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Evidence of deep subsurface sulfur cycle in a sediment core from eastern Arabian Sea

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Abstract

Anaerobic microbial sulfate reduction and oxidative sulfur cycling have been studied in long sediment cores mainly acquired as part of IODP explorations. The most remarkable observation in many of these studies is the existence of an active sulfur cycle in the deep subsurface sediments that have very low organic carbon content and are presumably refractory. Here we investigate the interstitial sulfate concentrations and sulfur isotope ratios in a 290 m long core collected from the eastern Arabian Sea at a water depth of 2663 m. Continuous decrease in pore water-sulfate concentrations with depth (up to 75 mbsf) coupled with enrichment in $\delta^{34}S_{SO4}$ values suggests organoclastic sulfate reduction (OSR) processes attributed to the activity of sulfate-reducing bacteria (SRB) and retention of labile organic substrates amenable to the SRBs. Below a depth of 75 mbsf, the absence of a further reduction in sulfate concentrations indicates insufficient labile substrate to drive SRB. An increase in sulfate concentrations at the deeper subsurface (below 128.5 mbsf) coupled with

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decreasing $\delta^{34}S_{SO4}$ values may be attributed to a ferric-oxyhydroxide driven oxidation of Fe-sulfide. This study reveals that even under deep aerobic water columns, organic matter may continue to be a source of labile organic substrates at significantly deeper subsurface. Enhanced sulfate concentrations in the deeper depths may be attributed to the oxidation of sulfides via ferric-oxyhydroxides buried deep within the sediment. A microbiological investigation may reveal further details of the sulfur cycle at the deep surface.

1. **Introduction**

The exploration of the sub-seafloor biosphere and redox zonation in sediments over the last few decades has enhanced our knowledge of the deep biospheric microbial distribution (Wasmund et al., 2017), substrates, energy utilization pathways (LaRowe and Amend, 2015) and diagenetic mineralization (Meister et al., 2019). Microbially mediated biogeochemical processes in marine sediments are fuelled by simple organic molecules (electron sources) and inorganic electron acceptors, including O_2, NO_3^-, Fe^{3+}, Mn^{4+}, SO_4^{2-} and CO_2. Degenerated and reorganized organic particulates deposited on the sea bed are further subjected to microbially mediated oxidative degradation and reworking by benthic organisms, enriching the sediment porewater with fresh dissolved organic matter (Ferdelman et al., 2011; Maliverno and Martinez, 2015; Bergauer et al., 2017; Luek et al., 2017). Hydrolysis and subsequent fermentation of complex organic molecules fuels a sequential utilization of terminal electron acceptors, typically in the order of O_2, NO_3^-, Mn^{4+}, Fe^{3+} and SO_4^{2-} followed by CO_2. At a depth of a few centimetres to meters below the seafloor, oxidative remineralization is taken over by strictly anaerobic, organoclastic sulfate reduction (OSR), which accounts for up to 29% of the remineralization of accumulated seafloor organic matter (Bowles et al., 2014).

The availability of simple organic compounds like volatile fatty acids (VFA), including formate, acetate, propionate, and H_2, in the sediment pore-fluid is crucial in sustaining OSR and the growth of sulfate-reducing bacteria (SRB). However, in the deep subsurface, due to depletion in the availability of labile organic molecules, sulfate reducers may use methanol, long-chain fatty acids, and aromatic compounds as electron sources (Sousa et al., 2018). Wellsbury et al. (2002) reported SO_4^{2-} reduction up to 100 mbsf in a deep-sea sediment core characterized by low organic carbon content (~0.4%) and attributed the SO_4^{2-} reduction process to the presence of culturable fermenters and acetogens in the deep subsurface. Micromolar acetate concentrations (4 – 14 µM) have been reported by D'Hondt et al. (2003) in marine deep subsurface sediments. Sulfate-reducing bacteria may metabolize, and even grow at extremely low rates under energy-limited conditions (Hoehler and Jørgensen, 2013; Bowles et al., 2014; Jørgensen and Marshall, 2016) through physiological adaptations including increased substrate uptake efficiency (Lever et al., 2015; Jørgensen and Marshall, 2016), and use of alternative electron carriers like rubredoxin and rubrerythrin for ATP generation (Wenk et al., 2017). Sulfate reducers may also adapt to sporulation in extreme deep subsurface conditions (Klemps et al., 1985; Kotelnikova and Pedersen, 1997). In addition, H_2 generated in porewater by radiolysis or anaerobic mineral reactions may also play an important role in deep-subsurface SO_4^{2-} reduction (Stevens and Mckinley, 1995; Schrenk et al., 2013).

