

Ocean biogeochemistry and atmospheric composition: Significance of the Arabian Sea

S. W. A. Naqvi* and D. A. Jayakumar

National Institute of Oceanography, Dona Paula, Goa 403 004, India

The Arabian Sea is an important site of biogeochemical ocean-atmosphere transfers, which play a crucial role in regulating the atmospheric chemical composition and the earth's climate. Widespread denitrification resulting from an intense oxygen-deficiency at mid-depths in this region modulates oceanic combined nitrogen inventory and consequently biological productivity. Due to a delicate biogeochemical balance the Arabian Sea is expected to be among the first to react to potential anthropogenic perturbations.

Oceanic carbon cycle

THE chemical composition of the earth's atmosphere greatly differs from those of its two immediate neighbouring planets in that while carbon dioxide forms the bulk (> 95%) of the atmospheres of Venus and Mars, nitrogen and oxygen are the two most abundant gases in the earth's atmosphere with CO₂ ranking a poor fifth (0.036%). This is primarily due to the presence of large amounts of *liquid* water on earth, which is the only body in the solar system endowed with this wealth, on account of being of the right size, having the right chemical composition, and located at the right distance from the sun. Because of these favourable conditions life originated and thrived on earth. This, in turn, drastically modified the earth's surface environment, particularly its atmospheric composition which, with the exception of argon, is controlled mainly by biological processes.

It is believed that during the early years of the earth's history, its atmosphere was also predominantly comprised of CO₂, which was produced as a result of oxidation of methane (CH₄) by O₂ generated through photolysis of water vapour. The resultant greenhouse warming probably maintained a very high (90°C) temperature at the earth's surface at that time¹. However, as the liquid water filled the depressions to form primitive oceans, it rapidly sequestered atmospheric CO₂. The property which differentiates CO₂ from most other atmospheric constituents is that it reacts with water to form carbonic acid (H₂CO₃), which undergoes dissociation to yield bicarbonate (HCO₃⁻) and carbonate (CO₃²⁻) ions. This chemical reactivity makes CO₂ highly soluble in water. The dissolved CO₂ facilitates

weathering of rocks. The CO₃²⁻ ions interact with cations, mainly Ca²⁺, to form sparingly-soluble carbonates. The carbonate production can occur both chemically and biochemically. In today's ocean, chemical precipitation is confined to just a few areas such as the Persian Gulf, but early in the earth's history it was an important mechanism that led to a decrease in atmospheric CO₂. The carbonates precipitated chemically on the young earth have since been recycled many times over, and the present carbonate deposits are mainly of biogenic origin¹. Many organisms secrete CaCO₃ to build their hard skeletal parts either in the form of aragonite (e.g. corals) or calcite (e.g. foraminifera). The oceanic surface waters are supersaturated with respect to both these polymorphs, especially in the tropical regions, facilitating biological CaCO₃ production.

The most important pathway through which the biota affects the carbon cycle is the fixation of inorganic carbon by organisms to build soft tissues. This is done by autotrophs, some of which can derive the energy needed for biosynthesis of organic matter through chemical reactions such as sulphide oxidation (chemosynthesis), but most use solar energy trapped with the help of pigments such as chlorophyll (photosynthesis). The annual rate of photosynthetic (primary) production on earth is estimated to be about 230 Tg C y⁻¹ (1 Tg = 10¹² g); of this the oceanic contribution is about 60 Tg C y⁻¹ (ref. 2). Most of the photosynthetic production in the sea is carried out by tiny organisms known as phytoplankton within the upper 100 m or so of the water column which is illuminated by sunlight. The phytoplanktons require some trace elements (nutrients) such as nitrogen and phosphorus for their growth, and the biological uptake leads to decreases in nutrient concentrations in surface waters. While most of the organic matter thus produced gets recycled in the surface layer, a significant fraction escapes to the deep sea through sedimentation where it is decomposed by bacteria. This process results in the consumption of O₂ and regeneration of carbon (as CO₂) and nutrients [as nitrate (NO₃⁻) and phosphate (PO₄³⁻)]. Thus, photosynthesis and respiration cause depthwise fractionation of nutrients, i.e. their near-surface depletion and deep-water enrichment. These gradients are maintained because the oceans are not well-mixed vertically, but are generally stratified. The stratification is most pronounced in the tropics where strong solar heating results in the generation of a well-mixed surface layer which is a few tens of metres thick. Below the mixed layer, temperature decreases rapidly

*For correspondence (e-mail: naqvi@csnio.res.nic.in)

with the zone of sharp temperature and consequently density gradients, known as the thermocline, inhibiting mixing between the surface and deep waters. It is only in the areas where the subsurface waters are brought up close to the surface through divergence of currents (upwelling), or where the thermocline is weakened by vertical mixing, the euphotic zone gets adequate supply of nutrients; such areas are biologically most productive.

Since the 'biological pump' involves continuous export of carbon from the surface to subsurface waters, it makes the deep sea the repository of the bulk (> 90%) of the carbon in the biosphere-atmosphere-hydrosphere system. However, as CO_2 is dissolved in sea water in very high concentrations (> 2 mM), the decrease in total dissolved inorganic carbon (DIC or ΣCO_2) in the surface layer relative to the deep sea is no more than 20% (Figure 1). On

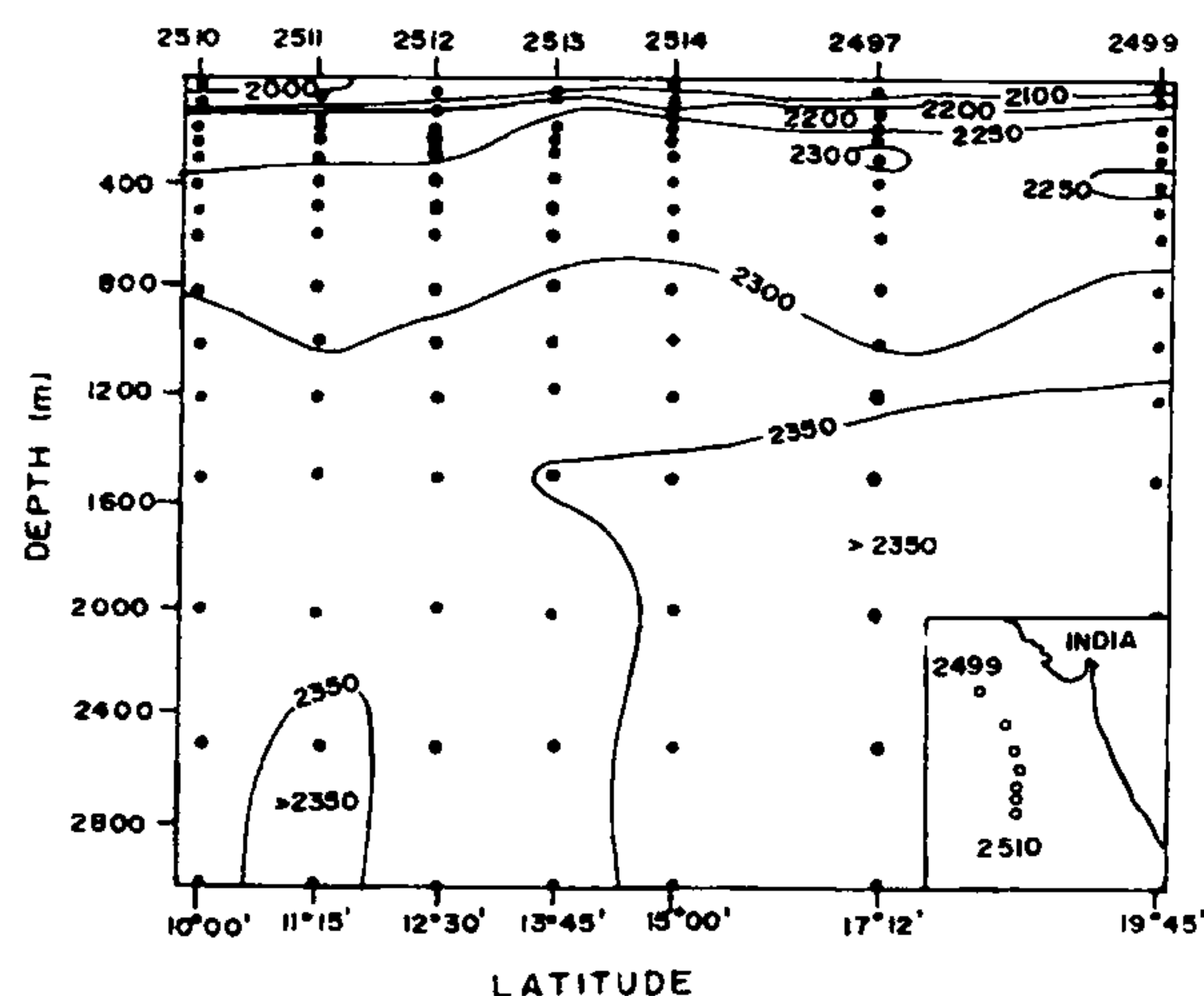


Figure 1. Vertical (north-south) section of ΣCO_2 (μM) in the Arabian Sea. Station locations are shown in the inset (from George *et al.*⁸).

the other hand, biological activity plays a more important role in regulating the speciation of DIC, which is strongly dependent on pH. In the pH range normally encountered in oceanic surface waters, HCO_3^- is the predominant species (90%); only about 1% of ΣCO_2 is present in the aqueous or hydrated form [$\text{CO}_2(\text{aq})$ and H_2CO_3] with the rest occurring as CO_3^{2-} . It is only the 'free' (unionized) form which can be exchanged with the atmosphere; its concentration is represented as $p\text{CO}_2$, the equilibrium partial pressure of CO_2 . It is this parameter which determines the direction, and in part the magnitude, of the air-sea CO_2 flux. The oceanic surface waters normally have $p\text{CO}_2$ values very close to that in the atmosphere (currently $\sim 360 \mu\text{atm}$). If $p\text{CO}_2$ in water is higher than this value, there is a net emission of CO_2 from water and vice versa. Both the physical and biological processes affect $p\text{CO}_2$. The cooling and deep-water formation at high latitudes result in lowering of surface water $p\text{CO}_2$ through an increase in CO_2 solubility and changes in H_2CO_3 dissociation constants; such areas serve as important sites of CO_2 removal from the atmosphere. Conversely, oceanic areas of divergence, such as the eastern boundary upwelling zones and the equatorial Pacific are principal sites of CO_2 efflux from the ocean (Figure 2)³. The net global air-sea flux of CO_2 is directed into the oceans, and it is estimated that the oceans are currently removing about 2000 Tg of $\text{CO}_2\text{-C}$ annually, which is about 25% of the rate at which CO_2 is being added to the atmosphere due to human activities (mainly fossil fuel combustion and deforestation)⁴.

