

Studies on the pore water sulphate, chloride and sedimentary methane to understand the sulphate reduction process in eastern Arabian Sea

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Sediment cores (~ 5 m length) from ten stations collected at water depths of 2665–3210 m in the eastern Arabian Sea were studied for pore water sulphate (SO₄²⁻), chloride (Cl⁻) and lighter hydrocarbons (methane: C₁, ethane: C₂ and propane: C₃) along with other parameters such as calcium carbonate (CaCO₃), total organic carbon (TOC) and porosity. Also, dissolved oxygen (DO) content in the near-bottom waters has been measured.

The CaCO₃ content of the sediments ranged from 33.6 to 69.9%, whereas TOC varied from 0.21 to 0.86%. Porosity of the sediments ranged from 54 to 57%, while DO of the near-bottom waters was in the range of 81 to 150 μM.

The sulphate content of the sediments in all the cores varies from 39.8 to 12.7 mM, indicating SO₄²⁻ reduction. Similarly, chloride concentration varies from 561 to 407 mM. The SO₄²⁻/Cl⁻ ratio is in the range of 0.025 to 0.072 with an average ratio of ~ 0.05, indicating that there is no significant loss of sulphate in the pore water. The down-core methane concentration in the sediment ranges from 1.5 to 12.5 nM. In addition, ethane and propane concentrations ranged from 0.04 to 1.2 nM and 0.09 to 0.46 nM respectively. The slow sulphate reduction process probably is due to a low content of C_{org}, moderate sedimentation rates as well as low porosity, in addition to the absence of strong anoxic environment in the sediments.

Keywords: Eastern Arabian Sea, methane concentration, sediment core, pore water sulphate studies, sulphate reduction.

GEOCHEMICAL studies of seabed sediments and their pore waters provide clues on the organic matter decomposition/diagenetic processes such as SO₄²⁻ reduction leading to the enrichment of methane (CH₄) due to methanogenesis. Methane in the sediments, the main component of hydro-

carbons, is largely used for tracing hydrocarbon deposits, including gas hydrates. Therefore, indirect geochemical proxy studies such as sulphate (SO₄²⁻) and chloride (Cl⁻) anomalies in pore waters were used in identifying these hidden resources¹. Barring the work of Böttcher *et al.*² and Prakash Babu *et al.*³ on pore waters for the isotopic composition of dissolved sulphate in the surface sediments (0–10 cm) from different water depths across the western continental margin of India, there is sparse information on this topic and also on sedimentary methane. As a major amount of methane is locked up in the form of gas hydrates⁴, it is important to study this part of the eastern Arabian Sea. Further, sulphate reduction process is an interesting issue in the Arabian Sea⁵, as sulphate reduction is subdued when compared to other upwelling margins with intense oxygen minimum zone (OMZ). Therefore, we report here pore water sulphate, chloride and sedimentary methane data to understand the sulphate reduction processes resulting from the early oxidation of organic matter in the shallow (5 m) sediment column of these hemi-pelagic sediments.

Study area

The study area (long. 70°30′–71°E; lat. 14°45′–15°30′N) in eastern Arabian Sea has oxic bottom waters (2665–3210 m) and is overlain by the well-established OMZ in mid-depths (200 to 1500 m). While narrating the geological framework, the occurrence of gas-charged sediments and the presence of bottom simulating reflectors (BSRs) possible gas-hydrate horizons have been deciphered along the western continental margin of India based on shallow seismic records⁶. The sedimentation rate reported in the vicinity of the study area is in the range of 1.8 to 8 cm/ky⁷. Sediment cores studied (GC 1, 2, 7, 9, 10, 19, 20, 21, 23 and 24) show moderate yellowish-brown colour sediments in the top 50 cm, while 50 cm to core bottom exhibits homogeneous grayish-olive colour.

