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An oceanic fixed nitrogen sink exceeding 400 Tg N a^{-1} vs the concept of homeostasis in the fixed-nitrogen inventory

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Abstract

Measurements of the N_2 produced by denitrification, a better understanding of non-canonical pathways for N_2 production such as the anammox reaction, better appreciation of the multiple environments in which denitrification can occur (e.g. brine pockets in ice), etc. suggest that it is unlikely that the oceanic denitrification rate is less than 400 Tg N a⁻¹. The total oceanic sink for fixed-N is, therefore, more than 400 Tg N a⁻¹. Because this sink term far exceeds present estimates for nitrogen fixation, the main source for oceanic fixed-N, there is a large apparent deficit (~200 Tg N a⁻¹) in the oceanic fixed-N budget. The size of the deficit appears to conflict with apparent constraints of the atmospheric carbon dioxide and sedimentary δ^{15}N records that suggest homeostasis during the Holocene. In addition, the oceanic nitrate/phosphate ratio tends to be close to the canonical Redfield biological uptake ratio of 16 (by N and P atoms) which can be interpreted to indicate the existence of a powerful feed-back mechanism that forces the system towards a balance. The main point of this paper is that one cannot solve this conundrum by reducing the oceanic sink term without violating an avalanche of recent data.

A solution to this problem may be as simple as an upwards revision of the oceanic nitrogen fixation rate, and it is noted that most direct estimates for this term have concentrated on nitrogen fixation by autotrophs in the photic zone, even though the gene for nitrogen fixation is widespread amongst heterotrophs. Another simple explanation may be that we are simply no longer in the Holocene and one might expect to see temporary imbalances in the oceanic fixed-N budget as we transition from the Holocene to the Anthropocene in line with an apparent denitrification maximum during the Glacial-Holocene transition. Other possible full or partial explanations involve plausible changes in the oceanic nitrate/phosphate and N/C ratios, an oceanic phosphorus budget that may also be in deficit, and oscillations in the source and sink terms that are short enough to be averaged out in the atmospheric and geologic records.

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1 Introduction

Because of its relationship with the planetary nitrous oxide distribution, biological productivity (e.g. Redfield et al., 1963) and the ocean's ability to sequester atmospheric carbon dioxide (e.g. Codispoti et al., 2001), there is more than academic interest in the oceanic fixed-N budget. Moreover, there has been considerable debate over the state of the oceanic fixed-N budget in recent years (Gruber and Sarmiento, 1997; Codispoti et al., 2001; Gruber, 2004). A major point of this paper is that attempts to bring the oceanic fixed-N budget more into balance by reducing the total sink term have to confront an avalanche of results suggesting that these previous estimates of oceanic fixed-N removal (e.g. Codispoti et al., 2001) may, if anything, be too low! We will suggest several possibilities for reconciling an oceanic sink for fixed-N of $>400\,\mathrm{Tg\,N\,a^{-1}}$ with constraints imposed by the atmospheric carbon dioxide record (Gruber and Sarmiento, 1997), the sedimentary nitrogen isotope record (Altabet, 2006; Deutsch et al., 2004) and by nitrate/phosphate relationships (Tyrell, 1999). With respect to nitrate/phosphate relationships, we will revisit our suggestion (Piper and Codispoti, 1975) that increases in denitrification are correlated with increased phosphate removal rates, and review some data and concepts that relate to the constancy (or lack thereof) of the oceanic nitrate/phosphate ratio. A constant refrain in this paper can be encapsulated by the phrase, "The more we look, the more we find", a comment made by A. Devol when he and the author of this paper were puzzling over ever-increasing estimates of oceanic denitrification years ago. Our emphasis will be on reconciling a large oceanic fixed-N sink with other data, and outlining pathways towards a reconciliation of the data on the oceanic fixed-N sink with prevailing concepts and beguiling notions such as steady-state, Redfieldian and homeostatic oceans. We suggest that both the estimates for denitrification and nitrogen fixation are likely to increase. Finally, we caution that the lessons from the past may be an uncertain predictor of the near-term ($\sim$100 yrs) future as we transition from Milankovich to Anthropogenic climate forcing, and as the already massive anthropogenic impingement on the marine environment increases

(e.g. Crutzen, 2002; Jackson and Sala, 2001; Watling and Norse, 1998).

2   Scientific background

2.1   General

Although there are other sources and sinks for oceanic fixed-N, there is general agreement that the oceanic fixed-N budget is dominated by internal biological cycling: a nitrogen fixation source and a sink that arises from the biological processes that convert fixed-N to N_2 (e.g. Table 1; Gruber and Sarmiento, 1997; Codispoti et al., 2005, Tyrell, 1999). There is also a consensus that the estimates for these source and sink terms made only a decade or two ago (e.g. Codispoti and Christensen, 1985) were far too low. With respect to nitrogen fixation, estimates of the global oceanic fixation rate by canonical genera (*Trichodesmium* and *Richelia endosymbioants*) have been revised upwards, and may require further upwards revision (Davis and McGillicuddy, 2006). In addition, there is now evidence for significant contributions from unicellular cyanobacteria and bacterioplankton (e.g. Montoya et al., 2004). Changes in our understanding of denitrification have perhaps been even more dramatic. We now better appreciate that in addition to "canonical denitrification" that is encapsulated in the following reaction sequence, $NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$, there are multiple biological pathways to N_2 (Fig. 1; Codispoti et al., 2005). One of these pathways, the anammox reaction ($NH_4^+ + NO_2^- \rightarrow N_2 + H_2O$), may be more important than the canonical route to N_2 under some circumstances (Kuypers et al., 2005; Thamdrup et al., 2006) and has been demonstrated to occur in both the water column and in sediments (Dalsgaard and Thamdrup, 2002; Dalsgaard et al., 2003; Kuypers et al., 2005). There is also recent evidence from the Arabian Sea that suggests that the biological production of dinitrogen (N_2) in the ocean exceeds estimates based on canonical stoichiometries for denitrification (Codispoti et al., 2001; Devol et al., 2006a; Naqvi et al., 2006), and J. W. Murray (personal communication) suggested that a similar situation exists in the Black

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Sea during his SPOT-ON presentation (Murray et al., 2005). Note that in this paper, we will use "denitrification" to denote the ensemble (Fig. 1) of biological processes that can convert fixed-N to dinitrogen (N_2).

2.2 Water column denitrification

Three major quasi-permanent sites for water column denitrification exist within suboxic (dissolved oxygen $<4\,\mu M$) portions of the thermocline in the Arabian Sea, the Eastern Tropical North Pacific (ETNP) and the Eastern Tropical South Pacific (ETSP). Although estimates vary, it is agreed that globally significant denitrification occurs in the three major zones (Fig. 2) even though they comprise only $\sim$0.1% of the oceanic volume (e.g. Codispoti et al., 2005; Gruber, 2004). Smaller reasonably well-studied sites exist in enclosed basins such as the Baltic and Black seas, and denitrification is known to occur off Namibia (Calvert and Price, 1971; Kuypers et al., 2005), as well as transiently during outbreaks of suboxia in shallow coastal waters such as has been documented over the West Indian Shelf (e.g. Naqvi et al., 2000). With increases in the outbreaks of coastal hypoxia/suboxia/anoxia that may arise from increasing additions of anthropogenic nutrients (e.g. Naqvi et al., 2000; Rabalais et al., 2000), it is possible that water column denitrification rates in the coastal ocean are on the increase. Globally significant increases in the denitrification rate in the ETSP appeared to have occurred in recent decades perhaps as consequences of a la Niña event (Codispoti et al., 1986), a regime shift (Chavez et al., 2003), and/or anthropogenic disturbance (Codispoti and Packard, 1980). Evidence for variability in the oceanic water column denitrification rate on glacial-interglacial time scales has been demonstrated for the eastern tropical Pacific (Ganeshram et al., 2002). Altabet et al's. (2002) examination of cores from the Arabian Sea suggests significant variability on glacial-interglacial, orbital, and $\sim$ millennial time scales.