The uptake of CO_2 for building soft tissues as well as hard skeletons affects the pH and alkalinity of sea water. Due to the acidic character of CO_2 , respiration and photosynthesis cause a decrease and an increase of sea water pH, respectively. The relatively high pH of oceanic surface waters keeps $p\text{CO}_2$ at moderately low levels (Figure 3). This is largely responsible for maintaining low

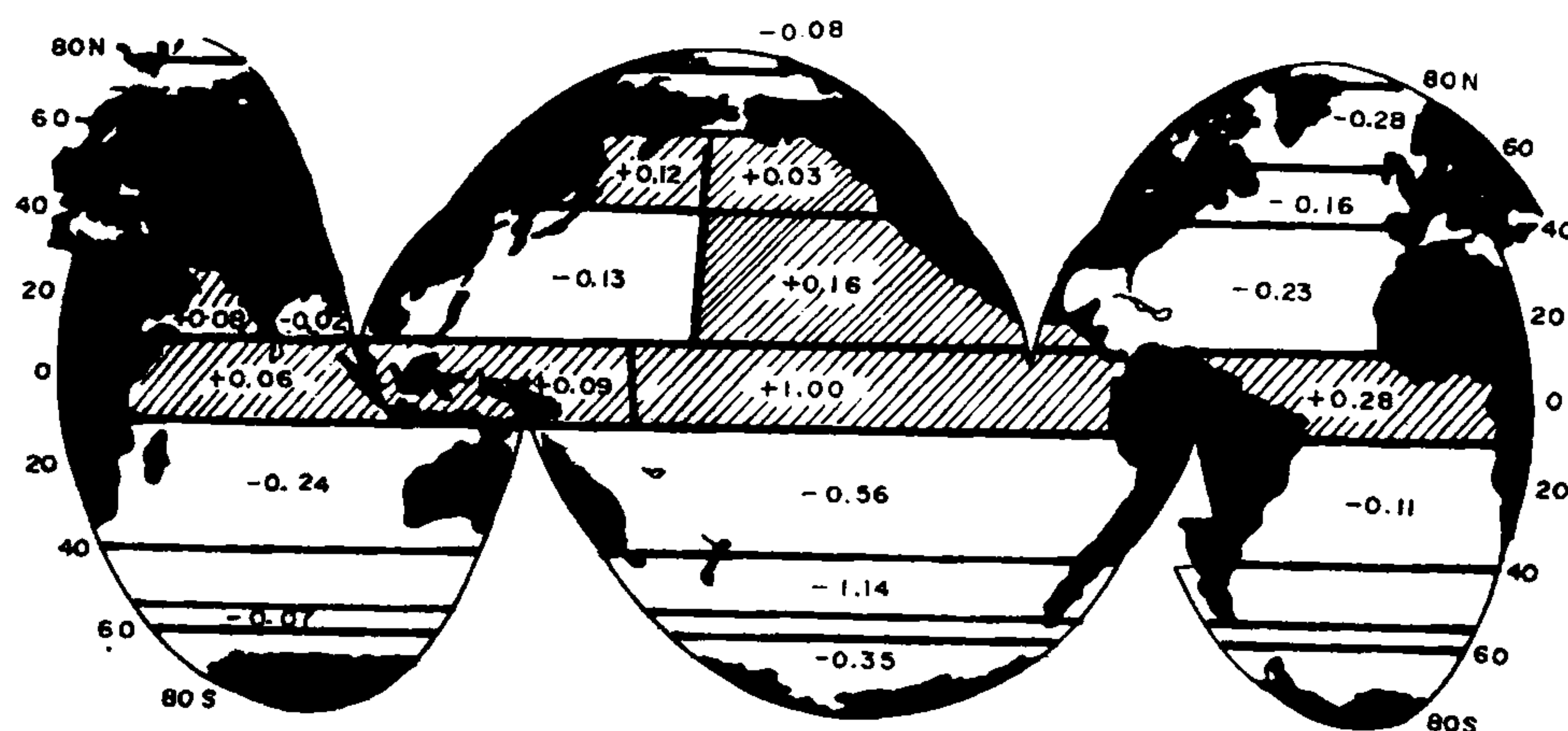


Figure 2. The mean annual net CO_2 exchange across the air-sea interface. Positive (negative) numbers within shaded (unshaded) areas indicate sea to air (air to sea) fluxes in Gg C y^{-1} (modified from Takahashi³).

levels of CO_2 in the atmosphere; in the absence of this mechanism the atmospheric CO_2 content would have been several-fold higher and consequently the earth would have been much warmer. Conversely, the high pCO_2 values in subsurface waters (particularly at intermediate depths) are the consequence of respiration. The production and dissolution of CaCO_3 , on the other hand, have opposite effects on pCO_2 – biological secretion of CaCO_3 in surface waters leads to an increase in pCO_2 . Fortunately, on an average, for each atom of carbon fixed into skeletal carbonate, about 4 atoms of carbon are utilized to build the soft tissue⁵, and so the biological activity results in a net decrease in pCO_2 at the sea surface.

As stated above, most of the removal of atmospheric CO_2 through the solubility pump occurs in the temperate or polar seas where dense surface waters sink and flow into the deep basins of all the oceans. Although the biological pump operates in all areas, the rate at which it removes CO_2 from surface waters varies a great deal due to the large geographical changes in biological productivity. Obviously the rate of biological removal should be the highest in regions of high biological production. However, the high biological production is itself sustained by upwelling and vertical mixing which tend to increase pCO_2 in surface waters, and so whether or not a given region serves as a net source or a net sink of atmospheric CO_2 depends upon the balance between the two opposing processes. In most cases the biochemical decrease of pCO_2 is overwhelmed by the physicochemical increase. The north-western Indian Ocean is one such area. It houses three centres located off Somalia, Arabia and south-west India where vigorous upwelling occurs during the south-west monsoon, making this region highly productive.

However, because of the high pCO_2 in the upwelled water the surface water pCO_2 levels are invariably higher than those in the atmosphere. In fact, the pCO_2 in the upwelling zones of this region is among the highest observed in the oceans. For example, values as high as $\sim 700 \mu\text{atm}$ have been recorded in the upwelling zone off south-west India. However, as upwelling is a spatially-confined, seasonal phenomenon, the distribution of pCO_2 shows large variability in both space and time^{6,7}. The seasonally-changing atmospheric circulation also brings about significant changes in the atmospheric pCO_2 over the Arabian Sea⁷. The highest pCO_2 values in water observed during the south-west monsoon are associated with low pCO_2 in the atmosphere, and since the winds are also the strongest during this season (which enhances the air-sea gas exchange), maximal emission of CO_2 from the Arabian Sea occurs during this season⁷. On an annual basis the emission rate of CO_2 from the Arabian Sea has been estimated as 79 Tg (ref. 8). Although this value is an order of magnitude lower than the flux from the equatorial Pacific³, the single largest source of atmospheric CO_2 , and consequently globally not so significant, the important point is that this is maintained in spite of a high rate of photosynthetic carbon fixation in the region.

Role of nitrogen

The Arabian Sea plays a more important role in regulating the atmospheric composition through controls on global nitrogen budget. Among the nutrient elements essential for the growth of plants, nitrogen is perhaps the most important. Although it is the most abundant constituent of the atmosphere, occurring predominantly as N_2 , this form of nitrogen is chemically inert, and only a few organisms have the capability to utilize or 'fix' it as such. Most organisms can only use nitrogen in 'combined' forms such as NO_3^- and ammonium (NH_4^+) which are less abundant in nature but are more easily assimilated. The availability of such forms often limits photosynthesis in the marine environment⁹.

The inventory of combined nitrogen in oceans is regulated by several processes. Inputs of nitrogen occur mainly through river runoff, atmospheric deposition and nitrogen fixation, while its loss is principally through conversion of the combined nitrogen to N_2 . This process, known as denitrification, takes place when the ambient O_2 concentrations are close to zero and bacteria begin to utilize NO_3^- instead of O_2 as an oxidant for decomposing organic debris¹⁰. Conditions favourable for denitrification commonly develop within sediments of shallow seas. In the water column, however, oceanic currents supply enough O_2 at all depths to prevent the development of anoxic conditions in most oceanic areas. However, there are three regions where unusual oceanographic processes cause the O_2 demand to exceed its supply leading to an almost

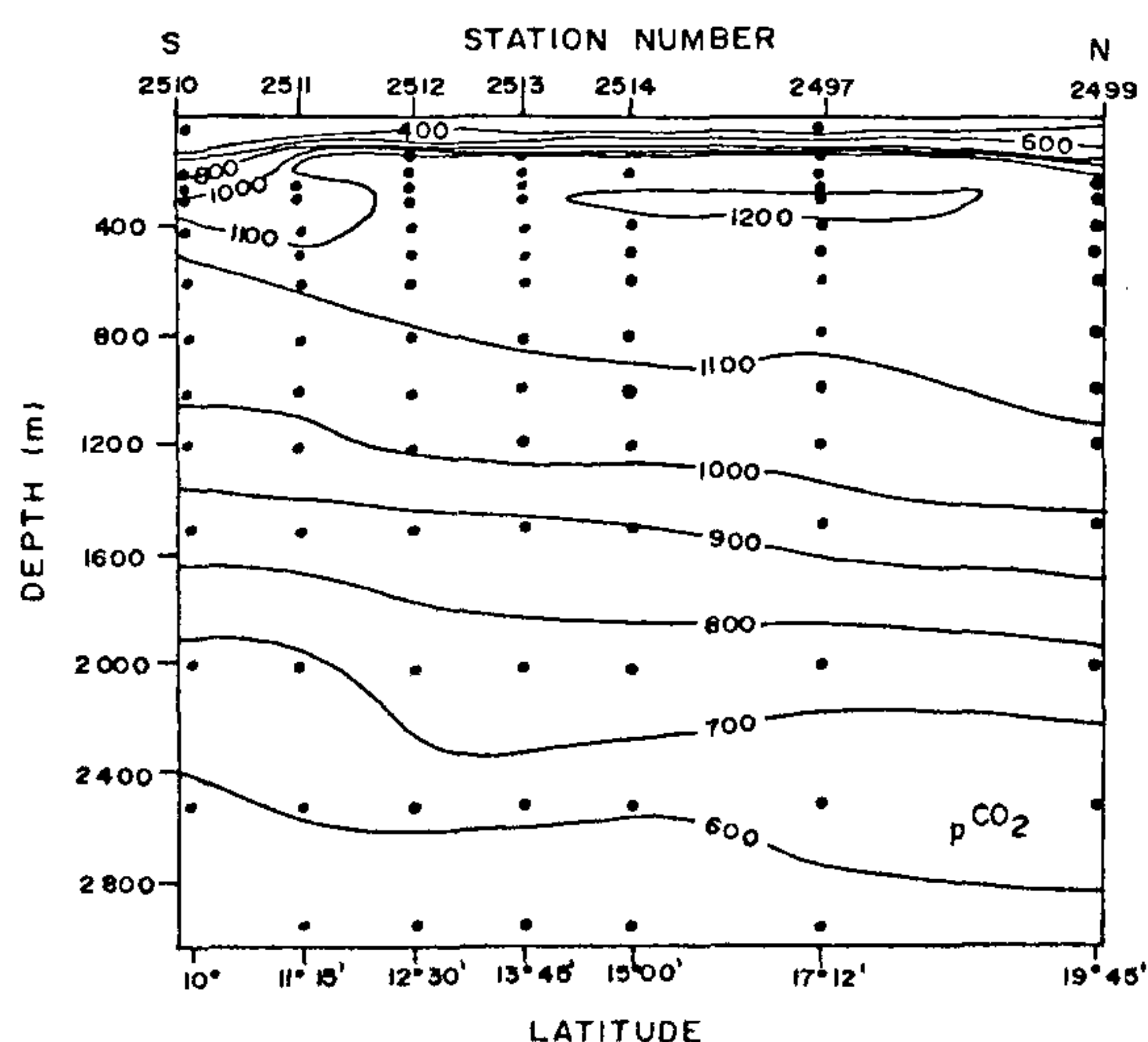


Figure 3. Vertical (north-south) section of pCO_2 (μatm) in the Arabian Sea. Station locations are shown in the inset of Figure 1 (from George *et al.*⁸).