Sulfate reduction typically decreases interstitial dissolved SO_4^{2-} concentrations as the sediment is buried beneath the seafloor, eventually reaching below detection levels within the sulfate-methane transition zone (Jørgensen and Kasten, 2006). The sulfate concentration profile is also accompanied by a distinct alteration in interstitial water compositions, including total alkalinity, HCO_3^-, NH_4^+, HS^- concentrations, and sulfur stable isotope ($\delta^{34}S_{SO4}$ and $\delta^{34}S_{HS}$) ratios. However, pore water analyses of long sedimentary cores from IODP or other expeditions often show anomalous SO_4^{2-} concentrations in the deeper sediment layers after initial drawdown (Meyers and Shaw, 1996) at shallower depths. These observations have been attributed to deep subsurface Fe-sulfide oxidation, disproportionation of S^0 (Riedinger et al., 2010), and brine flux from deeper sources (Meister et al., 2019). Recycling of sulfur species and the cryptic sulfur cycle has also been reported from the deep subsurface SO_4^{2-}-poor sediments (Holmkvist et al., 2011; Brunner et al., 2016) coupled with the continuous detection of functional genes of sulfate-reducing microbes (Leloup et al., 2007; Leloup et al., 2009; Blazejak and Schippers, 2011; Aoki et al., 2015). Chloroflexi is notable for being relatively abundant in deep sediments and could therefore hint at their roles in the deep subsurface sulfur cycle (Wasmund et al., 2016).

In the present work, we have attempted to explain the anomalous SO_4^{2-} concentrations and $\delta^{34}S_{SO4}$ profiles in the interstitial waters in a long sediment core collected from the eastern Arabian Sea (off the west coast of India) during the 2006 NGHP-01 Expedition on board ORV *JOIDES-Resolution*. The cruise was undertaken as part of the Indian gas hydrate exploration program (Collette et al., 2008).

2. Geology

The Western Continental Margin of India has evolved due to rifting of the Indian landmass from Madagascar and Seychelles islands, since the Middle Cretaceous (Norton and Sclater, 1979). Subsequent seafloor spreading between these landmasses formed the Arabian Sea (Chaubey et al., 1993). The Carlsberg Ridge divides the Arabian Sea into two major basins: the Arabian Basin to the east and the Somali Basin to the west (Mckenzie and Sclater, 1971). The Arabian Sea (3.862 million km²**)** has an average water depth of 2,734 m. It is bordered to the west by the Horn of Africa and the Arabian Peninsula, to the north by Iran and Pakistan, to the east by India, and to the south by the Indian Ocean.

The western continental margin of India, which forms the eastern boundary of the Arabian Sea, is a passive margin and characterized by (i) an NW-SE trending continental shelf (~200 to 50 km wide) (ii) a straight outer edge limited by 200 m isobath, (iii) a narrow continental slope bounded by the 200 and 2000 m isobaths, (iv) deep sedimentary basins viz., Kori-Comorin and Kerala-Konkan Basins and, (v) several structural features like Chagos-Laccadive Ridge, Laxmi Ridge and Pratap Ridge (Naini and Talwani, 1982). The N-S trending Chagos-Laccadive Ridge represents the trace of the Reunion hotspot (Duncan, 1981).

The Kerala-Konkan Basin forms the southern part of the western continental margin of India and extends from Goa to the tip of Cape Comorin. The coring site NGHP-01-01A is located in the Kerala-Konkan Basin at a water depth of 2663 m (Fig.1). NGHP-01-01A coring site lies on the western flank of the Chagos-Laccadive Ridge. Seismic lines show a prominent basement high beneath the site (Rao et al., 2001).

NGHP-01-01A core is characterized by a remarkably homogenous sequence of carbonate-rich oozes (Kumar et al., 2014) with variable clay content. The oozes include nannofossil ooze and foraminifera-bearing nannofossil ooze. The sediment core shows a varying degree of bioturbation, ranging from moderate to abundant (Collett et al., 2008).