Codispoti et al. (2001) suggested that a conservative estimate of oceanic water column denitrification in the present-day ocean was $\sim$150 Tg N a^{-1}. This upward revision was based largely on the determination that direct determination of the N_2 produced

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by denitrification in the Arabian Sea produced an excess N_2-N burden ~4x historical estimates of the nitrate deficit inventory and about 2x the nitrate deficit inventory arising from a new method presented by Codispoti et al. (2001).

2.3 Sedimentary denitrification

Middleburg et al. (1996) suggest an oceanic sedimentary denitrification rate (including continental shelves) between 230–285 Tg N a^{-1}. Brandes and Devol (2002) suggest that the oceanic nitrogen isotope budget requires a sedimentary denitrification rate during the Holocene of ~280 Tg N a^{-1} based on a nitrogen isotope budget. These are reasonable values, but perhaps a bit conservative. The discussion section of this paper (Sect. 3) suggests why. Here we will note, that many past estimates of oceanic sedimentary denitrification neglected the importance of coupled nitrification-denitrification in sediments (see Codispoti and Christensen, 1985) and that most have not explicitly accounted for some of the newly appreciated pathways to N_2 such as the anammox reaction (Fig. 1).

2.4 Nitrogen fixation

During the past decade or so there has been an accumulation of data to suggest that earlier estimates of oceanic nitrogen fixation require upwards revision. For example, estimates of upper water column nitrogen fixation based on *Trichodesmium sp.* and the diatom endosymbiont *Richelia intracellularis* (e.g. Capone, 2001) are matched or perhaps exceeded by nitrogen fixation in smaller microbes (e.g. Montoya, et al., 2004). In addition, the genome for nitrogen fixation appears to be widespread (Zehr et al., 1998), and it is likely that estimates for marine nitrogen fixation will continue to increase. Existing estimates for the total oceanic nitrogen fixation rate (e.g. Codispoti et al., 2005; Deutsch et al., 2005; Gruber, 2004), do not exceed 150 Tg N a^{-1}. This rate is based on observations and models, but direct observations of rates are concentrated in the photic zone and in coastal sediments. There does not appear to have been a

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comprehensive study of heterotrophic and chemolithotrophic nitrogen fixation rates in sub-euphotic zone waters and deeper sediments.

3 Discussion

3.1 The oceanic fixed-N budget

Table 1 presents simplified "pro forma" oceanic fixed-N budgets. The totals include all known processes, but only the nitrogen fixation and denitrification rates are explicitly indicated because it is the apparent imbalance between these rates that is at the core of the problem addressed in this paper. Note that our budgets (this paper, and Codispoti et al., 2001) include continental shelves and marginal seas such as the Mediterranean, Black and Baltic seas, but omit estuaries. It is obvious that there is considerable disagreement on the denitrification sink terms and whether or not the available information suggest a balanced or unbalanced budget. We will discuss this matter in some detail in the following sections. At the outset, we will note that as a result of discussions at the SPOT-ON, (Jickells, 2006) and also as a consequence of a recent study (Chuck et al., 2002) suggesting that the ocean is a source of alkyl nitrates, we now believe that the upwards revision in the atmospheric source term in the Codispoti et al. (2001) budget was in error and have reduced this term to bring it in line with the other budgets. The effect of this revision is to put the Codispoti et al. (2001) budget (Table 1) into an even greater deficit ($\sim$230 Tg N a^{-1}). We also note, that our budget's N$_2$O loss term (6 Tg N a^{-1}) is in accord with the work of Bange (2006) who estimates that a conservative estimate for the oceanic loss (including estuaries, in his case) would be 7$\pm$4 Tg N a^{-1}. We will not discuss this term further because a change of 2–3 Tg N a^{-1} from the canonical values while important for atmospheric chemistry has only a minor impact on the overall oceanic fixed-N budget.

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3.2 The problem

There is a consensus that traditional estimates of nitrogen fixation and denitrification were too low and that the oceanic turnover time for fixed-N is ~2500 years or less (Codispoti et al., 2005; Gruber, 2004; Middelburg et al., 1996). There is also agreement that the terms in the budget are poorly constrained (e.g. Gruber and Sarmiento, 1997 and 2002; Gruber 2004). The problem that this paper seeks to address is that the total sink terms posited by Codispoti et al. (2001), produce fixed-N deficits that would be unlikely to exist for more than several hundred years without violating apparent constraints imposed by the Holocene atmospheric carbon dioxide record (Gruber and Sarmiento, 1997) and the Holocene sedimentary ^{15}N record (Altabet, 2002; Deutsch et al., 2004). In addition, there exists the traditional "geochemist's" view that since the oceanic nitrate/phosphate ratio (~15 by N and P atoms; Falkowski, 2000) is quite similar to the canonical "Redfieldian" ratio of 16 in "plankton" (see Falkowski, 2000), and since the fixed-N budget is dominated by a biological source (nitrogen fixation) and sink (denitrification) there is a strong tendency for "homeostasis" (e.g. Gruber, 2004; Tyrell, 1999). The coupling of denitrification and nitrogen fixation over ocean circulation and shorter time-scales (Broecker and Peng, 1982; Codispoti, 1989) does provide negative feed-backs that favor homeostasis, but this paper will suggest that there are several possible factors that could weaken the influence of this mechanism, and that, to the extent that it does apply in today's ocean, it must account for a fixed-N sink term of $\sim 400 \, \text{Tg} \, \text{N} \, \text{a}^{-1}$.

3.3 Reducing the sink term is not the answer

As outlined above, Codispoti et al. (2001) made the case for an upwards revision of the denitrification rate in the oceanic water column, based partly on data from the Arabian Sea, suggesting that prior nitrate deficit calculations were too low necessitating a correction for the Arabian Sea. Even with an improved method for estimating nitrate removals, determinations of the excess N_2 arising from denitrification exceeded esti-

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mates of nitrate removal by a factor of ∼2, and there were suggestions that this might also be the case in the Eastern Tropical North Pacific Ocean (Brandes, personal communication). Murray et al. (2005) present results from the suboxic zone in the Black Sea suggesting a similar situation. Gruber (2004) in arguing for a lower water column denitrification rate questioned whether the baseline values used to calculate excess N_2 in the Arabian Sea were appropriate. These baselines were determined by looking at data just before water masses entered the Arabian Sea, and do not involve assumptions about equilibrium values for nitrogen and argon. They are more fully discussed by Devol et al. (2006a). In summary, a compelling reason for rejecting the recent data on excess N_2 has not been advanced.