complete O_2 depletion at mid-depths. Two of these sites are located in the eastern Pacific – one on each side of the equator – while the third is found in the northern Indian Ocean, particularly in the Arabian Sea. Although these regions account for < 2% of the total oceanic area, they make disproportionately large contribution to global biogeochemical cycles. This is because N_2 produced during denitrification makes up for the inputs of combined nitrogen from various sources. In the absence of this process, the atmospheric N_2 would be depleted in a few tens of million years. In fact, the most recent estimate of various source and sink terms of the combined nitrogen budget (Table 1)¹¹ indicates that the loss of N_2 through denitrification may actually exceed the net inputs by a substantial margin. The magnitude of imbalance is such that it would lead to a complete removal of combined nitrogen from oceans in a few tens of thousand years. Obviously such a state cannot persist over a long period of time, and the only way the atmospheric N_2 content and oceanic combined nitrogen inventory could have remained constant over geological time scales is that there should be times when the balance is the other way around. In other words, the oceans may alternately serve as a net source and a net sink of combined nitrogen depending on the relative rates of nitrogen fixation and denitrification⁹. Such fluctuations in oceanic combined nitrogen budget have the potential to substantially alter the combined nitrogen inventory on time scales of hundreds to thousands of years. Since nitrogen is the principal limiting nutrient, and the C : N ratio during phytoplankton uptake is high (6.6 by atoms), such changes in the oceanic combined nitrogen inventory can bring about large variations in biological productivity and hence in the rate at which CO_2 is removed from the atmosphere; this in turn can force climate changes¹². How the balance is achieved on geological time scales is an important problem that is currently attracting the attention of biogeochemists the

world over, and it is in this context that areas such as the Arabian Sea assume a lot of importance.

Oxygen-deficiency and denitrification

The mid-depth O_2 deficiency in the Arabian Sea is perhaps the most severe observed anywhere in oceans, as the concentrations within ~ 150–1000 m are less than 0.1 ml/l (4 μM) within a large part of the central and north-eastern Arabian Sea (Figure 4). This deficiency is caused by a high subsurface O_2 demand arising from high surface productivity coupled with low O_2 content of water flowing into the Arabian Sea from the south¹³. Vigorous denitrification, however, does not occur within the entire oxygen minimum zone (OMZ) as evident from the distribution of nitrite (NO_2^-), the first intermediate of the reduction sequence, that accumulates in the water column to produce what is often referred to as the secondary nitrite maximum (SNM). This feature, which is associated with pronounced deficiencies in NO_3^- , develops only when the O_2 levels fall below 0.015–0.02 ml/l (Figure 5). Such a strong dependence of redox processes on minor changes in ambient O_2 levels implies an extremely sensitive ecosystem with a delicately poised biogeochemical balance which is expected to react rapidly to anthropogenic perturbations.

An anomalous feature of the Arabian Sea OMZ is that the zones of the highest primary production and the most vigorous denitrification are geographically separated here¹⁴. This is demonstrated by both chemical and biochemical data. For example, the highest NO_2^- and lowest NO_3^- concentrations as well as the highest electron transport system (ETS) activities are observed not beneath the biologically productive surface waters close to the continental margin but in the oligotrophic central Arabian

Table 1. Oceanic combined nitrogen budget ($Tg\ N\ y^{-1}$) (from Codispoti *et al.*¹¹)

Inputs	
Riverine	45
Groundwater	10
Atmospheric (DON + DIN)	100
Nitrogen fixation	150
Total	305
Sinks	
Water column denitrification	110
Sedimentary denitrification	255
Burial	35
Export of organic N	16
Inorganic loss to atmosphere	13
N_2O loss to atmosphere	7
Total	436
Deficit	131

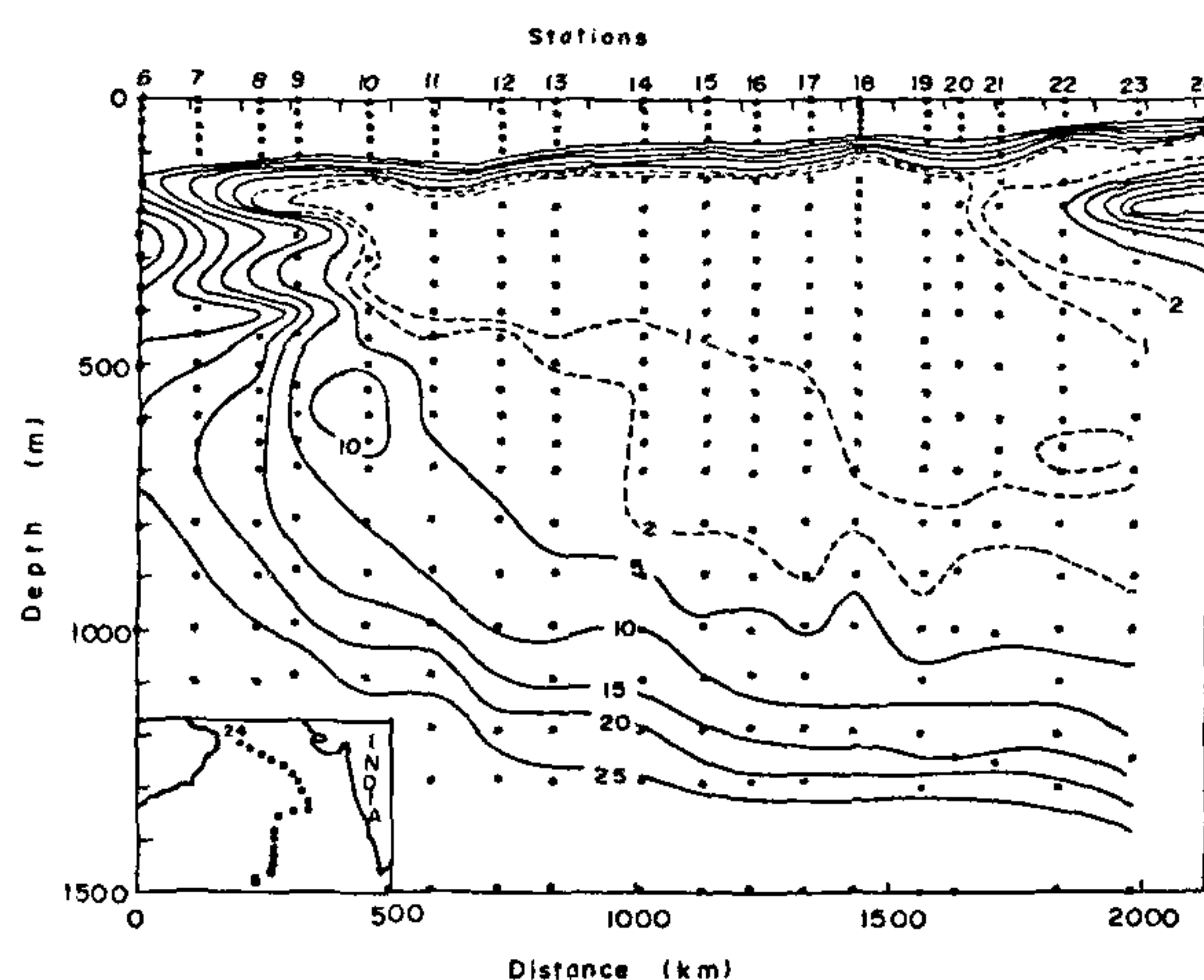


Figure 4. Vertical (north-south) section of dissolved O_2 (μM) in the Arabian Sea. Locations of stations worked during the US JGOFS (R.V. Thompson Cruise 39) are shown in the inset. O_2 concentrations above 25 μM are not shown.

Sea^{14,15}. Another unexpected result is that the ETS-based respiration rates are about an order of magnitude higher than the sinking flux of particulate organic carbon from the surface layer as measured by drifting sediment traps or estimated from global relationships between primary production and sinking carbon fluxes^{15,16}. Moreover, the rates in the suboxic waters are higher than those in the overlying and underlying oxic parts of the water column; in fact, the former are so high and the bacteria that carry out degradation proliferate to such an extent that there is a marked increase in water turbidity within the denitrifying zone (Figure 6)¹⁶. It is still not clear as to what produces this bacterial biomass maximum under energetically less favourable conditions and, given the apparent inadequacy of the sinking flux to meet the observed respiration rates, what is the additional mode of organic carbon input to the denitrifying layer. Two possible explanations have been offered: (a) Denitrifiers may efficiently utilize the dissolved organic matter supplied to the OMZ^{15,16} either quasi-horizontally from the continental margins or vertically through diurnal migrations of organisms particularly the mesopelagic fish such as myctophids¹⁷. Significantly, the Arabian Sea contains huge stocks (~ 100 million tonnes) of myctophids which are specially adapted to low (< 0.1 ml l⁻¹) ambient O₂ levels¹⁸. The presence of these

organisms is evident from the acoustic data (Figure 7)¹⁹ although how such a large biomass is sustained is another major question concerning the Arabian Sea biogeochemistry that is yet to be satisfactorily answered. (b) There may be an additional carbon pool in the form of transparent exopolymer particles (TEP) that could be formed from extracellular metabolites²⁰. The TEP levels within the OMZ are apparently more than enough to support the bacterial activities. The relative importance of the above processes in maintaining high metabolic rates and the consequent reducing environment remains to be assessed.

The rate of denitrification in the Arabian Sea has been quantified following physico-chemical and biochemical techniques. In the first approach, deficiencies in NO₃⁻ relative to the concentration expected from correlations with some other chemical tracers (such as O₂) are estimated, and these 'nitrate deficits' (cf. Figure 5) are combined with dynamic computations and suitable diffusion coefficients to work out the rate at which the deficits are exported out of the reducing zone through advection and mixing¹³. Assuming a steady state, this should be the same as the rate at which the deficits are produced. In the biochemical method, the denitrification rate is obtained from the ETS activity using suitable conversion factors¹⁵. In spite of the differences between the two methods and the uncertainties inherent in them, they have yielded remarkably similar estimates of denitrification rate – around 30 Tg N y⁻¹. This is about one-third the estimated global water column denitrification rate¹³, and its significance could be gauged from the fact that this rate can alter the total inventory of marine combined nitrogen by 0.5% in just a hundred years.