3. **Methodology**

Advanced piston coring (APC), extended core barrel (XCB), and pressure core (PCS) techniques were used on-board JOIDES Resolution (NGHP-01 cruise) under the aegis of the National Gas Hydrate Program of India. The core NGHP-01-01A (15°18.366’N, 070° 54.192’E) (Fig. 1) was sampled on-board following the IODP sampling protocol. Wholeround sediment samples were collected at variable resolutions for interstitial water analyses. A Manheim-type hydraulic press (Sayles et al., 1973; Gieskes, 1974) was used to squeeze out the porewater under nitrogen flow to avoid oxidation of hydrogen sulfide (HS^- + H_2S). The porewater aliquots were sealed in glass vials following N_2 purging for onshore measurements. Chloride (Cl^-) concentrations were measured onboard using a Metrohm IC (Collett et al., 2008). Porewater-SO_4^{2-} ion concentrations were measured using a Dionex-600 ion chromatograph at the CSIR-National Institute of Oceanography. A detailed analytical protocol is given in Mazumdar et al. (2007). Total alkalinity (Gieskes et al., 1986) was measured by the Gran titration method using a Metrohm Autotitrator (Titrino 799 GPT). Dissolved SO_4^{2-} in the porewater aliquot was precipitated as $BaSO_4$ using 1 ml of high-purity $BaCl_2$ (Mazumdar and Strauss, 2006). The acidified $BaSO_4$ suspension was boiled for a few minutes and allowed to cool down at room temperature, and the filtrate was subsequently dried in a hot air oven. The sulfur isotope ratio ($\delta^{34}S$) measurement of the $BaSO_4$ precipitate was carried out using an EA-IRMS (Thermo Delta V-Plus with EA1112) with a continuous flow system. IAEA-standards including SO-5, SO-6 ($BaSO_4$) and, S-1, S-2 (Ag_2S) were used as calibration standards for S-isotope ratio measurement. Sample reproducibility of $\delta^{34}S$ values was better than ± 0.3‰ VCDT (Vienna Canyon Diablo Troilite). Total inorganic carbon (TIC) contents in the sediment samples were measured using a UIC carbon coulometer (CM 5130). Ultrapure $CaCO_3$ (Sigma-Aldrich) was used as a TIC (wt%) measurement standard. Total carbon content (TC wt%) was measured using an elemental analyzer (Thermo EA1112). Reproducibility for TC and TIC measurements are 1% and 1.4%, respectively. Total organic carbon (TOC wt%) was calculated by subtracting TIC from TC.

4. Results and Discussion

4.1 Organoclastic sulfate reduction and sulfide oxidation

Based on SO_4^{2-} (Table-1) concentration and $\delta^{34}S_{SO4}$ isotope ratios (Fig. 2C & D), the sedimentary core NGHP-01-01A may be partitioned into four zones (I: 1.3-75.4 mbsf; II: 75.4 - 128.5 mbsf; III: 128.5 - 171.9 mbsf and IV: 171.9 - 290.8 mbsf). Within zone–I, SO_4^{2-} concentrations decrease from 28.4 (2.4 mbsf) to 19.1 mM at a depth of 75.4 mbsf. Within this zone, $\delta^{34}S_{SO4}$ values increase steadily down depth from a core top value of +22.8 to +43.9 ‰. Within zone–II, $\delta^{34}S_{SO4}$ varies from +42.9 to +47.3 ‰, whereas the SO_4^{2-} concentration varies from 18.4 to 20 mM. The $\delta^{34}S_{SO4}$ ratio drops from +48.9 to +36.2 ‰ within zone-III (128.5 to 171.9 mbsf) coupled with an increase in SO_4^{2-} concentration up to 24 mM. Below zone-III, the $\delta^{34}S_{SO4}$ values remain between +33.5 and +39.8 ‰. In contrast, SO_4^{2-} concentrations show significant scatter and range from 17.3 to 24 mM. The bulk organic carbon content ranges from 0.03 to 1.1% and is characterized by a logarithmic depth profile (Fig. 2A).

The marked variations in SO_4^{2-} concentrations and $\delta^{34}S_{SO4}$ values suggest active sulfur biogeochemistry involving microbial SO_4^{2-} reduction and sulfide oxidation in the deep subsurface of the eastern Arabian Sea. Microbial SO_4^{2-} reduction in the marine sediment involves organoclastic (Froelich et al., 1979; Treude et al., 2005; Jørgensen and Kasten, 2006; Riedinger et al., 2017; Beulig et al., 2018; Jørgensen et al., 2019) and anaerobic oxidation of methane (AOM) pathways (Froelich et al., 1979; Reeburgh, 1980; Valentine and Reeburgh, 2000; Boetius et al., 2000; Knittel and Boetius, 2009; Ouboter et al., 2022) represented by stoichiometric equations 1 and 2 respectively,