Gruber (2004) correctly critiqued one of the explanations offered to explain the Arabian Sea excess N_2 data. This explanation involved an enhanced ammonium flux as a consequence of the activities of sulfide oxidizing mat forming bacteria. These bacteria thrive at the interface between suboxic waters and sediments (Fossing et al., 1995; Jørgensen and Gallardo, 1999) and can obtain energy by using NO_3^- to oxidize sulfide. At present, the ratio of N_2 to NH_4^+ production by these bacteria is uncertain. Three genera of bacteria are involved. Schulz and Schulz (2005) suggest that *Thiomargarita* and *Beggiatoa* are important beneath the Benguela Upwelling area (SW Africa), and that *Thioploca* dominates off the coasts of Peru and Chile. These bacteria have vacuoles that can accumulate large amounts of nitrate. Codispoti et al. (2001) speculated that the activities of these bacteria would lead to a high ammonium flux into suboxic waters that could support the anammox reaction and lead to the production of excess N_2 that would not be detected by applying canonical stoichiometries. Gruber's (2004) critique correctly pointed out that since the ammonium arising from nitrate fermentation ($NO_3^- \rightarrow NH_4^+$) was produced from water column nitrate, then the signal for this process should be recorded by traditional stoichiometric parameters such as N*, but this critique assumes that the nitrate fermentation process is not accompanied by sedimentary phosphate sequestration. Another critique of this suggestion is that nitrate fermentation might not be the major source of ammonium in the sediments underlying

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suboxic waters. Off Namibia, most of the nitrate assimilated by the similar giant sulfur bacterium *Thiomargarita namibiensis* may be converted to N_2 (Zitzmann and Brüchert, 2005), but some ammonium is produced, and in both regions, ammonium fluxes out of the sediments are high due to the totality of suboxic/anoxic respiratory processes

5 (Graco et al., 2005; Zitzmann and Brüchert, 2005). Whether or not high ammonium fluxes from sediments into suboxic waters can lead to N_2 production that cannot be detected by N* involves the relationship between sedimentary ammonium and phosphate fluxes. Here we note, that suboxic sediments are known sites of enhanced phosphorite deposition (Piper and Codispoti, 1975; Ganeshram et al., 2002) and that Schulz

10 and Schulz (2005) have shown that *T. namibiensis* sequesters large amounts of phosphate which they suggest contributes importantly to phosphorite formation. Thus, it is possible that these sediments are net exporters of ammonium and net importers of phosphate from the immediately overlying waters. If so, the anammox process in overlying suboxic waters would help to explain, the excess N_2 values. In any case,

15 the recent *data* on excess N_2 cannot be dismissed on the basis of less than perfect *explanations.*

In attempting to produce a more balanced budget, Gruber (2004) also suggested that water column signals might sometimes arise from sedimentary denitrification and essentially be "counted twice". The possibility of ammonium fluxes from sediments

20 contributing to anammox in the water column leads to a hybrid sediment+ water column situation, and there may be some "double counting". Overall, however, this idea founders on several shoals. For example, it neglects the isotopic signals that separate water column from sedimentary denitrification (Brandes and Devol, 2002; Sigman, et al., 2003). It also ignores the implications of those nitrite maxima that occur at mid-

25 depths, separated from the coast (e.g. Codispoti, 1973; Naqvi, 1994) that may be positively correlated with denitrification rates (Codispoti and Packard, 1980). This notion is also at variance with estimates of water column denitrification based on ^{15}N incubations and electron transport activities (ETS) as reported by Codispoti and Richards (1976); Codispoti and Packard (1980); Naqvi and Shailaja (1992); and Devol et al. (2006b).

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In addition, it must deal with the small sedimentary areas in contact with some major suboxic water masses such as in the Eastern Tropical North Pacific. Finally there is a basic morphological argument. The sediments in contact with suboxic water masses comprise <3% of the total oceanic sedimentary area (Menard and Smith, 1966), and sedimentary denitrification is widespread depending more on the organic material supply than on the oxygen concentration of the overlying waters. Indeed, canonical denitrification is enhanced under oxygenated waters relative to suboxic waters because of the coupling of nitrification and denitrification (Codispoti and Christensen, 1985). Thus, it would appear that the problem of attributing sedimentary denitrification to water column processes does not have a major impact on present estimates of water column denitrification.

3.4 A water column denitrification rate of more than $150\,\mathrm{Tg\,N\,a^{-1}}$?

Having considered some of the arguments for reducing Codispoti et al.'s (2001) water column rate estimate of $\sim150\,\mathrm{Tg\,N\,a^{-1}}$, let us now turn to considerations that suggest that this estimate is actually too low. We can summarize them as follows:

3.4.1 Denitrification outside the boundaries of suboxic water masses

Existing estimates of water column denitrification are generally restricted to suboxic waters with nitrite concentrations $>0.1\,\mu\mathrm{M}$, but it is known that denitrification can proceed in the presence of dissolved oxygen (Codispoti et al., 2005; Zehr and Ward, 2002), and there is evidence for denitrification occurring within particles suspended in low (but not suboxic) waters; (Wolgast, 1998, Kuypers et al., 2005). Given that suboxic waters comprise only ~0.1–0.2% of the oceanic volume, there is a potential for a greatly increased water column denitrification rate if this process extends beyond the suboxic zone. Recently, Li et al. (2006) have suggested that significant N_2 production occurs in oxyclines in the water column and in suspended particles, by an ensemble of the processes that they refer to as "partial nitrification". Basically, they invoke those nitrifi-

cation pathways that lead to production of NO, N_2O, and N_2 (Fig. 1), and anammox as well as canonical denitrification within sediments to explain their results, and suggest that the zone in which N_2 is produced extends well beyond the suboxic portions of the water column.

3.4.2 Outmoded stoichiometries

Whether based on nitrate deficits, N*, ^{15}N incubations, or estimates of respiration rates using the ETS method (Codispoti et al., 2005) most estimates of water column denitrification assume canonical denitrification with only minor variations. Given the multiple pathways to free nitrogen shown in Fig. 1, and the excess N_2 values already discussed, it is likely that most existing estimates are too low.

3.4.3 Undersampling

No estimates for the oceanic significance of denitrification in the oxyclines associated with suspended particles/aggregates exist. Although, low inorganic-N concentrations have been associated with some hydrothermal vents and adjacent waters (Mehta et al., 2003), no estimate for the overall denitrification rate associated with hydrothermal vents/fluids exists. Denitrification has also been shown to occur in brine pockets in Arctic and Baltic sea ice (Rysgaard and Glud, 2004; Kaartokallio, 2001, 2005), at rates that are smaller but of the same magnitude as local sedimentary rates. Since the sedimentary denitrification rate exceeds the water column rate (see below), and since the average annual sea ice-extent of $\sim20\times10^6$ km^2 (Gloersen et al., 1992) is similar to the area of the global continental shelf ($\sim27\times10^6$ km^2; Menard and Smith, 1966), where the bulk of sedimentary denitrification may occur (Devol et al., 1997) it is possible that this newly discovered denitrification site can make an appreciable addition to the water column denitrification rate. Smaller contributions may be made by denitrification at the boundaries of anoxic hot brines such as found in the Orca Deep (Van Cappellen et al., 1998) and Bannock basin (Daffonchio et al., 2006), and no systematic attempt has

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been made to estimate the total rate associated with transient suboxic events, although rates for the seasonally occurring suboxia over the West Indian Shelf appear to be several $Tg\,N\,a^{-1}$ (Devol et al., 2006a; Naqvi et al., 2006). This writer concludes that the water column denitrification rate estimate is more likely to be raised than lowered
5 as we benefit from the results of ongoing research.