As mentioned above, in view of the extreme sensitivity of denitrification to small changes in ambient O₂ concentrations, large variability in its rate may be expected on a

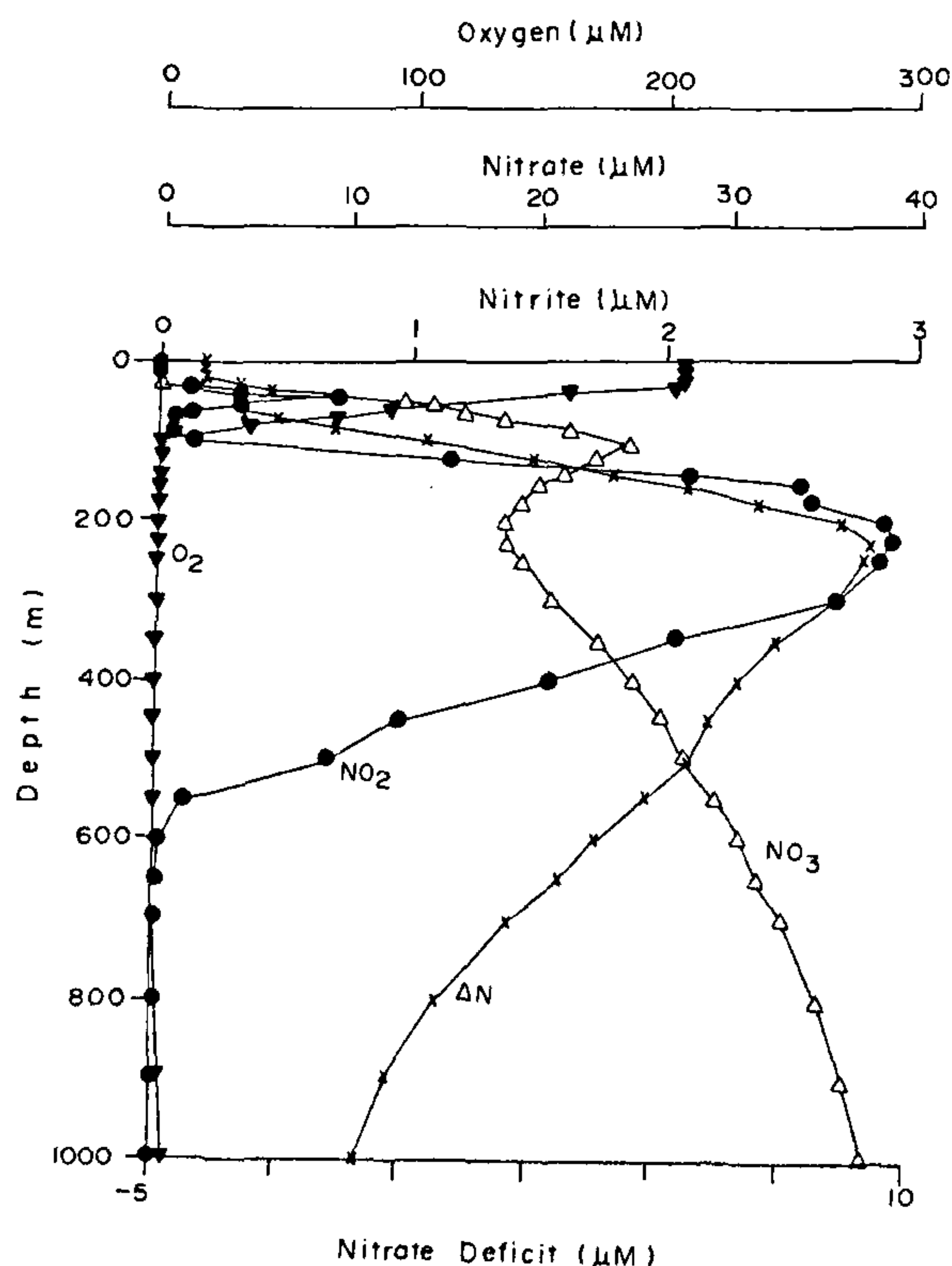


Figure 5. Vertical profiles of O₂, NO₂, NO₃ and NO₃ deficit at the US JGOFS Station N7 (19°N, 67°E, R.V. Thompson Cruise 39).

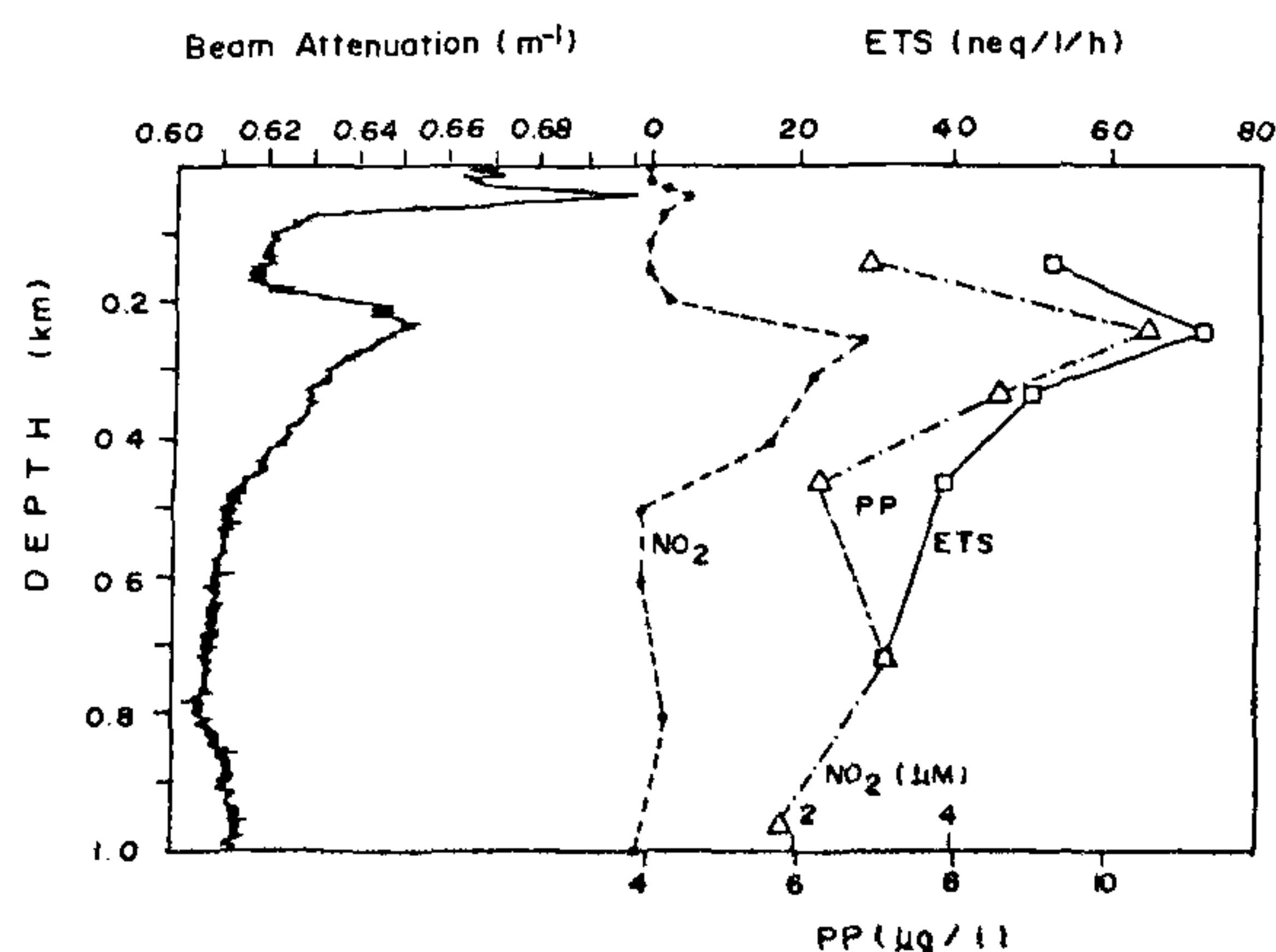


Figure 6. Vertical profiles of NO₂, ETS activity and particulate protein (PP) in relation to beam attenuation at Station SS 2496 (17°30'N, 67°30'E) (from Naqvi *et al.*¹⁶).

variety of time scales. Long-term trends in denitrification could be reconstructed utilizing the sedimentary record of nitrogen isotopes. This approach is based on the principle that various biologically-mediated processes involve mass-dependent fractionation of isotopes as a result of which the lighter isotopes are generally consumed preferentially and the residual reactants are enriched with heavier isotopes. For example, of the two natural isotopes of nitrogen with mass numbers of 14 and 15 (^{14}N and ^{15}N), NO_3^- containing ^{14}N is lost more easily than that containing ^{15}N during denitrification. Consequently N_2 , the end product of denitrification, gets depleted with ^{15}N while an enrichment of this isotope takes place in the residual NO_3^- (Figure 8). These data have been used to calculate the isotopic fractionation factor (ϵ) during denitrification from simple advection-reaction and diffusion-reaction models, yielding ϵ values of 22 and 25‰, respectively²¹. These estimates are similar to those computed for the eastern tropical Pacific Ocean indicating that the fraction factor may be independent of denitrification rate and local hydrography of the region.

In view of the large enrichment of ^{15}N in NO_3^- within the denitrifying layer, it is expected that the nitrogen incorporated in organic matter produced in the surface water overlying the reducing zones would be enriched with this isotope. Measurement of nitrogen isotope abundance in sinking matter collected by sediment traps and in the surficial sediments of the Arabian Sea provides obser-

vational support for this hypothesis (Table 2)²² – in both cases the $\delta^{15}\text{N}$ (a measure of the $^{15}\text{N}/^{14}\text{N}$ ratio) of organic nitrogen is much higher in the denitrifying Arabian Sea than the non-denitrifying Bay of Bengal. This property could thus be utilized to reconstruct past changes in the extent of denitrification.

A record of $\delta^{15}\text{N}$ covering the past 450,000 years has been generated by Altabet *et al.*²³ from a deep sea core raised from the western Arabian Sea (Figure 9). The modern or core-top $\delta^{15}\text{N}$ values are among the highest observed in the core indicating that denitrification in the Arabian Sea has been the most intense during the Holocene. By contrast, lighter isotopic values occur in sediments that accumulated during the last glacial maximum (approximately 20,000 years ago) and indeed during all glacial stages. These values are typical of non-reducing environments in today's ocean. This implies that the water column denitrification was either absent or it was much weaker during glacial times. Incidentally, the glacial stages were also characterized by lower CO_2 partial pressures in the atmosphere as revealed by the analysis of gases trapped in polar ice²⁴. A spectral analysis of the record showed a high degree of cyclicity associated with frequencies of the three Milankowitch bands of 100,000, 41,000 and 23,000 years. The association with the 23,000 year precessional band which dominantly regulates the monsoon strength is particularly strong. Thus the sedimentary record supports the view that large climatic changes in denitrification