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 53\ SO_4^{2-} \rightarrow 106\ HCO_3^- + 53\ HS^- + 16\ NH_3 + H_3PO_4 + 53\ H^+ \qquad \text{Eq.1}$$

$$CH_4 + SO_4^{2-} \rightarrow HCO_3^- + HS^- + H_2O \qquad \text{Eq.2}$$

The absence of detectable methane concentrations in the core sample (Collett et al., 2008) suggests that OSR is the most critical microbial pathway responsible for the drop in SO_4^{2-} concentrations. Additionally, the lack of chloride (Cl^-) anomaly (Fig.2B) indicates the absence of methane hydrate in the core sediments. Microbial SO_4^{2-} reduction results in ^{34}S enrichment (kinetic fractionation) of residual interstitial SO_4^{2-} owing to preferential partitioning of ^{32}S in the HS^-/H_2S phase (Canfield, 2001; Detmers et al., 2001; Wing and Halevy, 2014). Dissolved SO_4^{2-} in the modern ocean has a sulfur isotopic composition of about +20.5 ‰ (Böttcher et al., 2000). Compared to seawater, $\delta^{34}S_{SO4}$ values of the porewater-SO_4^{2-} (Fig 2D) indicate enrichment of ^{34}S (Böttcher et al., 2004). The absence of interstitial HS^-/H_2S is attributed to consumption via Fe-sulfide synthesis (Canfield and Thampdrup, 1994; Canfield, 2001; Claypool, 2004; Canfield et al., 2005; Jørgensen & Kasten, 2006; Jørgensen et al., 2019) or incorporation into organic molecules (Werne et al., 2008; Raven et al., 2016). The presence of pyrite in the NGHP-01-01A core was reported by Collett et al. (2008).

The activity of SRB driving the OSR in marine sediments is controlled by the composition and concentrations of buried labile organic molecules including simple dissolved fatty acids (acetate, lactate, formate), alcohol (methanol and ethanol), and H_2 in the interstitial waters (Glombitza et al., 2015; Jørgensen et al., 2019). The interstitial volatile fatty acids (VFA) and alcohols are fermentation/ acetogenesis products of hydrolyzed organic molecules buried below the oxygenated zone in the marine sediments (Jørgensen et al., 2019). Additional factors influencing SO_4^{2-} reduction rate and sulfur isotopic fractionation include bacterial groups/ population, temperature, and SO_4^{2-} concentrations (Canfield, 2001; Jørgensen and Karsten, 2006). The steady drop in interstitial SO_4^{2-} concentrations in zone-I thus indicates the availability of bioamenable organic substrates in the interstitial waters, which fuels SO_4^{2-} reduction. Intuitively, the lack of a noticeable drop in SO_4^{2-} concentrations within zone–II possibly indicates a significant limitation of substrate availability to sustain SO_4^{2-} reduction. The bulk organic matter content and reactivity markedly decrease down depth (Fig. 2A) with potential retention of refractory organic components (Parkes et al., 1994; Wellsbury et al., 1997; Jørgensen and Kasten, 2006; Johnson et al., 2014). Below zone-II, the SO_4^{2} concentrations show a moderate increase coupled with a drop in $\delta^{34}S_{SO4}$ values, suggesting possible oxidation of Fe-sulfide via the Fe^{3+} reduction pathway (Eq.- 3; McKibben and Barnes, 1986; Balci et al., 2007; Mazumdar et al., 2008). Ferric-oxide enrichment within this zone (Collett et al., 2008) supports the above contention. In the absence of microbial population data, the possible role of microbial activity in the oxidative phase of the sulfur cycle (Riedinger et al., 2010) remains speculative in this study. The decrease in carbonate alkalinity within zone-I and II (Fig. 2E) likely indicates HCO_3^- uptake by Ca-carbonate precipitation (Eq. 4), whereas, in zone-IV, the enhanced alkalinity trend may be attributed to $CaCO_3$ dissolution and HCO_3^- production (Eq. 5). The enhanced alkalinity in zone-IV is supported by increased calcium carbonate content (ranging from 22 to 86. wt%) reported by Johnson et al. (2014). The H^+ availability in the interstitial waters may be attributed to Fe-sulfide oxidation (Eq. 3). Enhanced bicarbonate alkalinity due to pyrite oxidation in carbonate-rich sediment has also been reported by Appelo et al. (1998).