3.5 Sedimentary denitrification

Codispoti et al. (2001) suggested an oceanic sedimentary denitrification rate of $\sim 300\,Tg\,N\,a^{-1}$. They used the estimate of 230–$285\,Tg\,N\,a^{-1}$ suggested by Middelburg et al. (1996) as a starting point, but pointed out that this range of values was based
10 on canonical stoichiometries that did not account for anammox or for the Mn mediated reactions that might produce N_2. We now have data that suggest that anammox occurs in sediments (Dalsgaard and Thamdrup, 2002; Thamdrup and Dalsgaard, 2002), and redox metal mediated denitrification may also occur (Codispoti et al, 2005; Luther et al., 1997). Anaerobic methane oxidation can also be coupled to denitrification (i.e. ni-
15 trate oxidizes methane; Raghoebarsing et al., 2006), and the direct N_2 contributions of *Thiomargarita, Thioploca, Beggiatoa* and other sedimentary bacteria that oxidize re-duced sulfur compounds with oxidized forms of N have yet to be comprehensively ad-dressed. In addition, a recent study of nitrate deficits in the Bering Sea (Lehmann et al., 2005) resulted in a denitrification rate in abyssal (2000 m and deeper) sediments more
20 than 3 times higher than existing high-end estimates of the average global sedimentary denitrification rate for the same depth interval. Based on *canonical stoichiometries,* a rate of $1.3\,Tg\,N\,a^{-1}$ was estimated for an area of only $0.9 \times 10^6\,km^2$ which is tiny com-pared to the total oceanic area $\geq 2000\,m$ of $300 \times 10^6\,km^2$ (Menard and Smith, 1966). Whether this high rate would be balanced by regions that should have lower than aver-
25 age rates such as the Eastern Mediterranean Sea (Krom et al., 2005) and the Canada Basin of the Arctic Ocean (Codispoti et al., 2005) is an open question, but we note the existence of several semi-enclosed basins in regions of moderate to high primary production for which regional denitrification rates in abyssal sediments have not been

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estimated (e.g. the Red Sea, Gulf of Mexico, etc.). In addition, the chemotrophic productivity associated with hydrothermal vents and cold seeps, should also be associated with high rates of respiration in deep sediments. No comprehensive denitrification rate estimate exists for such habitats, although Mehta et al. (2003) note the occurrence

5 of vent fluids with low nitrate and ammonium concentrations, and a bacterium from a hydrothermal vent chimney has been shown to grow via nitrate respiration with the production of N_2 (Nakagawa et al., 2003). Recent studies also suggest that coarse (silty and sandy) nearshore sediments that were previously discounted as sites of enhanced respiration because of low organic carbon contents, may in fact be sites of high respi-

10 ration including denitrification (Jahnke, 2006; Middelburg et al., 2005; Rao and Jahnke, 2006), and there are seasonal oscillations in water exchange between aquifers and the coastal ocean (Michael, et al., 2005) that might, in effect, expand coastal denitrifying sediments landward. In addition, there has been considerable recent interest in microbial activities that can be found deep in marine sediments (Parkes, et al., 2005),

15 and suboxic electron acceptors can be found more than 100 m below the surface in sedimentary columns presumably as a consequence of water circulating through the underlying basement rock (Hondt et al., 2004) that supplies oxygen and nitrate and produces an "upside-down" redox profile (Law, 2004). Once again, there has yet, to be an attempt to assess the overall impact of these processes.

20 Brandes and Devol (2002) suggested a sedimentary denitrification rate of $280\,\text{Tg N a}^{-1}$ for the Holocene. Their budget was based on an isotopic budget for oceanic fixed-N, a rate of $75\,\text{Tg N a}^{-1}$ for canonical denitrification in the water column, and the differences in isotopic fractionation between source and sink processes with canonical water column denitrification having a much larger fractionation factor. Their

25 rate was based on a whole ocean isotope budget, so it would apply to a time-scale similar to the $\sim 10^3$ year turnover time for fixed-nitrogen. While, at first blush, one might think that this rate should be scaled up dramatically if the $150\,\text{Tg N a}^{-1}$ water column rate is correct (Table 1), this is not the case. This is because the increase in the water column sink was attributable in large measure to N_2 production from organic-N

and ammonium oxidation that might be associated with low isotope fractionation due to substrate depletion, similar to sedimentary denitrification. In estimating their total water column denitrification rate of $150\,\mathrm{Tg\,N\,a^{-1}}$, Codispoti et al. (2001) assumed that such processes contributed one third of the N_2 to water column denitrification outside of the Arabian Sea (total=$90\,\mathrm{Tg\,N\,a^{-1}}$) and half of the biogenic N_2 produced during water column denitrification in the Arabian Sea (total=$60\,\mathrm{Tg\,N\,a^{-1}}$). If the 50% value applied everywhere their water column rate would have been $180\,\mathrm{Tg\,N\,a^{-1}}$ evenly divided between canonical denitrification and processes that might have fractionation factors similar to sedimentary denitrification. In this case the adjusted value for sedimentary denitrification based on the Brandes and Devol (2002) isotopic budget would be $246\,\mathrm{Tg\,N\,a^{-1}}$ (($90/75\times280$)–90). Applying the 33% proportion uniformly would reduce the Codispoti et al. (2001) water column rate to $135\,\mathrm{Tg\,N\,a^{-1}}$ of which 2/3 would be canonical denitrification. In this case, the sedimentary denitrification rate would be $291\,\mathrm{Tg\,N\,a^{-1}}$ (($90/75\times280$)–45). Holding the total water column rate at $150\,\mathrm{Tg\,N\,a^{-1}}$ and assuming that one third of the N_2 was produced via the non-canonical pathways would yield a sedimentary rate of $323\,\mathrm{Tg\,N\,a^{-1}}$ (($100/75\times280$)–50). Thus, reasonable scenarios for increased water-column denitrification do not massively effect the sedimentary denitrification rate based on Brandes and Devol's (2002) isotopic budget.

To conclude this section, it seems reasonable to suggest that the weight of the evidence supports an oceanic sedimentary denitrification rate of $\sim$250–300$\,\mathrm{Tg\,N\,a^{-1}}$. Even if the sedimentary rate was only 200–250$\,\mathrm{Tg\,N\,a^{-1}}$, however, it would not solve the problem of a deficit in the oceanic fixed-N budget (Table 1) that could not be maintained for more than a few hundred years without challenging current interpretations of the atmospheric CO_2 record (Gruber and Sarmiento, 1997) and the ^{15}N record in sediments (Altabet, 2002; Deutsch et al., 2004).

3.6 Interpretation of the oceanic N/P ratio

Arguments for a "homeostatic" oceanic fixed-N budget that is balanced within the uncertainties often involve (in part) interpretation of oceanic N/P ratios and intercepts in N-P scatter diagrams (e.g. Gruber, 2004; Tyrell, 1999). In practice, the ratios employed for the water column are normally nitrate/phosphate ratios. Below the upper several hundred meters, ammonium and nitrite concentrations are usually low, and it is also reasonable to assume that most of the organic N is refractory (Aluwihare et al., 2005). Similarly, in nutrient-depleted surface waters it might be reasonable to assume that, when nitrate or phosphate are ~0, the other biologically available forms of these elements are also close to 0 (e.g. Codispoti et al., 2005; Thingstad et al., 2005; Krom et al., 2005; Fig. 2). The oceanic average for the nitrate/phosphate (by atoms of N&P) ratio at depths of 500 m and greater is ~14.7 (Falkowski, 2000), vs nitrate and phosphate uptake ratios of ~16 (e.g. Redfield et al., 1963), and average planktonic N/P ratios of ~16 (Hedges et al. 2002). Following Redfield, (1958), many investigators (e.g. Gruber, 2004; Tyrell, 1999) have used the near correspondence between the oceanic N/P ratio, uptake ratios, and the average ratio in plankton, to suggest that nitrogen fixation and denitrification interact in the Holocene ocean to produce a "homeostasis" that keeps the ocean fixed-N budget balanced within observational uncertainty. A hopefully not too unfair simplification of this view would be that the oceanic fixed-N inventory lags phosphate by only an amount small enough to "excite" sufficient nitrogen fixation to keep the inventories close to the canonical 16/1 Redfield ratio. Some have also looked at the oceanic zero intercepts of the phosphate-nitrate scatter diagrams (e.g. Tyrell, 1999) to amplify this argument, since, on average, the phosphate intercept at 0 nitrate is only ~0.25 μM. With an atomic N/P ratio of 16 this corresponds to ~4.0 μM of fixed-N. Whether or not an average nitrate deficit of ~4.0 should be considered to be small relative to concentrations within 100 m of the photic zone is debatable, and there are the following additional complications.

