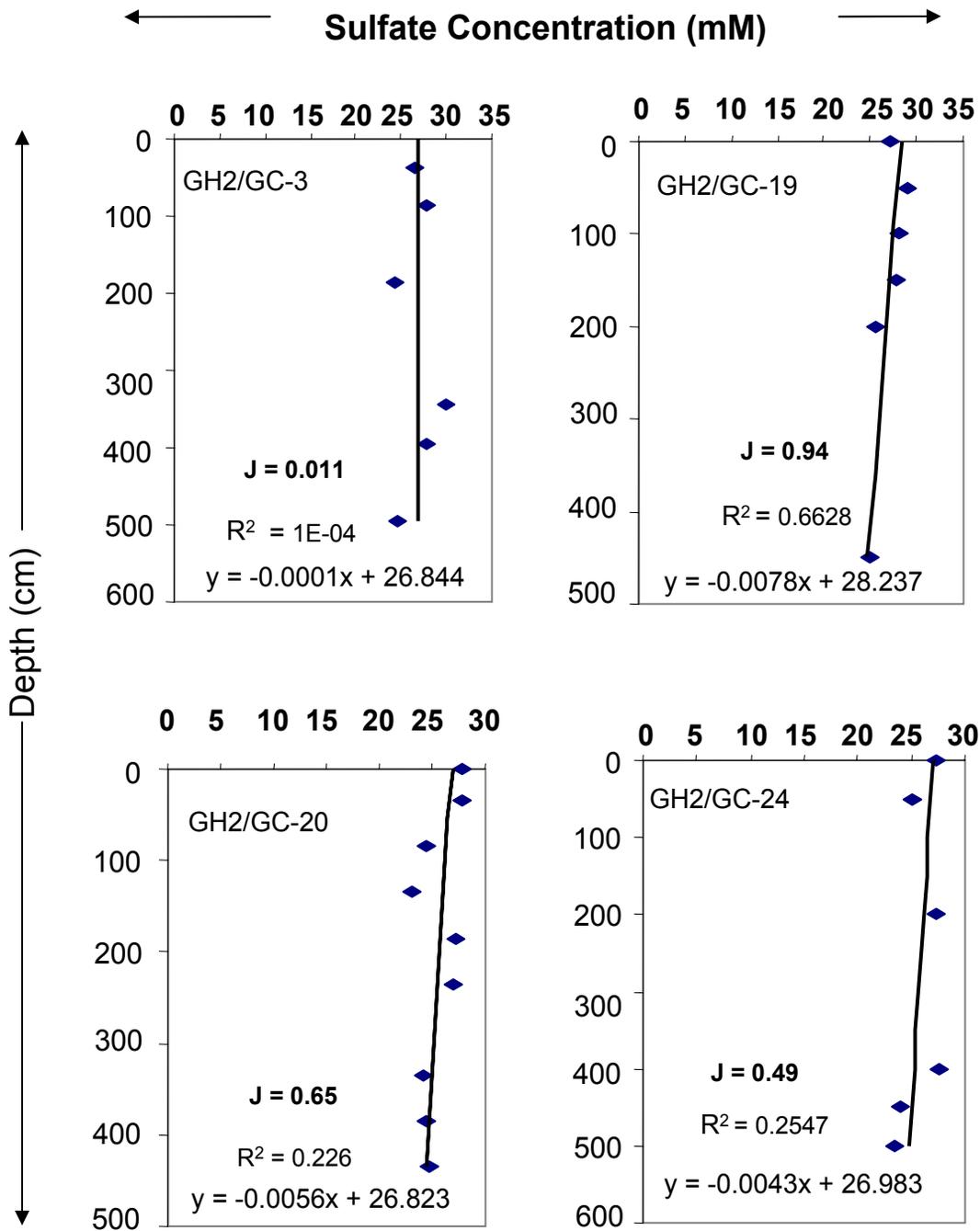


Figure 4B

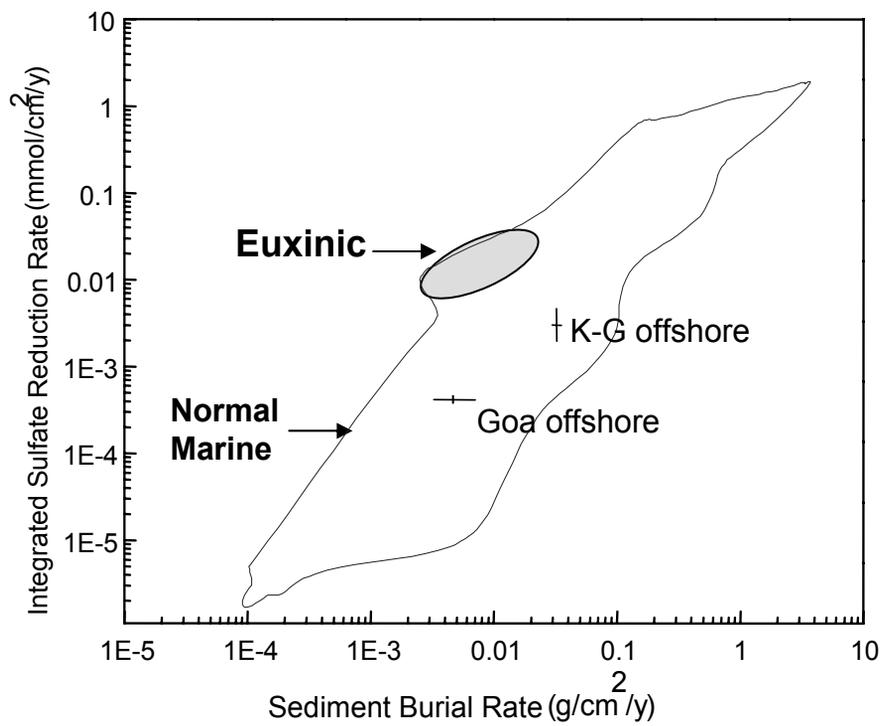


Figure -5

<b>Table-1A</b>						
<b>Sulfate concentrations (mM)</b>		<b>(K-G offshore)</b>				
<b>Mean Depth (cm)</b>	<b>GH4/GC1 (1327m)</b>	<b>GH4/GC2R (316m)</b>	<b>GH4/GC30 (1090m)</b>	<b>GH4/GC33 (951m)</b>	<b>GH4/GC48(1023m)</b>	<b>GH4/GC73(1450m)</b>
2.5	25.01	22.83	26.05	22.95	24.37	25.95
17.5						25.97
42.5				19.79		
52.5	23.61	16.36	18.04		18.59	
67.5						25.67
102.5	20.08	14.5	15.11		13.18	
117.5						22.7
142.5				15.01		
152.5	18.99	7.92	12.44		10.48	
167.5						22.43
192.5				12.42		
202.5	16.35	5.87	10.41		7.6	
217.5						20.28
242.5				10.11		
252.5	13.42	5.47	5.41		4.74	
267.5						17.36
282.5				6.05		
302.5	10.4	3.74			2.43	
317.5						18
342.5				3.85		
352.5	8.58	2.62				
367.5						16.74
402.5	4.96	1.57				
417.5						15.24
452.5	4.93	1.74				
467.5						15.57
517.5						14.63
567.5						13.09

<b>Table-1B</b>				
<b>Sulfate concentration (mM) Goa basin</b>				
<b>Depth</b>	<b>GH2/GC3 (2906m)</b>	<b>GH2/GC19 (2960m)</b>	<b>GH2/GC20 (2981m)</b>	<b>GH2/GC24 (2673m)</b>
2.5		27.10	27.83	27.33
35			27.90	
37	26.52			
50		28.92		25.21
85	27.73		24.44	
100		27.94		
135			23.07	
150		27.60		
185	24.31		27.36	
200		25.69		27.25
235			27.06	
335			24.07	
345	29.84			
385			24.56	
395	27.83			