$$FeS_2 + Fe^{3+} + 8H_2O \rightarrow 2Fe^{2+} + 16H^+ + 2SO_4^{2-} \qquad \text{Eq. 3}$$

$$HCO_3^- + Ca^{2+} \rightarrow CaCO_3 + H^+ \qquad \text{Eq. 4}$$

$$CaCO_3 + H^+ \rightarrow HCO_3^- + Ca^{2+} \qquad \text{Eq. 5}$$

4.2 Depositional environment and organic matter reactivity

One of the most interesting findings of this study is the microbially mediated deep-surface reductive and abiotic oxidative sulfur cycle. The SO_4^{2-} reduction process indicates the presence of microbially amenable simple organic molecules in organic carbon-depleted sediments deposited below the deep aerobic water column. The 2663 m water column at the study site is characterized by a top 100 m of productive zone followed by 850 m (150 to 1000 mbsl) of oxygen minimum zone (Mazumdar et al., 2007) and 1560 m of aerobic water with dissolved oxygen concentrations increasing from 0.5 to 3.2 ml/l. Phytoplankton, including diatoms and dinoflagellates, comprise the eastern Arabian Sea's dominant particulate biomass (Marra and Barber, 2005). Organic matter sinks from surface water to the seafloor via the biological pump (Ducklow et al., 2001). The dissolved and particulate organic matter undergoes a remarkable transformation during transit through the water depth (with increasing DO concentrations) due to direct utilization by the biota and/or solubilization via extracellular enzymatic activity by heterotrophic microbes (Brophy and Carlson, 1989; Bergauer et al., 2017). The quality and quantity of the organic matter in the bottom sediment, which fuels the biogeochemical reaction during burial, depends on the molecular transformation of the settling organic load (Zonneveld et al., 2010; Arndt et al., 2013) through the water column. Numerous factors like adsorption of organic matter on siliciclastic particulates, physical protection/isolation of organic matter by siliciclastics, rate of vertical fall (ballast effect), aggradation/degradation of particulate flocs, and temperature influence the rate and extent of breakdown of organic matter in the aerobic water column (Lee et al., 2004; Arndt et al., 2013). Only a small fraction of the organic matter is exported to the seafloor (Holland, 1978; Hedges and Keil, 1995; Berner, 2004; Arndt et al., 2013) since the majority of the organic matter is remineralized to CO_2 during its trajectory (Burdige, 2007). En route to the sea bed, the particulate organic matter rapidly and preferentially gets depleted

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in amino acids, carbohydrates, polyunsaturated fatty acids, and lipids by microbial and zooplankton activity. Whereas, marine and terrestrially derived refractory organic matter are preferentially transferred to the sea bed (Kharbush et al., 2020).

The sulfur dynamics observed in our study support the retention of microbially amenable simple organic molecules to fuel SO_4^{2-} reduction at least in the top 75 mbsf, which implies that despite extensive aerobic degradation in the water column, the organic particulates retain sufficient hydrolyzable compounds to fuel anaerobic fermentation to drive SO_4^{2-} reduction. This conjecture is supported by the reported retention of 10–20 % carbohydrates, 10 % nitrogenous compounds (mostly amino acids), and 5–15 % lipids in organic particulates (Hedges and Oades, 1997; Burdige, 2007). Agatova and Bogdanov (1972), Danovaro et al. (1993), and Dell'Anno et al. (2000) also reported hydrolysed protein and carbohydrate pools in deep-sea sediments.

5. Conclusions

Sulfate concentration and sulfur isotope ratio ($\delta^{34}S_{SO4}$) profiles of interstitial waters in the sediment core (NGHP-01-01A) from the eastern Arabian Sea show tell-tale evidence of OSR and sulfide oxidation attributed to deep subsurface biotic and abiotic processes respectively. Definite evidence of SO_4^{2-} reduction down to a depth of 75 mbsf may be attributed to the retention of labile organic molecules in sediment in despite burial and overlying 1560 m aerobic water column. The absence of a steady drop in SO_4^{2-} concentrations below 75 m may be attributed to the enhanced refractory nature of the organic matter (due to burial) and insufficient labile content to support active SO_4^{2-} reduction. Iron-oxyhydroxide-driven Fe-sulfide oxidation has been suggested as a possible mechanism to explain the enhanced SO_4^{2-} concentrations and drop in $\delta^{34}S_{SO4}$ values. A detailed microbiological study is required in future investigations to understand the possibility of the cryptic sulfur cycle and disproportionation processes in deep cores of the eastern Arabian Sea.

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Figure and Table Captions

Figure 1: Regional map showing the location of sediment core (NGHP-01-01A) in Kerala-Konkan Basin. The bathymetry map was generated using ocean data view software.