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Materials and methods

The CTD data were collected from eight stations (Table 1) during the 41st cruise of *AA Sidorenko* in January 2002, while the gravity sediment cores were collected from ten stations (Tables 2 and 3) during GH-2 cruise of *AA Sidorenko* in November 2002. Pore waters were extracted by centrifugation (12 min at 6000 rpm), filtered (0.45 μ m)

and stored at -18°C for onshore analyses. Dionex Ion Chromatograph, DX-600, calibrated with Dionex standard and working sulphate standard, was used for the determination of sulphate and chloride in the pore water samples with $\pm 5\%$ accuracy.

Total organic carbon (TOC) and CaCO_3 were estimated by coulometry, while dissolved oxygen (DO) was measured by Winkler's method⁸ after adapting proper internal measures.

Table 1. Location of hydrocasts along with details of water depth, temperatures at sea surface (SST), sea bottom (SBT), and dissolved oxygen (DO) at near-bottom waters

Hydrocast no.	Latitude (N)	Longitude (E)	Water depth (m)	SST ($^{\circ}\text{C}$)	SBT ($^{\circ}\text{C}$)	DO (μM)
1	15 $^{\circ}$ 09.4'	70 $^{\circ}$ 41.3'	3018	27.6	2.35	150
2	15 $^{\circ}$ 04.5'	70 $^{\circ}$ 57.0'	2600	26.5	2.35	140
3	14 $^{\circ}$ 51.6'	70 $^{\circ}$ 50.7'	2641	27.0	4.57	81
5	15 $^{\circ}$ 24.2'	70 $^{\circ}$ 52.9'	2876	27.1	2.25	94
8	14 $^{\circ}$ 46.1'	70 $^{\circ}$ 40.0'	3000	27.3	2.26	96
9	14 $^{\circ}$ 59.7'	70 $^{\circ}$ 45.8'	2835	27.0	2.35	105
10	14 $^{\circ}$ 56.5'	70 $^{\circ}$ 55.9'	2630	26.8	2.44	100
11	14 $^{\circ}$ 50.9'	70 $^{\circ}$ 50.8'	2640	26.9	2.40	118

Table 2. Location of sediment cores, water depth, TOC and CaCO_3 at three sections of the cores

Core no.	Location		Water depth (m)	Sediment depth (cm)	TOC (%)	CaCO_3 (%)
	Latitude (N $^{\circ}$)	Longitude (E $^{\circ}$)				
GC-01	15.5	70.6	3210	0	0.45	67.4
				185	0.38	41.6
				475	0.62	40.4
GC-02	15.1	70.7	2996	0	0.45	69.9
				166	0.48	46.3
				472	0.72	48.1
GC-07	15.3	70.7	2872	0	0.48	65.4
				230	0.52	33.6
				530	0.86	66.0
GC-09	15.5	70.7	3190	0	0.21	63.0
				200	0.62	36.8
				450	0.65	45.8
GC-10	15.5	70.7	3155	0	0.28	63.8
				200	0.83	43.9
				500	0.45	40.3
GC-19	15.5	70.8	2960	0	0.69	64.6
				200	0.48	37.2
				450	0.69	45.1
GC-20	15.5	70.8	2981	0	0.48	63.7
				185	0.55	44.6
				435	0.59	40.7
GC-21	15.4	70.8	2965	0	0.79	63.6
				185	0.65	49.11
				485	0.55	44.63
GC-23	15.3	70.9	2665	0	0.38	65.04
				200	0.45	40.13
				450	0.48	52.48
GC-24	15.1	70.9	2673	0	0.38	58.87
				200	0.48	42.28
				500	0.48	40.59

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Table 3. Station numbers, location, water depth with pore water SO_4^{2-} , Cl^- , ratio of $\text{SO}_4^{2-}/\text{Cl}^-$, and sedimentary methane (C_1), ethane (C_2) and propane (C_3) concentrations at different levels of ten sediment cores