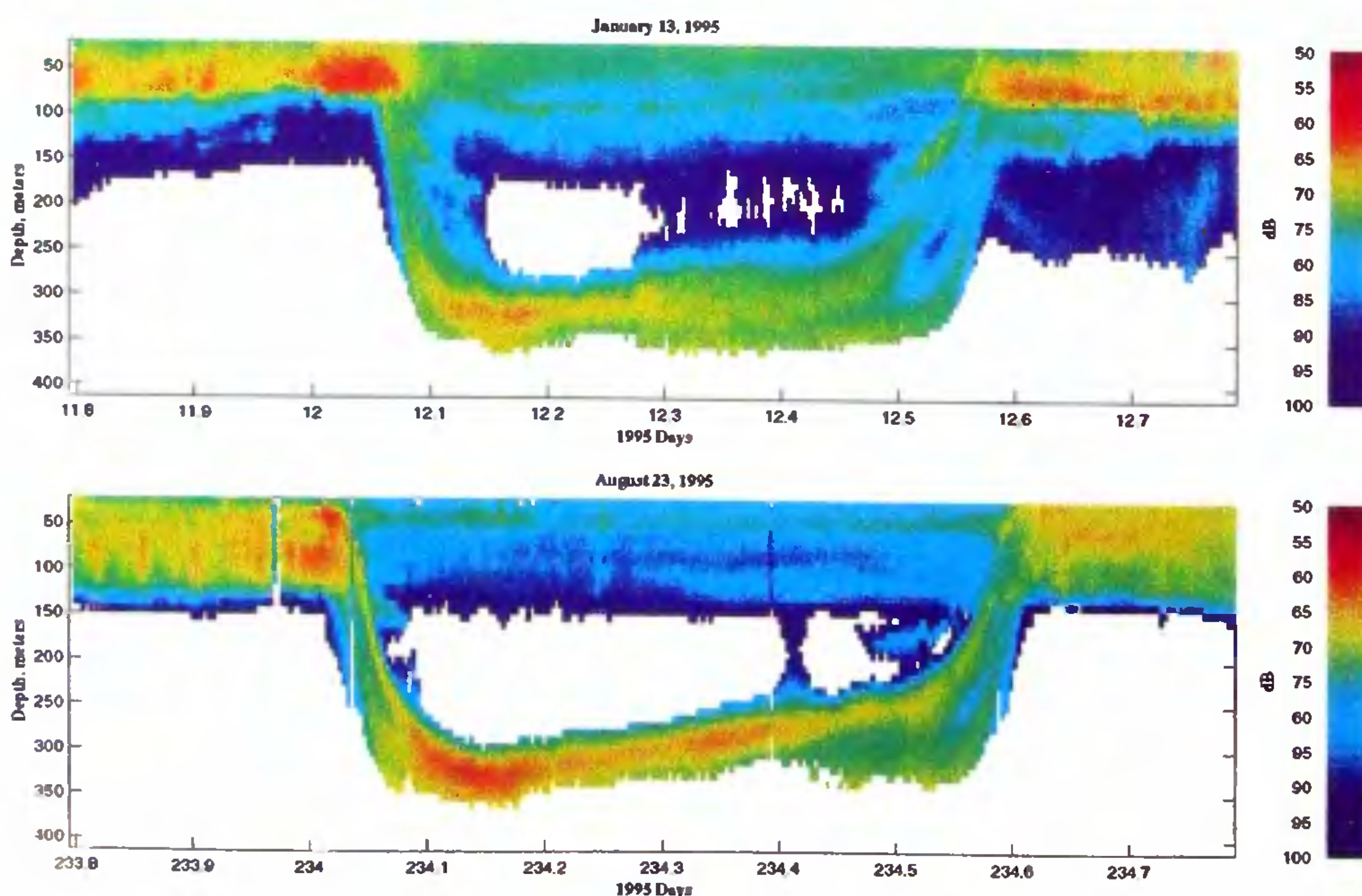


Figure 7. Acoustic backscatter for 24 h around US JGOFS Station N7 indicating diurnal migration of organisms (mostly myctophids) (from Morrison *et al.*¹⁹).

intensity were associated with climatic cycles resulting in cyclic fluctuations in the oceanic combined nitrogen balance. The latter are not only necessary for keeping the oceanic combined nitrogen inventory constant over extended time periods but probably also played an important role in modulating climatic cycles through controls on atmospheric CO₂ (refs 12, 23, 25).

Nitrous oxide cycling

Apart from nitrogen fixation and denitrification, the other important term in the nitrogen budget to which contribution from the Arabian Sea is very significant is N₂O efflux to the atmosphere. N₂O is not only an important greenhouse gas, but it also contributes to the stratospheric ozone depletion. The rate of N₂O loss in the stratosphere through photolysis and reaction with the excited atomic

oxygen [O(¹D)], which should be equal to the natural flux of N₂O to the atmosphere from all sources, is about 12 Tg N₂O-N y⁻¹ (ref. 26). Of this at least half seems to come from the oceans²⁷. But the N₂O efflux is not uniformly distributed over the oceanic surface with the eastern boundary environments underlain by low-O₂ waters making disproportionately large contributions²⁸. Measurements of N₂O in the upwelling zones off Oman²⁹ and Somalia³⁰ have revealed large surface saturations (up to 230 and 330%, respectively), indicating that the annual flux of N₂O from the Arabian Sea alone may be as much as 0.5–1 Tg N y⁻¹. More recent observations in the lesser-known third upwelling centre (off SW India) yielded more extreme data: at 23 stations (Lat. 8.58–11.85°N, Long. 74.34–76.32°E) sampled during the SW monsoon of 1995, surface concentrations and saturations were 11.2–62.5 nM (mean ± SD = 28.5 ± 14.7) and 193–953% (458 ± 223), respectively³¹. These values, among the highest observed in oceanic surface waters, were associated with low sea surface temperatures (minimum 22.8°C) and high NO₃⁻ (maximum 16 µM) indicating intense upwelling. The accumulation of N₂O in very high concentration in areas such as the Arabian Sea is because its cycling is greatly affected by ambient O₂ levels in the low range (< 0.5 ml l⁻¹). While its concentration peaks as the O₂ levels approach but do not reach suboxia, in strongly reducing environments such as those found within the core of the denitrifying zone, N₂O itself is reduced to N₂ by bacteria²⁸. Thus, the vertical profiles of N₂O in the Arabian Sea exhibit two maxima separated by a minimum; the minimum coincides with the secondary nitrite maximum while the maxima are located at the peripheries of this feature (Figure 10)³². Since the upper N₂O maximum is located just below the surface mixed layer, it sustains fairly large inputs of N₂O to the surface layer, in turn supporting a large atmospheric flux from this region^{32,33}. The occurrence of intense sources and sinks in close proximity of each other is expected to lead to a turnover rate which may be the most rapid on our planet^{31,32}.

The cause of the unusually large N₂O buildup in oceanic OMZs is still not fully understood. This is because

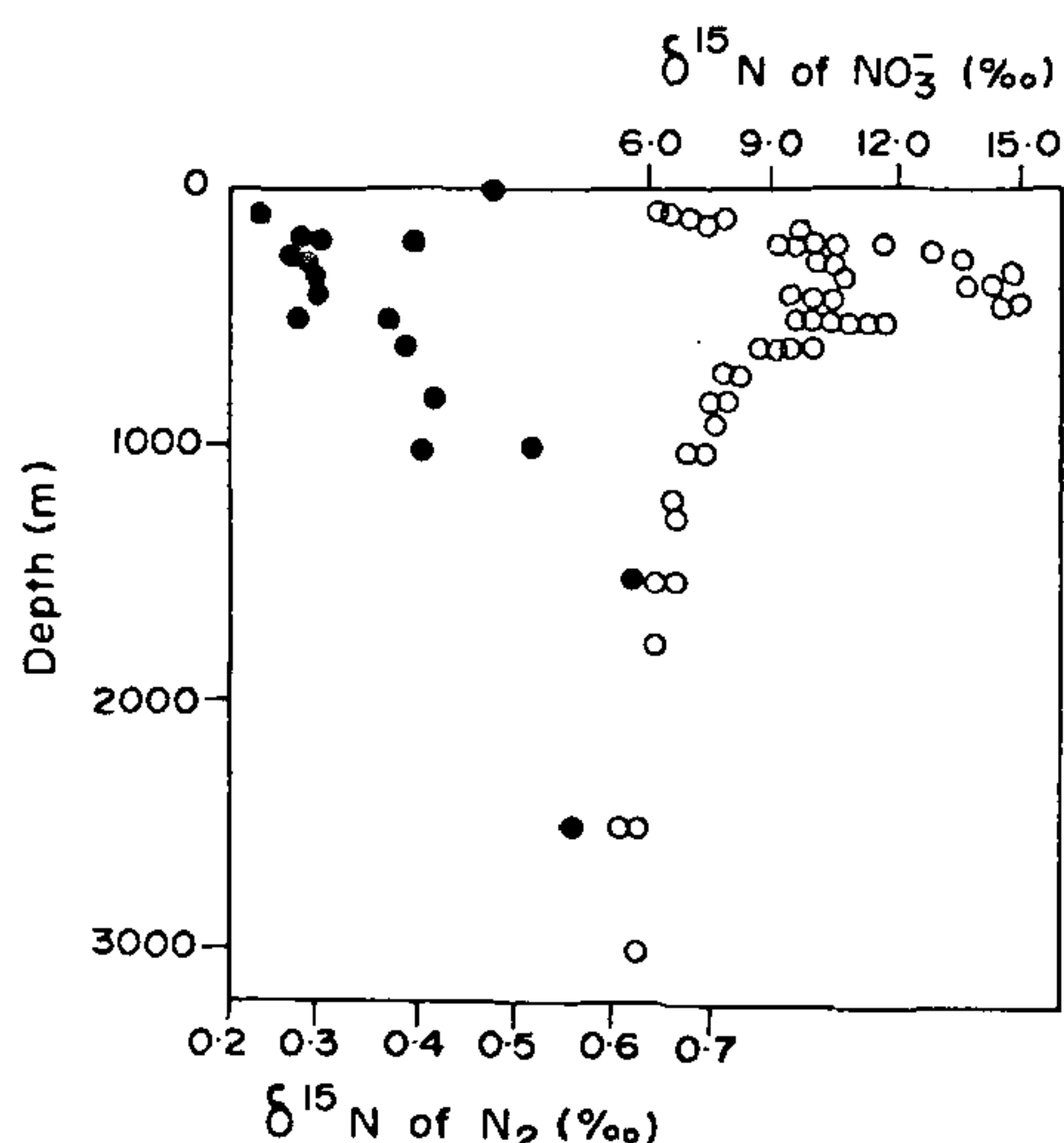


Figure 8. Nitrogen isotopic composition (expressed as ‰ δ¹⁵N relative to atmospheric N₂) of NO₃⁻ (solid circles) and N₂ (open circles) plotted vs depth in the Arabian Sea suboxic zone (from Brandes *et al.*²¹).