3.6.1 Multiple controls on nitrogen fixation

Several recent studies (e.g. Wu et al., 2000) suggest that iron limitation of nitrogen fixation, can complicate the elegant and simple feed-back mechanism originally proposed by Redfield (1958). In regions such as the North Atlantic where Saharan dust
5 creates a relatively abundant iron supply, phosphate limitation (Sañudo-Wilhelmy et al., 2001) and co-limitation of nitrogen fixation by iron and phosphorus (Mills et al., 2004) may occur. In other regions such as the HOTS site off Hawaii, iron is more likely to limit nitrogen fixation (e.g. Wu et al., 2000). Capone (2001) concluded that "Iron and phosphorus are the likely factors controlling oceanic nitrogen fixation and their relative
10 influence may vary among ocean basins". Other trace metals such as zinc, a cofactor in many alkaline phosphatases (e.g. Mills et al., 2004), may also impact nitrogen fixation rates. In addition, nitrogen fixation is energy intensive, and the pelagic nitrogen fixation identified, so far, is restricted mainly to tropical and sub-tropical waters (Carpenter and Romans, 1991). Another complication vis a vis the traditional Redfieldian view is that
15 nitrogen fixation proceeds in North Atlantic waters that reach the surface with >16/1 nitrate/phosphate ratios (Wu et al., 2000) and that the organic material that is produced during nitrogen fixation has N/P ratios considerably higher than 16/1 (e.g. Gruber and Sarmiento, 1997; Karl et al. 1997). These facts suggest that nitrogen fixation does not respond to an excess of phosphate in a simple fashion and that nitrogen fixation
20 may continue beyond the point at which the Redfield ratio of 16/1 is attained. Since the factors that govern phosphate, and iron concentrations, and water temperature differ, it is likely that the processes that permit nitrogen fixation to compensate for losses of fixed-N are complex and, may take longer than might be inferred from the original Redfield proposal.

3.6.2 Interpreting intercepts

There is considerable regional variability in the values of nitrate and phosphate intercepts in scatter diagrams of the two variables. We can find positive nitrate intercepts

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in the Mediterranean Sea and in portions of the North Atlantic (Wu et al., 2000) etc., and we can find phosphate values at 0 inorganic-N much higher than 0.25 μM in regions such as the Peruvian Upwelling and the Chukchi and East Siberian seas (Fig. 2; Codispoti et al., 1991). Positive nitrate intercepts at 0 P are often attributed to nitrogen
5 fixation. An alternative involving weak sedimentary denitrification and high N/P ratios in dust inputs has, however, been proposed for the extremely oligotrophic eastern Mediterranean (Krom et al., 2005). High phosphate values at 0 inorganic-N can reasonably be attributed to the effects of far-field and local denitrification. In the Chukchi Sea, Pacific waters entering via Bering Strait are already deficient in inorganic-N as
10 a consequence of external denitrification, and additional denitrification occurs locally (Devol et al., 1997). Early in the growing season (Fig. 3a) the phosphate value at 0 nitrate in these waters is ~0.7 μM, but we see a "march towards 0 phosphate" after the phytoplankton bloom in surface waters (Fig. 2b). If ammonium values were included we would even see some positive intercepts for inorganic-N during post-bloom conditions
15 (Fig. 2b). This brings us to the next complication, "luxury consumption". Redfield et al. (1963) suggested "luxury consumption" of phosphate to explain a phosphate-nitrate scatter diagram similar to Fig. 2b. Luxury consumption of inorganic-N can also occur when phosphate is depleted (Arrigo, 2005; Klausmeier and Litchman, 2004; Klausmeier et al., 2004; Krom et al., 2005). A similar situation exists with respect to carbon
20 uptake after depletion of one or more nutrients (e.g. Sambrotto et al., 1994). Early growing season conditions in the Chukchi Sea were quite similar in 2002 (Codispoti et al., 2005) to the 2004 conditions shown in Fig. 2a suggesting that the system "resets" itself on an annual basis. This is in line with theoretical considerations (Peinert et al., 1989) that suggest that the unusual nutrient ratios associated with "luxury con-
25 sumption" are transients that have little effect on the overall oceanic N/P ratio. The complication of "luxury consumption", therefore, introduces uncertainty into the use of nitrate and phosphate intercepts per se as indicators of "homeostasis" in the oceanic N/P ratio.

3.6.3 Variability in N/P ratios?

The variability in intercepts suggests that denitrification and nitrogen fixation are frequently out of balance regionally, and whatever homeostasis does exist is dependent to an extent on coupling of denitrification and nitrogen fixation via ocean circulation (e.g. Broecker and Peng, 1982, Codispoti, 1989). Chukchi Sea data (Fig. 2) provide an interesting juxtaposition of regional differences, because the Pacific waters that occupy the upper ~150 m overlie deeper waters that change little with respect to their nutrient concentrations and ratios (Codispoti et al., 2005) since entering the Arctic Ocean from the North Atlantic. Thus, we have waters in the upper ~150 m that have ratios of nitrate/phosphate <10 with a slope (Δnitrate/Δphosphate) of <13, overlying Atlantic waters with ratios of ~15. In contrast to the low ratios in the upper layers of the Chukchi Sea, regions where nitrogen fixation is thought to be important have high ratios. For example, regeneration ratios (Δnitrate/Δphosphate) in the Red Sea exceed 20 (Naqvi et al., 1986); N/P ratios in sinking particulate matter during a ~ decadal period of net nitrogen sequestion at the HOTS time-series station in the North Pacific subtropical gyre N/P were generally >16/1 and at times >40 (Karl et al., 2001); and nitrate/phosphate ratios in the Mediterranean Sea increase from ~22 to 28 (Krom et al., 1991; Krom, 2004) proceeding eastward from the Alboran Sea to the Cyprus Eddy. Finally, phosphate limitation is more prevalent in fresh water (including pristine fresh water lakes) than in the ocean (Howarth, 1988; Howarth and Marino, 2006, Falkowski, 2003). This raises the question of why the ocean is generally deficient in N and lakes deficient in P if one takes the view that a small excess of P is all that is required to maintain systems close to the canonical Redfield ratio.