Core nos	Location (lat. N°/long. E°)	Water depth (m)	Core depth (cm)	SO_4^{2-} (mM)	Cl^- (mM)	$\text{SO}_4^{2-}/\text{Cl}^-$	Methane C_1 (nM)	Ethane C_2 (nM)	Propane C_3 (nM)
GC-01	15.5; 70.6	3210	0	25.3	551.3	0.046	3.8	0.37	0.16
			45	—	551.3	—	—	—	—
			140	—	551.4	—	—	—	—
			185	25.4	532.2	0.048	10.9	0.95	0.33
			230	—	561.0	—	—	—	—
			320	27.3	551.4	0.049	—	—	—
			375	25.6	541.7	0.047	—	—	—
			420	26.7	551.4	0.048	—	—	—
			475	18.4	—	—	9.9	0.09	—
GC-02	15.1; 70.7	2996	0	25.8	541.7	0.048	4.1	0.37	0.12
			16	—	541.7	—	—	—	—
			56	25.6	551.3	0.046	—	—	—
			116	22.3	532.2	0.042	—	—	—
			166	23.7	532.2	0.045	7.3	0.7	0.26
			266	13.1	—	—	—	—	—
			320	13.2	—	—	—	—	—
			368	—	—	—	—	—	—
			472	21.2	465.0	0.046	5.0	0.46	0.19
GC-07	15.3; 70.7	2872	0	—	—	—	2.5	0.11	—
			32	26.2	551.3	0.048	—	—	—
			80	25.3	551.3	0.046	—	—	—
			130	17.9	551.3	0.033	—	—	—
			230	17.3	541.7	0.032	9.1	0.83	—
			280	14.4	—	—	—	—	—
			380	15.9	513.0	0.03	—	—	—
			430	24.2	522.5	0.05	—	—	—
			530	27.8	551.3	0.05	—	—	—
GC-09	15.5; 70.7	3190	0	—	—	—	3.3	0.32	0.12
			50	26.0	445.8	0.058	—	—	—
			100	—	551.4	—	—	—	—
			150	39.8	551.4	0.072	—	—	—
			200	23.1	532.2	0.043	4.7	0.42	0.18
			300	25.8	493.8	0.052	—	—	—
			350	21.0	455.4	0.046	—	—	—
			400	—	413.0	—	—	—	—
			450	26.2	532.1	0.049	3.8	0.41	0.15
GC-10	15.5; 70.7	3155	0	27.8	551.3	0.048	3.29	0.32	0.12
			50	27.6	551.3	0.046	—	—	—
			100	36.2	541.7	0.033	—	—	—
			200	28.6	522.5	0.032	—	—	—
			250	23.5	551.4	—	4.71	0.42	0.18
			300	—	561.0	—	—	—	—
			350	—	561.0	—	—	—	—
			400	25.1	522.5	0.051	—	—	—
			500	—	—	—	3.77	0.41	0.15
GC-19	15.5; 70.8	2960	0	27.1	522.5	0.052	1.461	—	—
			50	28.9	551.3	0.052	—	—	—
			100	27.9	541.7	0.052	—	—	—
			150	27.6	541.7	0.051	—	—	—
			200	25.7	551.3	0.047	—	—	—
			450	24.7	551.3	0.045	1.77	0.04	—
GC-20	15.5; 70.8	2981	0	27.8	551.4	0.050	12.48	—	—
			35	27.9	551.4	0.051	—	—	—

(Contd...)

Table 3. (Contd...)