Table 2. ¹⁵N/¹⁴N ratio in sinking organic matter (from Schafer and Ittekkot²²)

Site	Depth (m)	$\delta^{15}\text{N}$ settling particles (‰)		$\delta^{15}\text{N}$ sediment (‰)
		Range	Mean	
<i>Bay of Bengal</i>				
Northern	1700–2100	3.0–4.6	3.5	7.4
Central	2300	2.0–6.2	4.2	7.7
Southern	3000	3.8–5.9		
<i>Arabian Sea</i>				
Western	3000	5.3–8.8	7.1	9.2
Central	2900–3100	6.3–8.7	7.4	11.0
Eastern	2800–2900	4.7–8.0	5.9	9.7
Lofoten Basin	3000	2.7–8.8	4.2	
Sargasso Sea	3200	0.1–2.8	1.2	

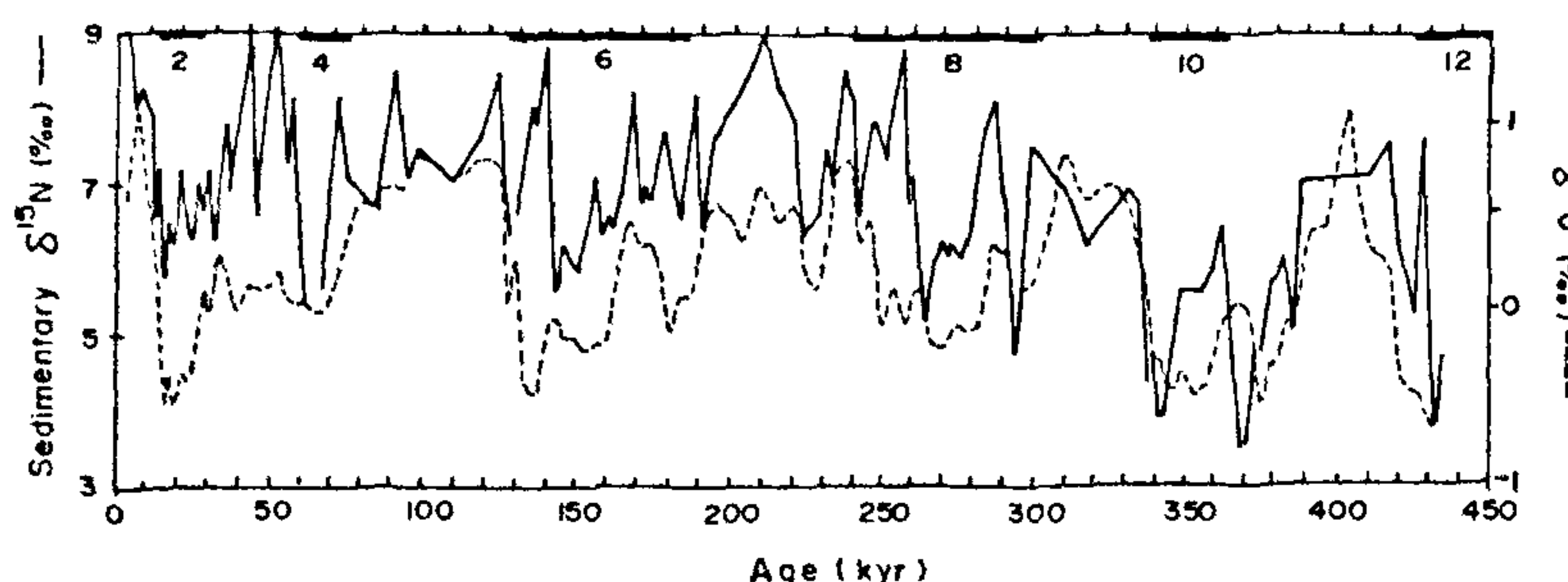


Figure 9. Downcore profiles of isotopic compositions of nitrogen in organic matter and oxygen in the shells of planktonic foraminifera in RC27-61 raised from the Owen Ridge (16°39.5'N, 59°31.4'E). Solid bars at the top of the figure marked by even numbers represent cold oxygen isotope stages (modified from Altabet *et al.*²³).

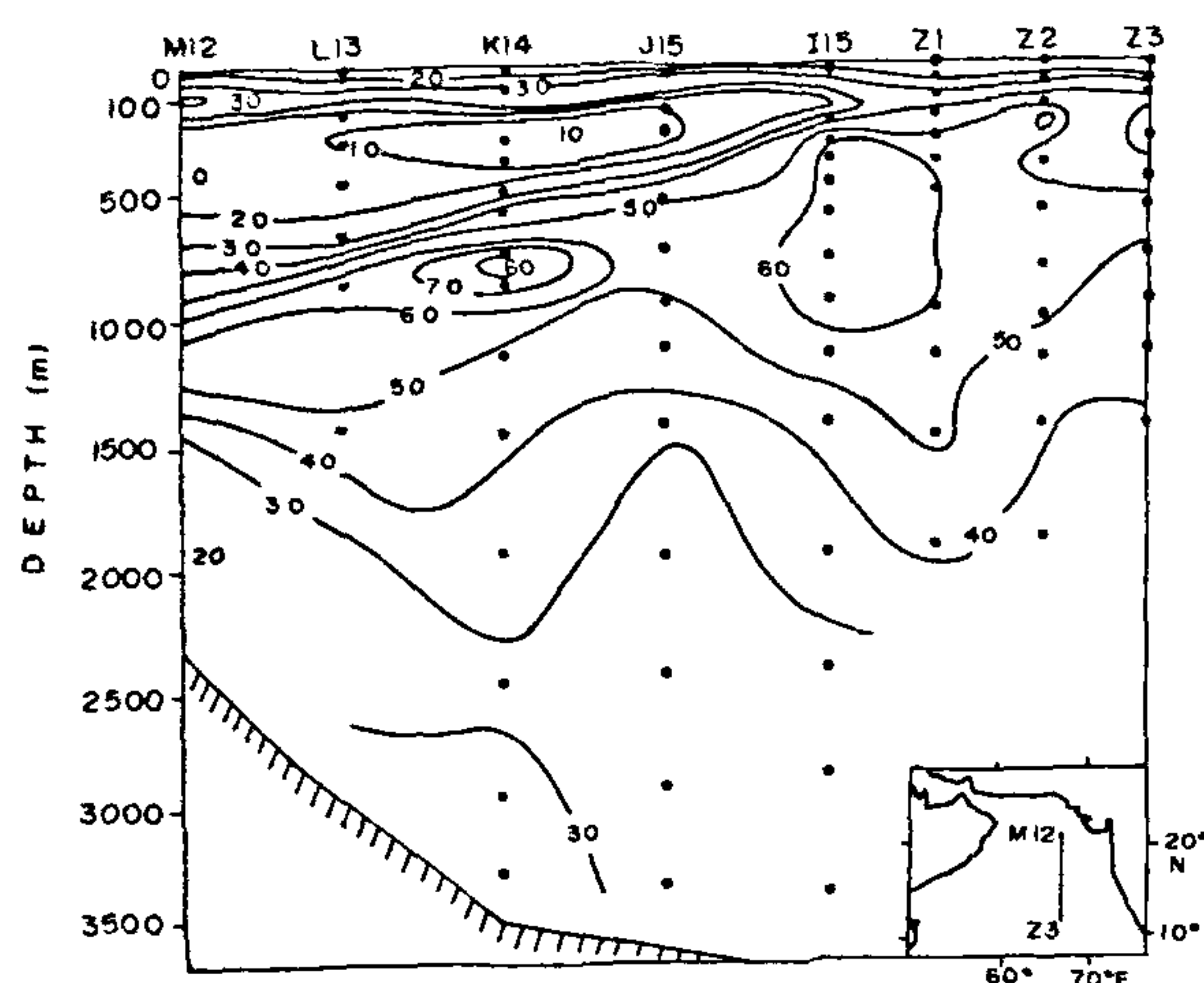


Figure 10. Vertical (north-south) section of N_2O (nM) in the Arabian Sea. Station locations are shown in the inset (from Naqvi and Noronha³²).

N_2O is an intermediate or a byproduct of both the oxidative (nitrification) and reductive (denitrification) pathways of nitrogen transformations²⁸. These pathways are expected to lead to different isotopic signatures and therefore a study of natural abundance of nitrogen and oxygen isotopes in dissolved N_2O may provide insights into its production mechanisms^{34,35}.

Results of recent measurements of $^{15}N/^{14}N$ and $^{18}O/^{16}O$ in N_2O in surface waters of the Arabian Sea reveal a negative correlation between $\delta^{15}N$ and per cent saturation with N_2O in the upwelled waters off south-west India being the most depleted in ^{15}N (Figure 11)³¹. Although these $\delta^{15}N$ values are the lowest ever reported for sea water [also substantially lower than the $\delta^{15}N$ of tropospheric N_2O (7‰, ref. 35)], these are much higher than the expected $\delta^{15}N$ of N_2O produced through nitrification³⁴. By contrast, $\delta^{18}O$ does not exhibit a discernible relationship with per cent saturation, and with the exception of one sample, all $\delta^{18}O$ values are

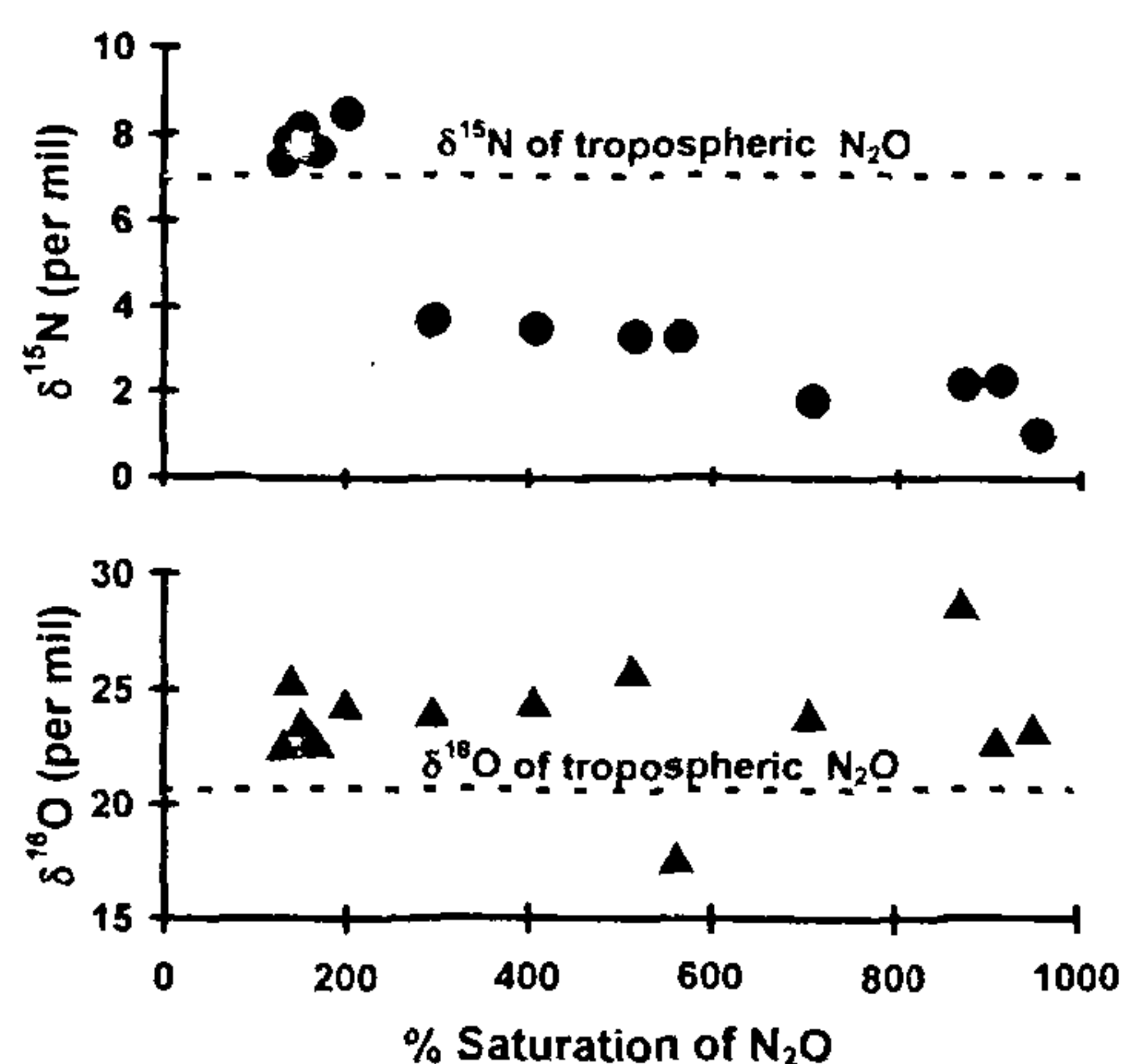


Figure 11. Nitrogen and oxygen isotopic composition of N_2O vs per cent saturation at the sea surface (depth < 5 m). Horizontal dashed lines indicate the composition of N_2O in marine air³⁵. Values with moderate saturation and $\delta^{15}N$ close to the tropospheric value are from the northern Arabian Sea; all other data are from the coastal upwelling zone off SW India (from Naqvi *et al.*³¹).

consistently higher than the $\delta^{18}O$ of tropospheric N_2O (20.7‰, ref. 35).