Accurate and comprehensive nitrate/phosphate ratios for the world ocean have only been available for the last ~50–75 yrs, a period of considerable global change. What if these ratios slowly change and could have been higher in the past? We have already noted that the sinking organic matter associated with regions of high nitrogen fixation in today's ocean may have N/P ratios in excess of 20 (Naqvi et al., 1986; Karl

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et al 2001). Suppose, the ocean can have an average N/P ratio as high as 25 as suggested by Broecker and Henderson (1998) for glacial conditions. With average present-day nitrate and phosphate concentrations of 30 and $2\,\mu$M, respectively (Gruber and Sarmiento, 1997), a gedankenexperiment that has the nitrate/phosphate ratio
5 decrease from 25 to 15, would decrease nitrate concentrations by $20\,\mu$M (30/2=15; 50/2=25). With an oceanic volume of $1.35\times10^{18}\,\mathrm{m}^3$ (Menard and Smith, 1966) and recognizing that $20\,\mu\mathrm{M}=20$ millimoles $\mathrm{m}^3=0.28\,\mathrm{g\,N\,m}^3$, we arrive at a total nitrate removal of $3.8\times10^5\,\mathrm{Tg\,N}$, an amount that could sustain the imbalance in our "pro forma" budget for $\sim$1500 years!
10 The above calculations raise the issue of the constancy of N/P ratios, and whether Redfield's (1958) interpretation that the plankton control rather than respond to the oceanic nitrate/phosphate ratio (see Falkowski, 2000) is correct. The results that we have reviewed, so far, suggest that it is possible for nitrogen-fixers to produce organic material with N/P ratios higher than the Redfield ratio of 16/1. What about the rest
15 of the phytoplankton? We have already noted the phenomenon of "luxury consumption", but this process generally occurs within a community that does not export large amounts of organic material, and therefore does not have a large impact on observed subsurface regeneration ratios, that seem remarkably close to the 16/1 Redfield ratio. After a literature review Codispoti (1989) concluded that with possible exceptions in
20 coastal waters, there was considerable evidence for an average oceanic phytoplankton uptake ratio and a regeneration ratio close to 16:1. Even if we examine the data from the Chukchi Sea where considerable excess phosphate seems to exist, the "low" regeneration ratio of $\sim$13:1 (see above) can reasonably be attributed to the effects of sedimentary denitrification suggesting a ratio in the material exported from the photic
25 zone during the growing season similar to 16:1. These facts stand in contrast to an accumulation of evidence suggesting that phytoplankton groups can have uptake rates that stray far from the canonical Redfield ratio. For example, empirical laboratory data suggest that phytoplankton can be divided into superfamilies (Quigg et al., 2003) with markedly different N:P and C:P ratios and smaller but still significant differences in C:N

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ratios. Laboratory studies also suggest differences in N:P ratios that may arise from physiological variables (e.g. Klausmeier and Litchman, 2003). Field studies can produce similar results. For example, Arrigo et al. (1999) found an overall disappearance (∼uptake?) ratio in nitrate and phosphate replete Antarctic waters close to the Redfield
5   ratio, but when they broke down their data regionally, they found a *Phaeocystis* dominated community with a nitrate/phosphate disappearance ratio of ∼19 and a diatom dominated community with a ratio of ∼10. This study was followed by that of Sweeney et al. (2000) who found similar results to Arrigo et al's early in the growing season, but found that as the growing season progressed ratios in the diatom dominated community
10   became more "Redfieldian". These observations are in line with suggestions (Arrigo, 2005, Klausmeier et al., 2004) that nutrient ratios in phytoplankton can be affected by growth strategies and adjustment to environmental conditions in addition to the already noted "familial" differences. Arrigo (2005) suggested that "survivalists" have high N:P ratios, "bloomers" low N:P ratios, and "generalists" ratios close to the canonical Red-
15   field ratio. Since diatoms in the Ross Sea early in the growing season should be in the "blooming" mode, their low N:P ratios could, in hindsight, be anticipated. Klausmeier et al.'s (2004) views are similar, but they also noted that P-limited environments favor slightly less P allocation to assembly than N-limited or light-limited environments. Their model predicted that optimal phytoplankton N:P ratios could vary from 8.2 to 45.0, and
20   structural ratios from 7.1 to 43.3, with a median of 17.7, tantalizingly close to the canonical Redfield ratio. They suggest that ".... the canonical Redfield N:P ratio of 16 is not a universal biochemical optimum, but instead represents an average of species-specific N:P ratios." They also discuss the particularly high ratios in nitrogen-fixing species, noting an N:P range of 42-125 for *Trichodesmium* blooms. They provide a mechanistic
25   explanation for the high N:P and N:C ratios in nitrogen fixing phytoplankton that involves the need for more light-harvesting N rich machinery to power N fixation. They also suggest that the Redfield ratio is not a universal value based on either empirical data or their model, that it is possible that N:P ratios in the ocean could vary over time and that Broecker and Henderson's (1998) suggestion that the ratio could rise to 25

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during glacial periods is possible.

Here, we will take the position that the ocean-wide sinking flux of organic material in today's ocean is close to 16:1, and that nutrient replete "communities" do tend to export organic material with an N:P ratio similar to the canonical Redfield ratio. Given the high N:P ratios associated with nitrogen-fixation, however, one can wonder if an ocean in which nitrogen fixation was "easy" and in which denitrification is reduced might not have an N:P ratio close to 25. Broecker and Henderson (1998) suggested this possibility for a glacial ocean with an enhanced iron supply (see also, Wolff et al., 2006) that favored nitrogen fixation. In addition, we have already noted that one explanation for the high N:P ratios in today's Eastern Mediterranean involves decreased denitrification and a high N:P ratio in airborne inputs, and there is evidence to suggest that denitrification was reduced during glacial periods (e.g. Altabet et al., 2002; Ganeshram et al. 2002; Deutsch et al., 2004). Thus, it is possible that the overall oceanic N:P ratio can fluctuate significantly. A reasonable range for the Holocene might be ~14–25, values that can be found within large basins in today's ocean. In today's ocean, the evidence suggests that the N:P ratios in material exported from the photic zone are close to the canonical Redfield ratio except in zones of active nitrogen fixation.

3.6.4 Concurrent changes in P&N sinks may help stabilize N/P ratios

Piper and Codispoti (1975) suggested that increased denitrification might be associated with increased phosphate deposition in the form of phosphorite (mainly carbonate fluorapatite or CFA). Much has been learned about denitrification and about oceanic P deposition since the time of that paper, but the following quote is still worth considering. "*Ultimately any impoverishment of combined nitrogen, caused by increased denitrification should cause marine nitrogen fixation rates to rise or should cause respiration rates at depth in the ocean to decrease because of reduced primary productivity, or both. Over geologic time, the nitrogen/phosphorus ratio may be maintained reasonably constant by such a feedback mechanism in the nitrogen cycle, aided by the increased phosphorite precipitation which according to our proposal should accom-*