Core nos	Location (lat. N°/long. E°)	Water depth (m)	Core depth (cm)	SO ₄ ²⁻ (mM)	Cl ⁻ (mM)	SO ₄ ²⁻ /Cl ⁻	Methane C ₁ (nM)	Ethane C ₂ (nM)	Propane C ₃ (nM)
			85	24.4	522.5	0.047	–	–	–
			135	23.1	551.4	0.042	–	–	–
			185	27.4	538.7	0.051	7.1	–	–
			235	27.1	407.4	0.066	–	–	–
			335	24.1	541.7	0.044	–	–	–
			385	24.6	493.7	0.050	–	–	–
			435	24.8	426.6	0.058	9.27	–	–
GC-21	15.4; 70.8	2965	0	27.1	541.8	0.050	4.05	0.38	–
			35	–	532.2	–	–	–	–
			85	–	522.6	–	–	–	–
			135	24.3	532.2	0.046	–	–	–
			185	26.4	532.2	0.050	–	–	–
			235	25.1	541.7	0.046	14.74	1.19	0.46
			285	23.6	532.2	0.044	–	–	–
			335	28.6	532.2	0.054	–	–	–
			385	24.3	551.4	0.044	–	–	–
			485	25.6	532.2	0.048	–	–	–
GC-23	15.3; 70.9	2665	0	27.8	532.2	0.052	2.48	0.21	–
			50	31.0	561.0	0.055	–	–	–
			100	23.9	551.3	0.043	–	–	–
			200	27.6	512.9	0.054	–	–	–
			250	26.9	541.7	0.050	2.15	–	0.22
			350	22.7	551.3	0.041	–	–	–
			400	14.6	532.2	0.027	–	–	–
			450	12.7	513.0	0.025	–	–	–
GC-24	15.1; 70.9	2673	0	27.3	561.0	0.049	2.58	0.24	–
			50	25.1	551.3	0.046	–	–	–
			100	–	541.7	–	–	–	–
			150	–	561.0	–	–	–	–
			200	27.2	538.7	0.051	4.93	–	–
			250	–	561.0	–	–	–	–
			300	–	445.7	–	–	–	–
			350	–	–	–	9.62	–	–
			400	–	532.2	–	–	–	–
			450	24.1	541.7	0.045	–	–	–
			500	23.5	493.7	0.048	–	–	–

Combined gases, equal to the sum of adsorbed gas and un-escaped free gas from the pore volume⁹, were extracted from wet sediment samples using vacuum degassing system fabricated by Schmitt *et al.*¹⁰.

Methane content in the gas phase was determined with a Carlo Erba (Model CE 8000 Top) Gas Chromatograph fitted with 30 m long GS-Q-coated quartz capillary column and flame ionization detector (FID). The GC system was calibrated with standard mixtures of methane obtained from Linde Pruf Gas, UK. The concentration is given in nanomoles per litre (nM).

Results and discussion

Total organic carbon

TOC values are low and range in between 0.21 and 0.86% (Table 2). TOC values in the similar range were also re-

ported^{2,7,11,12} in the Arabian Sea. This perhaps could be due to oligotrophic nature of the area and low primary productivity $\sim 166 \text{ g C m}^{-2} \text{ y}^{-1}$ (ref. 7).

Calcium carbonate

The CaCO₃ content is variable and ranges from 33.6 to 69.9% (Table 2). Similar variability has been reported^{3,11,12} in the Arabian Sea and is attributed to factors such as variable biological productivity and dilution by terrigenous material.

Bottom-water dissolved oxygen values

Using hydrocasts we have obtained sea surface temperature (SST: 26 to 27°C), sea bottom temperature (SBT: 2.3 to 4.6°C) and DO (81 to 150 μM) data (Table 1). Results show that two stations show comparatively higher DO

values from 140 to 150 μM , while other stations record concentrations from 81 to 118 μM .

Sulphate gradients

Sulphate distribution in the study area is given in Table 3 and Figure 1. Out of ten sediment cores analysed, only three cores (GC 2, 7 and 23) show down-core SO_4^{2-} depletion, while the remaining show no significant change in values. It is known that average sea water sulphate value is 28.8 mM, and often bottom waters can have sulphate up to 30 mM (Borowski, pers. commun.). The pore water sulphate concentration varies between 39.8 and 12.7 mM. Maximum concentrations of 39.8 and 36.2 mM are observed in two cores (GC 9 and 10). Otherwise, sulphate concentration ranges between 31 and 12.7 mM. Sulphate concentration in the surface sediments ranges from 25.3 to 27.8 mM, and is close to sea water concentration.