Vertical profiles of carbon and oxygen isotope ratios at two stations in the central Arabian Sea are shown in Figure 12. One of these (SS 3201) was located within the zone of intense denitrification while the other (SS 3204) was situated at its periphery. The N_2O minimum observed at 200–500 m at SS 3201 coincided with an intense SNM and a pronounced peak of $\delta^{15}N-NO_3$. Preferential loss of lighter N_2O to N_2 within this layer evidently led to enrichments of ^{15}N and ^{18}O in residual N_2O which are by far the greatest reported from any natural environment³¹. The N_2O concentration minimum was embedded between two maxima, but the isotopic compositions of these N_2O -rich layers were very different. Going upward from the OMZ, the $\delta^{15}N$ and $\delta^{18}O$ values fell sharply across the oxic-

suboxic boundary with the former generally lower than the tropospheric value in the upper 150 m. In contrast, although $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ also decreased below SNM, their levels remained much higher than the tropospheric values down to 1500 m. A similar pattern was also seen at the mildly reducing SS 3204 although the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ increases within the OMZ were smaller. An important aspect of the data is that the $\delta^{15}\text{N}$ of NO_3^- is consistently lower than that of N_2O at depths exceeding ~ 200 m, and higher at shallower depths at both stations. This indicates that the intense N_2O accumulation in the upper and lower parts of the OMZ may be through different mechanisms. Greater enrichment of $\delta^{15}\text{N}$ in N_2O relative to NO_3^- appears to be characteristic of denitrification. This pattern is most pronounced within N_2O -depleted SNM at SS 3201. Its persistence even below SNM at SS 3201 and at depths exceeding ~ 200 m at SS 3204 suggests significant N_2O production through denitrification. This observation is consistent with the view that denitrification may lead to a net N_2O accumulation under certain conditions³⁶.

While the isotopically lighter N_2O in waters above the suboxic zone is apparently not produced by denitrification, the pathway $\text{NH}_4^+ \rightarrow \text{NO}_2^- \rightarrow \text{N}_2\text{O}$ also cannot fully explain the observed data for two reasons. Firstly, the $\delta^{15}\text{N}$ values are much higher than that reported for nitrification³⁴. Secondly, the observed $\delta^{18}\text{O}$ is much higher than the value for nitrification ($< -3\text{‰}$) expected from $\delta^{18}\text{O}$ of H_2O and O_2 (ref. 37). A more likely pathway of N_2O production in the upper layer which can account for both the isotope and concentration data is a nitrification–denitrification coupling ($\text{NH}_4^+ \rightarrow \text{NH}_2\text{OH} \rightarrow \text{NO} \rightarrow \text{N}_2\text{O}$)³⁸. Whatever be the mechanism of enhanced N_2O production in low O_2 waters, the large temporal changes in the extent of the oxygen-deficient zones imply that the N_2O production rate in the Arabian Sea and in other similar areas may vary greatly with time, and this could

have contributed significantly to changes in the atmospheric N_2O content revealed by the ice core data³⁹.

Isotopic data from the Arabian Sea also have an important implication for the atmospheric N_2O budget. Analysis of stratospheric N_2O has shown large enrichments of heavier isotopes ($\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values of ~ 21 and 35‰ , respectively), and it is believed that the resultant large fluxes of ^{15}N and ^{18}O (400 and 500 Tg N‰ y^{-1} , respectively) from the stratosphere to the troposphere are balanced largely through exchange with the ocean where isotopically light N_2O may be produced by nitrifying bacteria^{26,40}. However, opposing trends in ^{15}N and ^{18}O and modest departures from tropospheric isotopic composition observed in the surface waters of the Arabian Sea clearly indicate that air–sea exchange cannot – given the heavy isotopic signature of N_2O derived from the stratosphere – allow the tropospheric budget of N_2O to be closed without invoking hitherto-unknown N_2O sources and sinks.

Other trace gases

The Arabian Sea is also a region where the emission rate of CH_4 , the second most important greenhouse gas, is several times higher than the global average^{41–43}. However, unlike N_2O these emissions are not large enough to affect the global CH_4 budget (the estimated flux of $\sim 0.04 \text{ Tg C y}^{-1}$ is merely 0.01% of CH_4 emission rate to the atmosphere from all sources⁴⁴). A pronounced subsurface maximum in CH_4 concentration, observed in most oceanic areas, is also found in the Arabian Sea. However, it seems to be intensified by the acute O_2 deficiency (Figure 13), and may be formed *in situ* due to CH_4 production within anoxic interiors of particles⁴³. The coastal waters of the eastern Arabian Sea have generally high CH_4 concentrations particularly close to the river

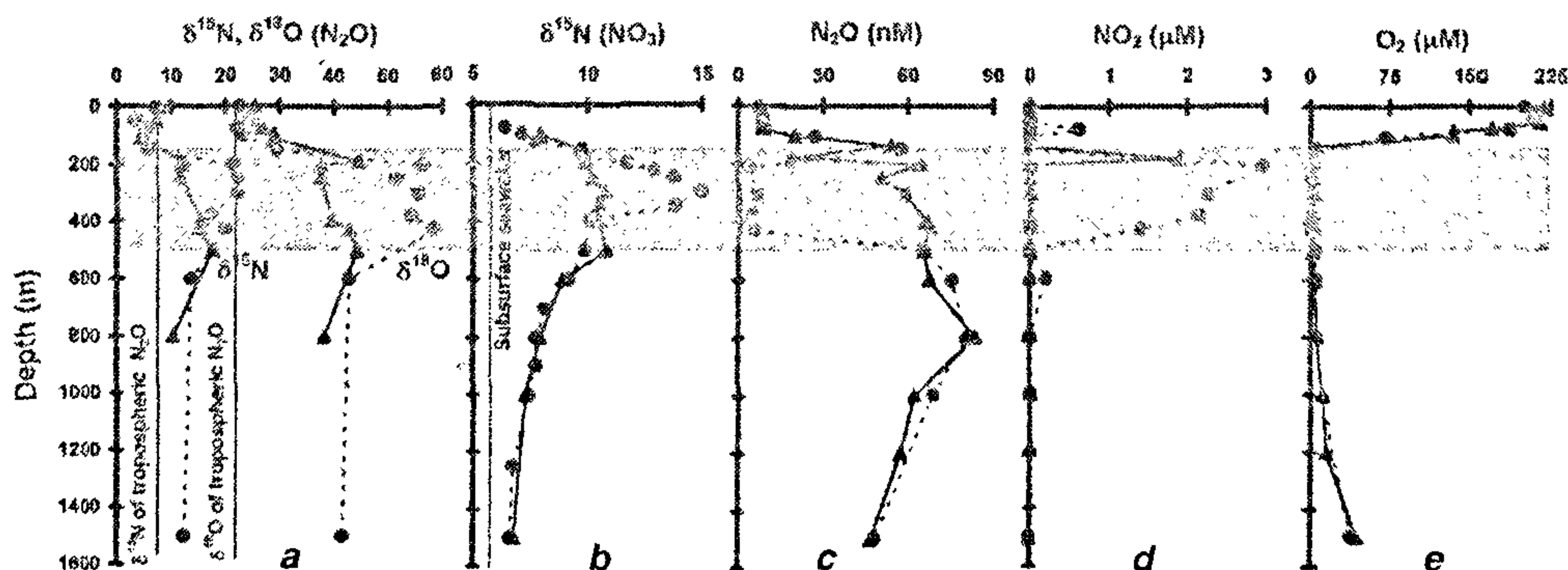


Figure 12. Vertical profiles of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ (‰ relative to air) of N_2O (a); $\delta^{15}\text{N}$ of NO_3^- (b); and concentrations of N_2O (c), NO_2^- (d) and O_2 (e) at stations SS 3201 (17°N , 68°E ; circles joined by dotted lines) and SS 3204 ($19^\circ 45'\text{N}$, $64^\circ 37'\text{E}$; triangles, joined by continuous lines). The shaded region represents secondary nitrite maximum at SS 3201. Vertical lines indicate $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of tropospheric N_2O (a) and mean $\delta^{15}\text{N}$ of NO_3^- in subsurface sea water²¹ (b) (from Naqvi *et al.*³¹).