Figure 2: Geochemical composition NGHP-01-01A core. A. TOC (wt. %) with logarithmic regression fit. B. Chloride concentration in interstitial waters (data from Collett et al., 2008). C. Interstitial SO_4^{2-} concentrations (mM). D. S-isotope ratio ($\delta^{34}S_{SO4}$) of interstitial SO_4^{2-}. E. Total alkalinity (TA) concentrations (mM) in the interstitial water. The horizontal dashed lines demarcate Zone I to IV. Vertical dashed lines demarcate the average seawater compositions.

Table 1: Concentrations and isotope ratios of pore water SO_4^{2-} and total alkalinity (TA) of the core NGHP-01-01A.

Table 2: Total organic carbon content of the core NGHP-01-01A.

Figure 1

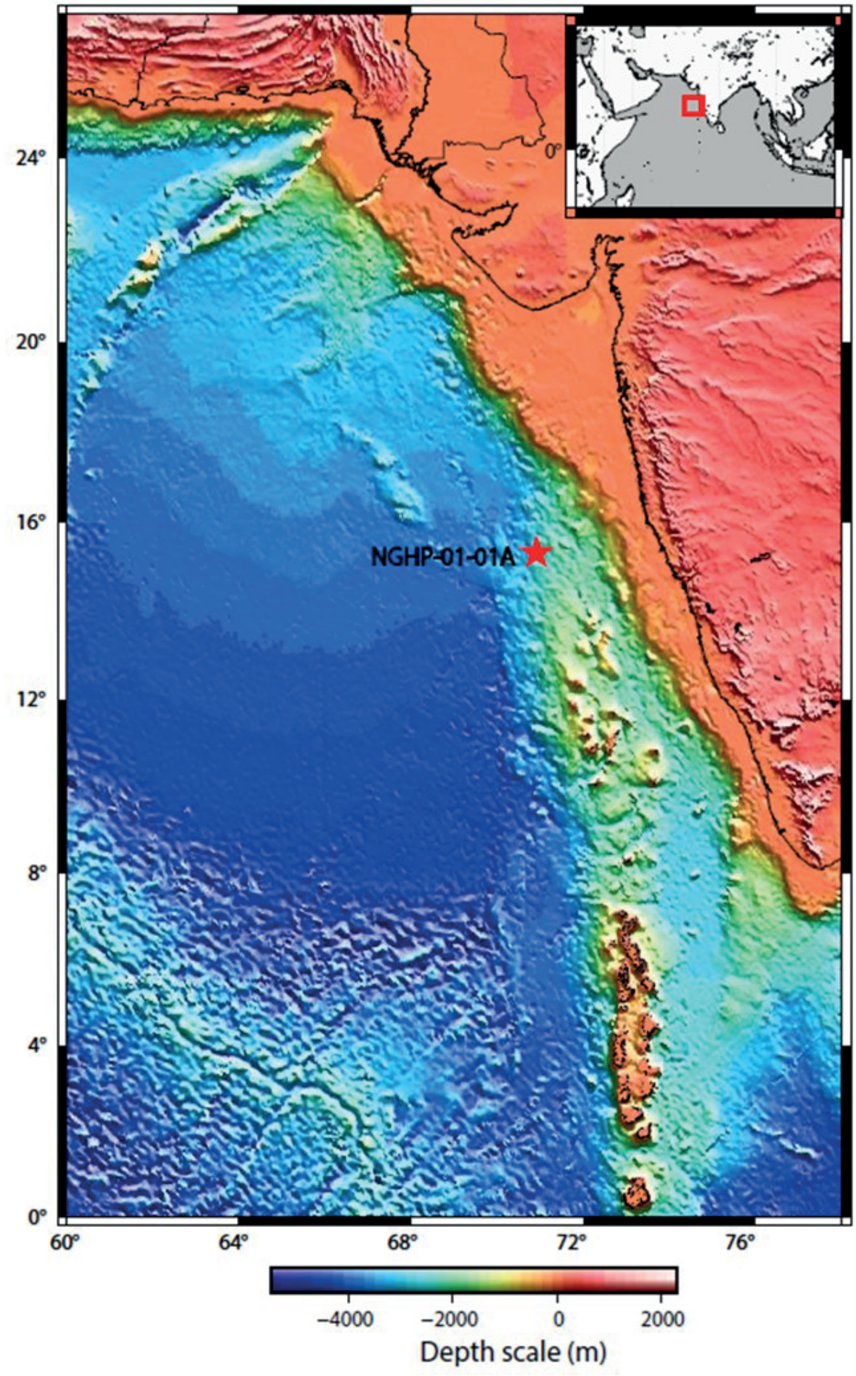
24°
20°
16°
12°
8°
4°
0°
60°
64°
68°
72°
76°
NGHP-01-01A
−4000
−2000
0
2000
Depth scale (m)