pany increased denitrification." (underlines added). At that time, most of the identified denitrification in the ocean, was associated with suboxic waters, and P&C noted the association of such waters in the Eastern Tropical Pacific with phosphorite deposits. Phosphorus diagenesis is complex, and some experiments have been interpreted as suggesting an enhanced P flux from such sediments (e.g. Ingale and Jahnke, 1994). Such observations tend to be at variance with other studies. For example, Compton et al. (2000) suggest that the Peru/Chile margin is the site of a "phosphorite giant" formation and that the present-day burial fluxes of P are high there and on the SW African Shelf, another site of water column denitrification (Kuypers et al., 2005). Babu and Nath (2005) show that P is enriched in sediments within the depth range of the OMZ in the Arabian Sea, and Schulz and Schulz (2005) present exciting results from the Namibian shelf suggesting that the sulfide oxidizing bacteria *Thiomargarita namibiensis* can sequester large amounts of phosphate and enhance phosphorite deposition. They suggest that close relatives such as *Beggiatoa spp.* that is also abundant in Namibian sediments, and *Thioplaca spp.* that occur in the upwelling zone off Chile and Peru may have a similar enhancing effect on phosphorite deposition. Because these bacteria can form thick mats, one might suspect that they are under-represented in cores, and bottom lander experiments that would also tend to avoid any CFA pavements that might be found in sediments overlain by suboxic waters (A. Devol, personal communication). One can also muse on the short-term effect of a "bottom lander" impact on bacterial mats that are rich in P. Confusion may arise also because anoxia and suboxia have quite different impacts on the oxidation state of iron. At the suboxic/anoxic interface in the Black Sea, for example, we see a phosphate minimum in the suboxic zone presumably from the uptake of P by particles formed via the oxidation by nitrate of reduced Fe and perhaps Mn that diffuses into the layer from the suboxic zone (Codispoti et al., 2005). Ganeshram et al.'s (2002) analysis of a core taken beneath suboxic waters in the Eastern Tropical North Pacfic suggests that the heavy δ^{15}N arising from water column denitrification occurs during interglacials and that P enriched layers in the sediments were also confined to the interglacials. They suggest similar conditions for the Arabian

Sea and Peru margins. We believe that the weight of the evidence does suggest a positive correlation between water column denitrification and phosphorite deposition. Because the glacial-interglacial changes in phosphorite deposition that Ganesharm et al. (2002) estimated were relatively small (equivalent to $\sim 3\,\mathrm{Tg\,N\,a^{-1}}$ using a 16/1 N/P atomic ratio) compared to the sink and source terms in the oceanic fixed-N budget (Table 1), their view was that this process had only a small impact on the oceanic N/P ratio, and a major point of their paper was that phosphate limitation would limit postulated increases in glacial nitrogen fixation assuming a constant Redfield ratio. With respect to the oceanic N/P ratio and the suggestion of P&C, this process would, indeed, help to maintain a constant ratio, but the effect would be small. One question worth investigating, however, is whether their estimate of the magnitude of the changes in phosphorite deposition might need to be revised in light of the results of Schulz and Schulz (2005), and given the limited number of cores that have been examined.

As is the case for upward increases in the fixed-N sink term, and in line with the "more we look, the more we find" theme of this paper, modern studies (Wheat et al., 1996) have shown that globally significant removals of P occur in association with mid-ocean ridge-flank hydrothermal processes. They produce an oceanic P budget that can be in deficit by by ~ 4–$14 \times 10 \times 10^{10}\,\mathrm{moles\,P\,a^{-1}}$ which (using a Redfield atomic N/P ratio of 16) translates into a deficit 9–$31\,\mathrm{Tg\,N\,a^{-1}}$. They suggest, "This situation would require a transient oceanic or terrestrial source term that potentially dominated during glacial periods, but not during interglacials."

To conclude, it is quite possible that increases in oceanic P removals may accompany increased denitrification and help to stabilize the oceanic N/P ratio, but whether the effect is minor or moderate will require further study.

3.7 The atmospheric carbon dioxide and sedimentary ^{15}N constraints

As already noted, Gruber and Sarmiento (1997) suggested that deficits of $\sim 100\,\mathrm{Tg\,N\,a^{-1}}$ in the post-glacial oceanic combined nitrogen budget maintained for a thousand years would deplete the oceanic fixed-N inventory by $\sim 30\%$ and change

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atmospheric CO_2 by 50 ppm, an amount that exceeds the observed variability during the entire Holocene. This argument is worth considering, but there are some complications that they did not consider explicitly. For example, they did not account for compensating changes in terrestrial sequestration, or for the possibility that C/N uptake ratios can vary. As outlined above, photosynthetic nitrogen-fixers have N:P and N:C ratios that are high relative to "Redfieldian" plankton. If the ocean can oscillate between strong and week nitrogen fixing phases such that the average N:P ratio can attain values of 20–25, during strong nitrogen fixation, the amount of C sequestered per N would decrease and this would dampen the effect on the atmospheric carbon dioxide record.

Another potential constraint on the oceanic fixed-N budget of the ocean arises from the sedimentary δ^{15}N record (Altabet, this volume). This record appears to undergo glacial-interglacial (orbital forcing) and ~millenium scale variability during glacial Dansgaard-Oeschger events (Altabet et al., 2002). The δ^{15}N record, during the Holocene, however, is more constant. Altabet (2006) suggests that to maintain constancy in the sedimentary δ^{15}N signal in the face of significant changes in the oceanic fixed-N inventory requires that the ratio of water column to sedimentary denitrification remains constant. This is because high isotope fractionation of N is associated with canonical water column denitrification and much lower fractionation is associated with sedimentary denitrification. Altabet suggests that maintenance of a constant ratio is unlikely. Once again, the basic idea has merit, but there are a number of complications. The real distinction should be between those fixed-N sinks that tend to have a large impact on the ^{15}N enrichments of the remaining fixed-N and those that have a small effect. To a large extent, this depends on whether the initial fixed-N substrate is depleted or remains abundant. Thus, during open-ocean canonical denitrification ($NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$) nitrate is often present in concentration of >15 μM and the remaining NO_3^- is heavily enriched in ^{15}N. In today's ocean, we can find examples of complete denitrification in the water column (e.g. Codispoti et al., 1986; Naqvi et al. 2000), although the percentage contribution of this type of denitrification is small.

What may be more important are the non-canonical water column pathways to N_2. These alternate pathways (Fig. 1) involve labile organic-N and NH_4^+ that are present in limiting concentrations. Therefore with respect to isotopic fractionation their effect on oceanic ^{15}N might be similar to sedimentary denitrification. To the extent (see calculations in Sect. 3.5) that water column N_2 production mimics sedimentary denitrification there would be an alleviation of the sedimentary ^{15}N record constraints. Moreover, the same processes that cause increases in water column denitrification (increased primary production, lower dissolved oxygen concentration) would, in many instances favor increased, sedimentary denitrification. In addition, the number of cores that have been analyzed in detail for $\delta^{15}N$ are relatively few; there is some evidence for the occurrence of water column denitrification in the North Pacific during the glaciations (Galbraith, 2006); there are diagenetic alterations of $\delta^{15}N$ that are not well-understood (Galbraith, 2006); the estimates for the fractionation of NO_3^- during canonical denitrification vary a bit (Brandes, et al., 1998; Altabet, 2006); and given the newly appreciated pathways for conversion of fixed-N to N_2 (Fig. 1) much needs to be done with regard to determining appropriate fractionation factors. This may also be true for the nitrogen-fixation source term and Naqvi (2006a) points out that although the denitrification term is larger, nitrogen fixation and denitrification both occur at significant rates in the water column of the Arabian Sea such that the $\delta^{15}N$ of local sediments is controlled partially by the ratio between water column denitrification and nitrogen fixation. Thus, while the sedimentary ^{15}N record is sufficient to erect the hypothesis that the oceanic fixed-N inventory has been ~ constant during the Holocene, it would probably be unwise, at this point, to let it color our estimates of the denitrification rate in today's ocean without further substantiation.