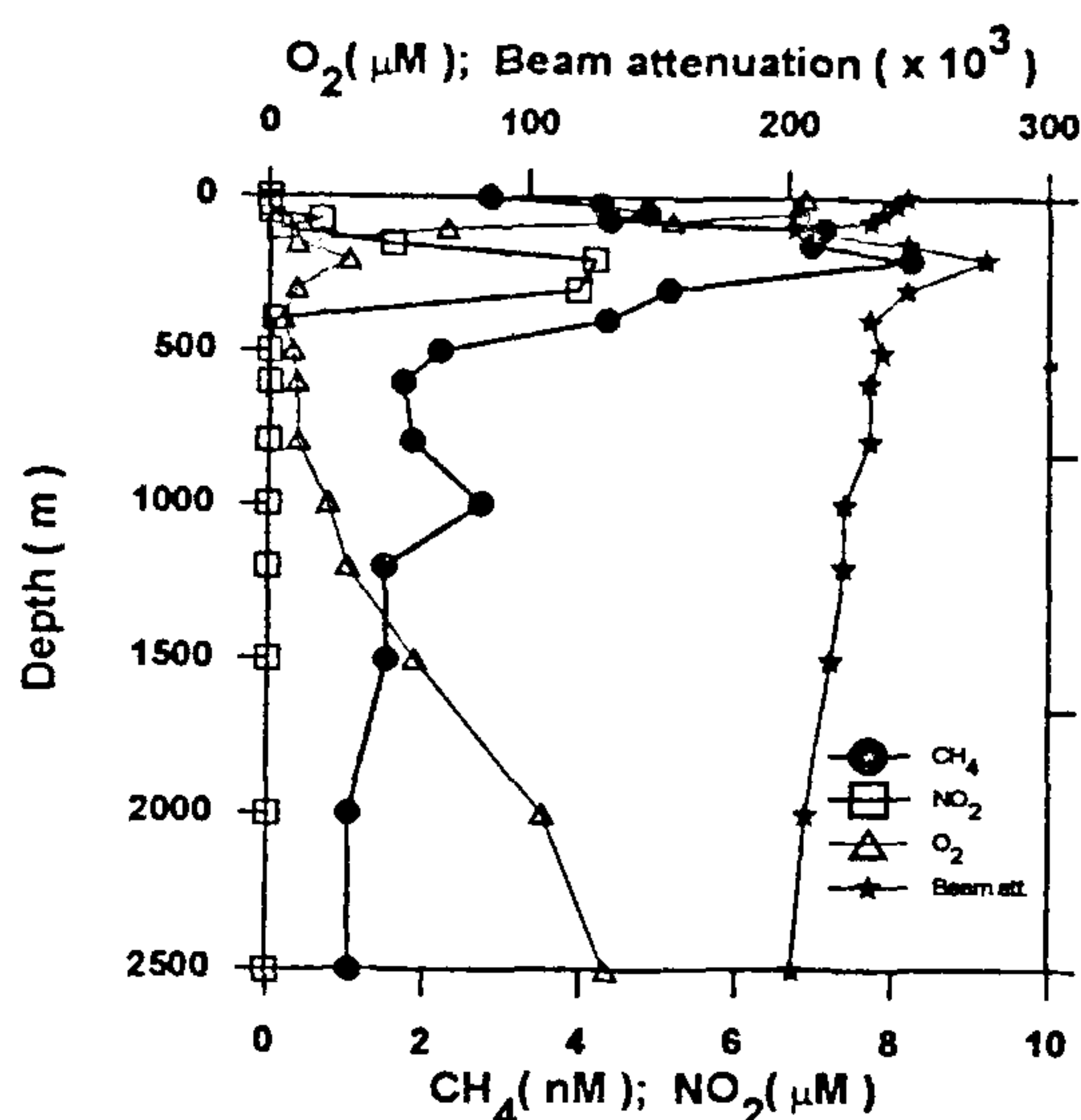


Figure 13. Vertical profiles of CH_4 in relation to NO_2 , O_2 and beam attenuation at SS 3441 (15°N , 69°E) (from Jayakumar *et al.*⁴³).

mouths. But large near-bottom anomalies, such as those observed in areas of known hydrocarbon seepage, are not seen even in the inner shelf region, where the presence of gas charged sediments is shown by geophysical data⁴⁵, indicating that sedimentary supply does not dominantly control CH_4 distribution in coastal waters. Instead, the available data strongly suggest that coastal wetlands, particularly mangrove swamps, generate large amounts of CH_4 , and probably make an important contribution through freshwater discharge to CH_4 cycling in the coastal region⁴³.

The Arabian Sea is also expected to contribute substantially to the fluxes of dimethyl sulphide (DMS) from oceans due to the presence of large coccolithophorid populations⁴⁶. Being the main source of non sea salt sulphate in the atmosphere, DMS provides cloud condensation nuclei. Currently there is no published report on its cycling in the Arabian Sea. However, this deficiency is expected to be remedied soon with information generated during the JGOFS Arabian Sea Process Study.

Concluding remarks

With an extremely delicate biogeochemical balance that exists in the oceanic O_2 -deficient zones, areas such as the Arabian Sea will perhaps be among the first to react to potential anthropogenic perturbations such as global warming and increased nutrient/organic loading. Because of this it has been suggested that the Arabian Sea could serve as an ocean scale barometer of global climate change⁴⁷. Any alterations in the rate of mid-depth water

renewal or in subsurface oxygen demand may bring about large changes in chemical fluxes including those of the climatically important gases, thus providing a climatic feedback. Similarly, an expansion of the OMZ, particularly towards the coastal zone, may also have deleterious consequences on biological resources as evident from mass mortality of fish reported from the south-west coast of India⁴⁸. It is still not clear as to how the suboxic ecosystem in the Arabian Sea will respond to changes induced by man. Future work must therefore focus on prediction of the magnitude and direction of these impacts.

1. Emiliani, C., *Planet Earth*, Cambridge University Press, Cambridge, 1992, p. 719.
2. Staley, J. T. and Orians, G. H., in *Global Biogeochemical Cycles* (eds Butcher, S. S., Charlson, R. J., Orians, G. H. and Wolfe, G. V.), Academic Press, London, 1992, pp. 21–54.
3. Takahashi, T., *Oceanus*, 1989, **32**, 22–29.
4. Bigg, G. R., *The Oceans and Climate*, Cambridge University Press, Cambridge, 1996, p. 266.
5. Broecker, W. S. and Peng, T.-H., *Tracer in the Sea*, Eldigio, Palisades, NY, 1982, p. 690.
6. Kumar, M. D., Naqvi, S. W. A., George, M. D. and Jayakumar, D. A., *J. Geophys. Res.*, 1996, **101**, 18121–18125.
7. Goyet, C., Millero, F. J., O'Sullivan, D. W., Eiseheid, G., McCue, S. J. and Bellerby, R. G. J., *Deep-Sea Res. I*, 1998, **45**, 609–623.
8. George, M. D., Kumar, M. D., Naqvi, S. W. A., Banerjee, S., Narvekar, P. V., de Sousa, S. N. and Jayakumar, D. A., *Mar. Chem.*, 1994, **47**, 243–254.
9. Codispoti, L., *Productivity of the Ocean: Present and Past* (eds Berger, W., Smetacek, V. and Wefer, G.), John Wiley, 1989, pp. 377–394.

10. Richards, F. A., in *Chemical Oceanography* (eds Riley J. P. and Riley, G.), Academic Press, 1965, vol. 1, pp. 611–645.
11. Codispoti, L. A., Devol, A., Minas, A., Paerl, H., Naqvi, S. W. A., Christensen, J., Becker, P. and Yoshinari, T., *Caribb. J. Sci.*, 1996, **32**, 284–285.
12. McElroy, M. B., *Nature*, 1983, **302**, 328–329.
13. Naqvi, S. W. A., *J. Mar. Res.*, 1987, **49**, 1049–1072.
14. Naqvi, S. W. A., *Oceanolog. Acta*, 1991, **14**, 281–290.
15. Naqvi, S. W. A. and Shailaja, M. S., *Deep-Sea Res. II*, 1993, **40**, 687–695.
16. Naqvi, S. W. A., Kumar, M. D., Narvekar, P. V., de Sousa, S. N., George, M. D. and D' Silva, C., *J. Geophys. Res.*, 1993, **98**, 16469–16479.
17. Banse, K., *Proc. Indian Acad. Sci. (Earth Planet. Sci.)*, 1994, **103**, 125–161.
18. US GLOBEC, Report No. 9, US GLOBEC Office, University of California, Davis, 1993.
19. Morrison, J. M., Codispoti, L. A., Wishner, K., Flagg, C., Gardner, W. D., Gaurin, S., Naqvi, S. W. A., Manghnani, V., Prosperie, L. and Gundersen, J. S., *Deep-Sea Res. II*, 1999, **46**, 1903–1931.
20. Kumar, M. D., Sarma, V. V. S. S., Ramaiah, N., Gauns, M. and de Sousa, S. N., *Geophys. Res. Lett.*, 1998, **25**, 81–84.
21. Brandes, J. A., Devol, A. H., Jayakumar, D. A., Yoshinari, T. and Naqvi, S. W. A., *Limnol. Oceanogr.*, 1998, **43**, 1680–1689.
22. Schafer, P. and Ittekkot, V., *Mitt. Geol.-Palaeontol. Inst. Univ. Hamburg*, 1996, **78**, 67–93.
23. Altabet, M. A., Francois, R., Murray, D. W. and Prell, W. L., *Nature*, 1995, **373**, 506–509.
24. Barnola, J. M., Raynaud, D., Korotkevich, Y. S. and Lorius, C., *Nature*, 1987, **329**, 408–414.
25. Ganeshram, R. S., Pederson, T. F., Calvert, S. E. and Prell, W. L., *Nature*, 1995, **376**, 755–758.
26. McElroy, M. B. and Jones, D. B., *Global Biogeochemical Cycles*, 1996, **10**, 651–659.
27. Bange, H. W., Rapsomanikis, S. and Andreae, M. O., *Global Biogeochem. Cycles*, 1996, **10**, 197–207.
28. Codispoti, L. A. and Christensen, J. P., *Mar. Chem.*, 1985, **16**, 277–300.
29. Bange, H. W., Rapsomanikis, S. and Andreae, M. O., *Geophys. Res. Lett.*, 1996, **23**, 3175–3178.
30. de Wilde, H. P. J. and Helder, W., *Deep-Sea Res. II*, 1997, **44**, 1319–1340.
31. Naqvi, S. W. A., Yoshinari, T., Jayakumar, D. A., Altabet, M. A., Narvekar, P. V., Devol, A. H., Brandes, J. A. and Codispoti, L. A., *Nature*, 1998, **394**, 462–464.
32. Naqvi, S. W. A. and Noronha, R. J., *Deep-Sea Res.*, 1991, **38**, 871–890.
33. Law, C. S. and Owens, N. J. P., *Nature*, 1990, **346**, 826–829.
34. Yoshida, N., *Nature*, 1988, **335**, 528–529.
35. Kim, K.-R. and Craig, H., *Nature*, 1990, **347**, 58–61.
36. Betlach, M. R. and Tiedje, J. M., *Appl. Environ. Microbiol.*, 1981, **42**, 1074–1084.
37. Yoshinari, T., Altabet, M. A., Naqvi, S. W. A., Codispoti, L., Jayakumar, A., Kuhland, M. and Devol, A., *Mar. Chem.*, 1997, **56**, 253–264.
38. Naqvi, S. W. A., *Nature*, 1991, **349**, 373–374.
39. Leuenberger, M. and Siegenthaler, U., *Nature*, 1992, **360**, 449–451.
40. Kim, K.-R. and Craig, H., *Science*, 1993, **262**, 1855–1857.
41. Owens, N. J. P., Law, C. S., Mantoura, R. F. C., Burkill, P. H. and Llewellyn, C. A., *Nature*, 1991, **354**, 293–296.
42. Patra, P. K., Lal, S. and Venkataramani, S., *J. Geophys. Res.*, 1998, **103**, 1167–1176.
43. Jayakumar, D. A., Naqvi, S. W. A., Narvekar, P. V. and George, M. D., *Mar. Chem.*, (in press).
44. Crutzen, P. J., *Nature*, 1991, **350**, 380–381.
45. Karisiddaiah, S. M. and Veerayya, M., *J. Geophys. Res.*, 1996, **101**, 25887–25895.
46. Codispoti, L. A., in U.S. JGOFS Planning Report No. 13 (ed. Smith, S. L.), Woods Hole Oceanographic Institution, Woods Hole, MA, 1991, pp. 75–85.
47. Mantoura, R. F. C., Law, C. S., Owens, N. J. P., Burkill, P. H., Woodward, E. M. S., Howland, R. J. M. and Llewellyn, C. A., *Deep-Sea Res. II*, 1993, **40**, 651–671.
48. Naqvi, S. W. A., George, M. D., Narvekar, P. V., Jayakumar, D. A., Shailaja, M. S., Sardesai, S., Sarma, V. V. S. S., Shenoy, D. M., Naik, H., Maheswaran, P. A., Krishna Kumari, K., Rajesh, G., Sudhir, A. K. and Binu, M. S., *Curr. Sci.*, 1998, **75**, 543–544.

ACKNOWLEDGEMENTS. We are grateful to our colleagues and all co-authors of publications cited here, who have contributed in generating most of the information summarized in this article.