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Figure 2

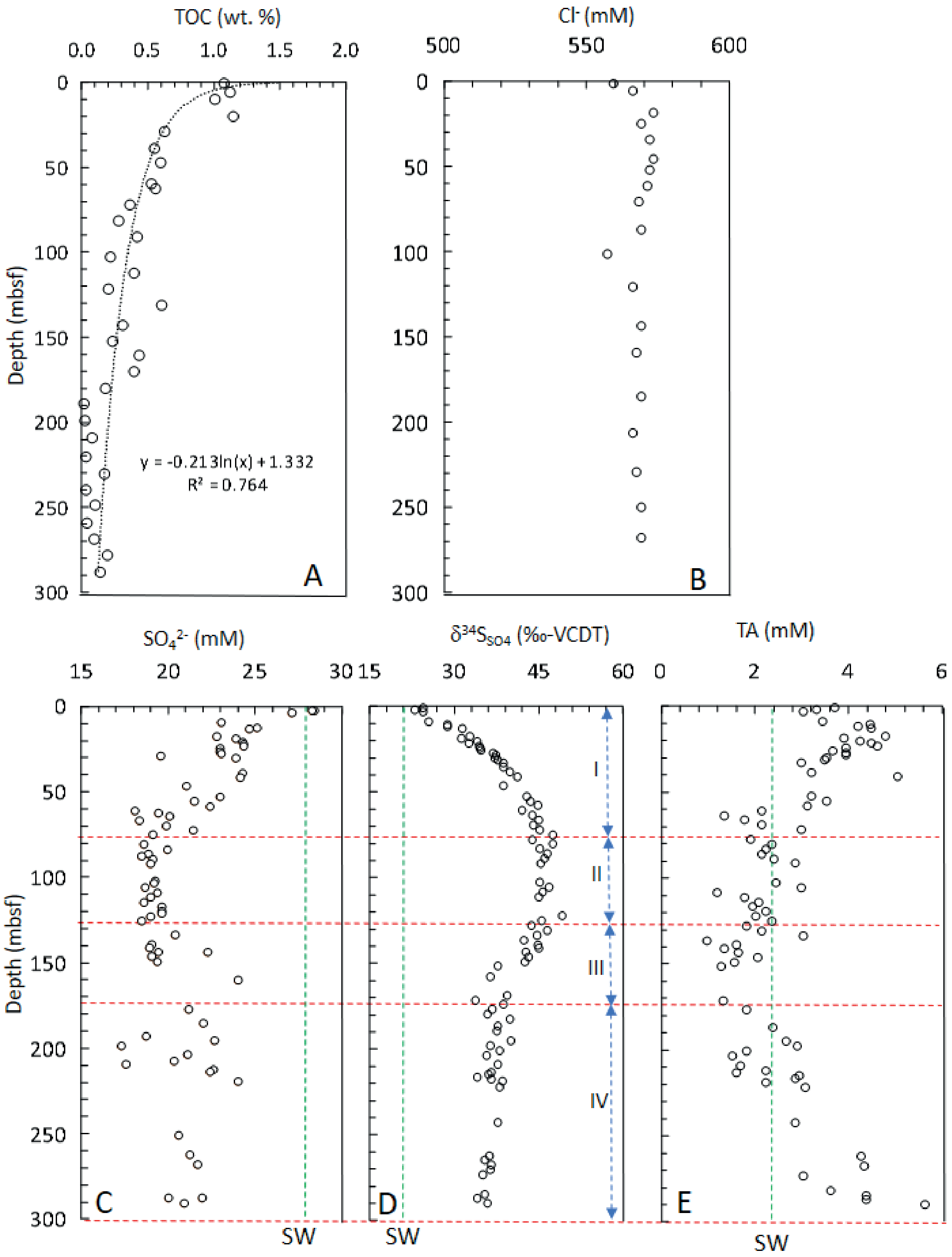

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Table 1

Sl. No	Depth	Sulfate	$\delta^{34}S$	Alkalinity
	(mbsf)	(mM)	(‰-VCDT)	(mM)
1	1.3		24.3	3.7
2	2.4	28.4		
3	2.7	28.3	22.8	3.3
4	4	27.1	24.3	3.0
5	9.7	23.1	25.2	3.4
6	11		28.6	4.4
7	12.4	25.1	28.6	4.2
8	13.4	24.7	31.3	4.5
9	18	22.8	32.5	4.8
10	19.2	23.9	31.1	3.9
11	20.8	24.3	33.9	4.2
12	22.2	24.3	32.5	4.5
13	23.6	24.3	34.2	4.6
14	25	23.0	34.3	3.9
15	26.4	23.0	34.6	3.6
16	27.8	23.1	36.7	3.9
17	29.2	19.5	37.3	3.9
18	30.6	23.9	37.1	3.5
19	32		37.5	3.5
20	33.4		38.5	3.0
21	36.2		38.6	
22	39	24.3	39.7	3.2
23	41.8	24.1	41.1	5.0
24	46.7	21.1	38.6	
25	53	23.0	42.8	3.2
26	55.8	21.5	43.3	3.5
27	58.6	22.4	44.7	3.1
28	61.4	18.1	41.9	2.1

29	62.3	19.4		
30	64.2	20.1	43.7	1.3
31	67	18.3	44.9	1.8
32	69.8	19.9	43.9	2.1
33	72.6	21.4	45.0	3.0
34	75.4	19.1	47.3	
35	78.2		43.7	1.9
36	81	18.6	47.3	2.3
37	83.8	20.0	44.9	2.2
38	86.6	18.9	46.3	2.1
39	87.8	18.5		
40	89.4	19.1	45.9	2.4
41	92.2	19.0	45.1	2.9
42	102.3	19.2		
43	103.4	19.1	45.0	2.4
44	106.2	18.7	46.6	3.0
45	109	19.4	45.5	1.2
46	111.8	19.0	44.9	1.8
47	114.6	18.6		2.1
48	117.4	19.6		1.9
49	120.1	19.6		2.2
50	121.3	19.6		
51	122.9	19.0	48.9	2.0
52	125.7	18.5	45.3	2.3
53	128.5		43.4	1.8
54	131.3		46.3	2.1
55	134.1	20.4	44.5	3.0