Sediment core GC 7 shows a decreasing trend of sulphate from 26.2 to 14.4 mM in between 0 and 380 cm. It then shows an increasing trend from 16 to 28 mM between 380 and 480 cm, indicating an additional sulphate source/supply. Similar trends are also observed in GC 2 with depletion up to 320 cm and increased concentration at 472 cm. GC 23 shows a typical depletion from 12.8 to 31 mM to a depth of 450 cm. GC 24 has limited data and sulphate concentrations are close to normal sea water values. GC 9 and 10 show sulphate concentration of 21 to 39.8 mM, with maximum concentration of 39.8 mM at 150 cm in GC 9 and 36.18 mM at 100 cm in GC 10. Except these two values, the sulphate concentrations vary between 21 and 28.57 mM in these cores. GC 01 shows concentration of 25.3 to 27.3 mM up to 420 cm and 18.4 mM at 475 cm. Core 19 records concentration between 24.8 and 29 mM, while nearby cores GC 20 and 21 show sulphate concentration in the range of 23.07 to 28.61 mM.

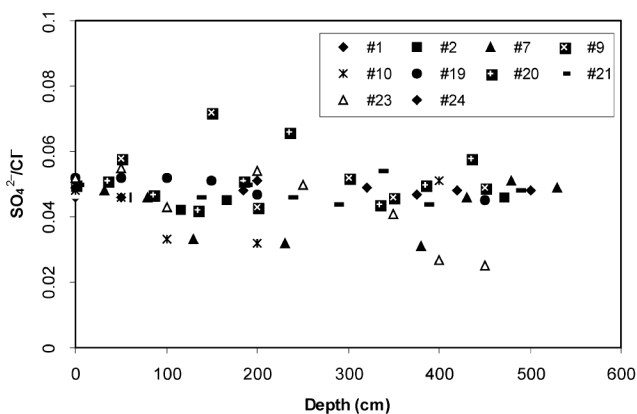


Figure 1. Plot showing ratio of $\text{SO}_4^{2-}/\text{Cl}^-$ versus depth (cm) in the sediment cores.

In the study area significant sulphate reduction in three cores (GC 2, 7 and 23) and insignificant sulphate reduction in all other cores have been observed. Such a variability over a small area has also been observed by Böttcher *et al.*¹³, who opined that due to re-oxidation and transportation processes in marine sediments, total sulphate reduction rates are typically much higher than the net rates reflected by dissolved sulphate. The constant trend of sulphate in some cores may be explained by inactive participation of sulphate reduction during the decomposition of organic matter¹⁴.

It is widely accepted that the available organic matter and associated metabolic activity in sediments are the two most important factors controlling sulphate reduction rates^{13,15}. Hence we consider their views to explain the low sulphate reduction in the study area.

Veto *et al.*¹⁶ opine that factors such as rate of sedimentation, primary productivity and water depth influence the rate of sulphate reduction in the sediments. Organic matter is generally abundant in continental margin deposits. Hence energy yield by anaerobic processes (sulphate reduction) is less than by oxygen reduction¹⁷. Biological decomposition of organic matter occurs both in the presence and absence of DO in the water column and pore waters¹⁸. It was assumed that aerobic microbial decomposition occurs more rapidly than anaerobic degradation. The constancy of sulphate concentration throughout the cores can be ascribed to the absence of strong anoxic conditions¹⁷. The colour of sedimentary facies in the study area is yellowish-brown and indicates oxic environs in the subsurface sediments. The slow sulphate reduction thus can be attributed to the low organic carbon content coupled with moderate sedimentation rates.

We observe that in the absence of or nano mole level methane in the 5 m sediments, the upward diffusion of methane is ruled out and sulphate reduction seems to be caused by *in situ* microbial degradation of organic matter¹³.