400				27.66
435	24.80			
450		24.76		24.11
495	24.66			
500				23.49

Table 2A. K-G offshore TOC%						
Mean Depth (cm)	GH4/GC-2R	GH4/GC-1	GH4/GC-30	GH4/GC-48	GH4/GC-33	GH4/GC-73
2.5	0.83	0.74	1.4	1.21	0.8	0.85
17.5						1.1
42.5					0.76	
52.5	0.73					
67.5						1.29
92.5					0.94	
102.5	0.67					
117.5						1.1
142.5					0.8	
152.5	0.76					
167.5						1.03
192.5					0.9	
202.5	0.69					
217.5						1.22
242.5		0.98	1.07	1.14	0.94	
252.5	0.97					
267.5						1.38
292.5					0.92	
302.5	0.89					
317.5						1.4
342.5					1.06	
352.5	0.97					
367.5						1.42
392.5					0.9	
402.5	0.62					
417.5						1.68
452.5	0.96	1.47	1.55	1.28	0.99	
467.5						1.72
517.5						1.4
<b>Average</b>	0.81	1.06	1.34	1.21	0.90	1.30
<b>Std. Dev.</b>	0.13	0.37	0.25	0.07	0.09	0.26

Table 2B. Goa offshore TOC%				
Mean Depth (cm)				
	<b>GH2/GC-3</b>	<b>GH2/GC-19</b>	<b>GH2/GC-20</b>	<b>GH2/GC-24</b>
1	0.71	0.48	0.48	
2.5	0.62			0.6
32.5	0.04			
42.5	0.71			0.80
92.5	0.60			0.74
142.5	0.71			0.87
182.5	0.48			
192.5	0.64			0.53
200			0.55	
232.5	0.71			
242.5				0.92
250		0.559		
252.5	0.39			
282.5	0.62			
292.5	0.48			0.64
322.5	0.57			
327.5	0.64			
341.5	0.44			
342.5				0.44
392.5				0.6
450			0.59	
442.5				0.41
492.5				0.71
550		0.69		
542.5				0.5
<b>Average</b>	0.56	0.58	0.54	0.66
<b>Std. Dev.</b>	0.18	0.11	0.06	0.17