56	136.9		42.3	1.0
57	139.7	19.0	44.6	1.6
58	141.7	18.9	44.9	1.3
59	143.9	19.5	42.6	1.6
60	146.7		43.1	2.1
61	144.1	22.3		
62	146.7	19.0		

63	149.5	19.4	42.4	1.5
64	152.3		37.5	1.3
65	158.5		36.2	
66	160.3	24.0		
67	169.1		39.3	
68	171.9		33.5	1.3
69	174.7		38.5	
70	177.5	21.1	36.6	1.8
71	180.3		35.7	
72	183.1		39.8	
73	185.7	22.0		
74	187.3		37.6	2.4
75	190.1		37.4	
76	192.9	18.7		
77	195.7	22.6	39.8	2.6
78	198.5	17.3	36.3	2.9
79	201.3		37.8	1.8
80	204.1	21.1	35.5	1.5
81	207.4	20.3		
82	209.7	17.6	37.6	1.7
83	212.5	22.6		2.2
84	213.9	22.4	36.3	1.6
85	215.3		35.9	2.9
86	217.1		33.8	2.9
87	218.1		36.3	
88	219.5	24.0	38.3	2.2
89	222.7		37.9	3.1
90	243.2		37.5	2.8
91	251.1	20.6		
92	262.8	21.3	36.0	4.3
93	265.1		35.1	
94	268.4	21.7	36.3	4.3
95	271.2		36.2	
96	274		34.9	3.0

97	282.4			3.6
98	285.2		35.3	4.4
99	287.6	20.0		
100	288.0	21.9	33.9	4.4
101	290.8	20.9	35.8	5.6

Table 2

Sr. no	Depth	TOC
	(mbsf)	(wt. %)
1	0.5	1.07
2	5.7	1.12
3	9.8	1.00
4	19.8	1.14
5	29.2	0.62
6	38.7	0.55
7	47.2	0.60
8	59.7	0.53
9	62.7	0.56
10	72.2	0.36
11	81.7	0.28
12	91.2	0.42
13	102.7	0.22
14	112.2	0.39
15	121.7	0.20
16	131.2	0.60
17	142.7	0.31
18	152.2	0.23
19	160.7	0.43
20	170.4	0.39
21	180.1	0.18
22	189.2	0.01
23	199.3	0.02
24	209.4	0.08
25	220.5	0.03
26	230.2	0.17
27	239.8	0.03
28	248.5	0.10
29	259.1	0.04
30	268.8	0.09

31	278.4	0.19
32	288.0	0.14