Alternatively, Van der Weijden *et al.*¹⁹ reported little or no evidence of sulphate reduction in northeastern Arabian Sea, which they attribute either to the availability of other post-oxic metabolic pathways (Fe-cycling) or to the absence of reactive organic matter that is susceptible to re-mineralization via this pathway.

Sulphate depletion due to the influx of freshwater and the impact of meteoric water is ruled out in the study area; however, the role of microbial consumption in sulphate depletion cannot be ruled out.

Oxygen content and sulphate reduction

A comparison of bottom water DO data with the reported ones reveals that the bottom water in the study area is more oxygenated. Our observation of slow sulphate reduction in the oxygenated bottom waters is similar to that of Cowie⁵ for the Arabian Sea.

Chloride concentration and pore water $\text{SO}_4^{2-}/\text{Cl}^-$ ratio

Chloride concentrations are in the range of 522 to 561 mM at the surface level. They remain constant up to 480 cm depth in most sediment cores, but down-core concentrations of chloride are at a lesser range of 407–446 mM in cores GC 9, 20 and 24. In sea water, chloride concentrations are generally 20 times greater than sulphate values. Dividing chloride values by 20, yields the expected sulphate concentration if dilution is the only process affecting sulphate concentration. The calculated difference between the measured pore water sulphate and the predicted sulphate concentration should equal the component of sulphate decrease due to microbial consumption²⁰. In addition, clay mineral diagenesis could be one of the causes for depletion of chloride content²¹.

The values of $\text{SO}_4^{2-}/\text{Cl}^-$ ratio for all the cores are shown in Figure 1 and Table 3. The plot of $\text{SO}_4^{2-}/\text{Cl}^-$ against water depth recast the diagenetic behaviour of sulphate and chloride ions in the area. The ratio of sulphate to chloride concentration is in the range of 0.025–0.072 (Table 3) with an average ratio of ~0.05, which resembled the bottom water value. As pore water chloride is inert, the constancy of the ($\text{SO}_4^{2-}/\text{Cl}^-$) ratio in the present study indicates that there is no significant loss of sulphate from the pore water systems. Böttcher *et al.*² also elaborated similar views.

Sedimentary methane

The concentration of gases, methane (C_1), ethane (C_2) and propane (C_3) extracted from the representative subsamples of the sediment cores is shown in Table 3. A general oceanic background concentration of methane is in the range²² of 2–3 nM. The water column-dissolved methane profiles at four open ocean stations in the Arabian Sea at and beyond 1500 m water depth, show²³ methane values in the range of 0–2 nM. One of the stations 3441, falling in the present study area shows methane value up to 2 nM at 2500 m water depth. However, the contribution of sedimentogenous methane to the dissolved methane in the water column was ruled out by Jayakumar *et al.*²³.

The origin of gases in shallow sediments can be attributed to either biogenic and or thermogenic processes²⁴. In our study we observed the presence of nano mole level of sedimentary methane and it could be due to limited sediment core length (about 5 m). Thus the sediment cores raised appear to be well within the anaerobic methane oxidation (AMO) zone. Sedimentary pore waters show linear decrease of sulphate from sediment–water interface to the sulphate–methane reaction zone, and then increase in methane levels below that zone leading to methanogenesis¹³. Presence of methane, ethane and propane led us to think about a possible origin and migration of meth-

ane perhaps from dissociation of gas hydrates (?) in subsurface layers.

Conclusion

We conclude that down-core sulphate profiles show constancy in sulphate concentrations in seven cores, while only three cores show down-core variation. Thus, intense sulphate reduction process in the study area is confined to a limited region. Whereas majority of cores show a process of negligible or slow sulphate reduction, as shown by Cowie⁵ in the Arabian Sea. This slow sulphate reduction is probably due to factors such as availability of less metabolizable organic carbon and slow sedimentation rate. The remaining three sites where sulphate reduction is intense, are potential regions for further detailed studies. Nano-mole level sedimentogenous methane values noticed in the study area reflect that these samples are well above the sulphate methane interface, hence they cannot be used to characterize sulphate depletion through AMO.

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