4 Reconciliation

Given the relatively stable climate during the Holocene, Gruber and Sarmiento (1997), Gruber (2004), and Altabet (2006), may well be correct in asserting that the oceanic

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fixed-N budget is ∼ balanced throughout the Holocene and that if any large changes occur, they must be of a duration short enough to be averaged out in the atmospheric CO_2 and sedimentary N records. The data reviewed herein, however, suggest a fixed-N sink, much larger than suggested in Gruber and Sarmiento's (1997) and Gruber's (2004) budgets. The following factors may permit reconciliation of these apparently divergent views:

4.1 Increasing the estimate of the oceanic nitrogen fixation rate

If the estimates of nitrogen fixation were raised significantly, the views of an approximate fixed-N inventory balance during the Holocene and of an oceanic fixed-N sink of >400 Tg N a^{-1} could both be accommodated. In this regard, it is worth noting that the oceanic nitrogen fixation rate has increased considerably in recent years. More than a decade ago, Codispoti (1989) suggested that an increase in the oceanic nitrogen fixation rate would be needed to balance the fixed-N budget, and since that time the consensus estimate has increased by a factor of 4–5. Recently, an approximate doubling of the incubation based estimates has been suggested in order to account for previously neglected contributions of smaller sized nitrogen fixers (Montoya et al, 2004), and Davis and McGillicuddy (2006) suggest that the abundance of the larger canonical nitrogen fixer *Trichodesmium* has been underestimated. In addition, significant nitrogen fixation may occur in close proximity to zones of water column denitrification (Deutsch et al., 2005; Naqvi, 2006a) that is difficult to detect with bulk parameters because the signal is swamped by higher denitrification rates. The signal does appear in some models (Deutsch et al., 2005) and in vertical δ^{15}N-NO$_3^-$ distributions in the Arabian Sea where unusually "light" NO$_3^-$ overlying unusually heavy δ^{15}N NO$_3^-$ occurs (Brandes et al., 1998; Naqvi, 2006a; Devol et al., 2006a). Brandes et al. (1998) suggest that nitrogen fixation in the Arabian Sea is ∼6 Tg N a^{-1} or about 20% of the water column rate for canonical denitrification. Interestingly, because of the high N:P and N:C ratios during nitrogen fixation, Devol et al. (2006a) suggest that the decomposition of

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the biogenic material produced by this nitrogen fixation could account for as much as 57% of the "extra excess N_2" found in the Arabian Sea that has caused an increase in the estimate of the water column denitrification rate (see above). Finally, Coles and Hood (this volume) point out that some models of nitrogen fixation based on N* will

5   actually yield net rates of nitrogen fixation and not the gross rates employed in our budgets (Table 1), because of denitrification within the model domain (e.g. sedimentary denitrification in the North Atlantic).

   Most direct estimates of nitrogen fixation rates in the ocean have been confined to the photic zone, yet genetic studies suggest that the capability for nitrogen fixation is

10   widespread throughout the water column. Zehr et al. (1998) for example have shown that the genes that support nitrogen fixation can be found within zooplankton and that these genes differ significantly from the genes found in free-living nitrogen fixers. Earlier experiments with shipworms showed that in some ways they were analogous to termites insofar as their symbiotic flora fixed-N when they were fed a diet of wood (Car-

15   penter and Culliney, 1975). Mehta et al. (2003) present genetic data suggesting that nitrogen fixation may be enhanced in the vicinity of thermal vents, etc. Two quotes from Zehr et al. (1998) that are worth considering are (1) "This report shows that there are far more diverse nitrogen-fixing populations and diverse habitats which can support nitrogen fixation in the open ocean than previously documented." and (2) "The intriguing

20   finding that nitrogen fixation in the open ocean may occur in marine invertebrate guts is analogous to nitrogen fixation in guts of terrestrial insects and marine shipworms. Sequences of this cluster are not found in the bulk water samples, indicating that the organisms from which these sequences were derived may be permanent residents of the zooplankton gut and may even be symbiotic with zooplankton." Therefore one has

25   to ask whether or not expanding the horizons of studies of oceanic nitrogen fixation from photic zone hotspots, to the remaining >97% of the oceanic volume may lead to greatly increased estimates of oceanic nitrogen fixation.

4.2 The Holocene to Anthropocene transition

As already mentioned, Altabet et al. (2002) suggest that the δ^{15}N record in cores from the Arabian Sea suggest some sharp (~millennial scale) changes during the last glaciation. Thus, relatively rapid changes in the oceanic fixed-N inventory may be possible. The question then arises, of how to compare the sedimentary Holocene record with relevant observations from the ocean. Here it is worthwhile noting that a widely adopted and reasonably accurate nitrate method did not become available until the 1960s and oceanographic dissolved oxygen methods were not rationalized until that time as well (Carritt and Carpenter, 1967). Thus, our oceanographic observations are restricted to the last ~50 years, a period when human impacts on the planet have become ever more important. Some investigators suggest (e.g. Crutzen, 2002; Crutzen and Ramanathan, 2000) that we have transitioned out of the Holocene in which change may have been dominated by orbital forcing to the "Anthropocene" where the activities of the human race are imposing significant and unprecedented types of forcing on the planetary ecosystem. It is in the nature of exponential growth that the latter doublings tend to have the greatest impact, and the last 50 years, and the next several decades, may be the period of the greatest increase in human population that will ever occur. As one example of a process that may impact ocean ecosystems, bottom trawling sweeps an area equal to ~25% of the global continental shelf every year (Watling and Norse, 1998), and yet there are no studies that directly address how this process might effect sedimentary denitrification. Anthropogenic additions of nutrients to the coastal ocean must also have some effect, and Naqvi et al. (2000) suggest that such inputs may have increased denitrification and led to extremely high nitrous oxide production rates over the West Indian Shelf, etc. Thus, it is not clear how applicable paleo records are to an ocean that is experiencing significant and unprecedented anthropogenic forcing.

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5 Conclusions

A review of the literature suggests that there is no reason to reduce the oceanic denitrification rate below ~400 Tg N a^{-1}, and that this rate may be conservative. The three most likely factors that could reconcile this rate with paleo records are as follows:

1. Oceanic nitrogen fixation has been significantly underestimated.

2. There is a significant mis-match between the sedimentary record and ocean observations with the former largely confined to the Holocene and earlier, and the latter confined to the Anthropocene: today's ocean may be in a transient state.

3. Century scale and shorter oscillations occur and are averaged out in the paleo record (Altabet, 2006; Gruber and Sarmiento, 1997).

In addition, plausible changes in oceanic N/P and N/C ratios could mute the effects that imbalances in the oceanic fixed-N budget would have upon the sedimentary and atmospheric record, and the co-occurrence of water column nitrogen fixation and denitrification may complicate interpretation of the sedimentary record.

It is difficult to review the recent literature on denitrification and nitrogen fixation and not suspect that the phrase "the more we look, the more we find" will continue to apply at least for the next few decades. Given these exciting discoveries, the need for expanding our geographic and intellectual horizons seems evident. To paraphrase a famous quote, the nitrogen cycle is more complicated than we imagined a few years ago, and perhaps more complicated than it is possible for us to imagine! More research is required to provide data and model outputs that will help our beleaguered imaginations!

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Table 1. Simplified Pro-Forma[1] Present-Day Oceanic Fixed-N Budgets.

Process	G&S 2002	G2004	C et al. 2001	C2006
Nitrogen Fixation	132	135	132	135+++
Benthic Denitrification	95	180	300	300+
Ratio Benthic/Water Denit.	1.2	3.6	3.5 50	3.5 50
Water Column Denit.	80	50	150	150++
Totals (all sources&sinks)	**+34**	**+5**	**-188**	**-234**

[1]This table is simplified insofar as the smaller sources and sinks are omitted except in the totals. "Pro-forma" is used to suggest that all of these budgets are going to be shown to be incorrect as we learn more. G&S 2002 = Gruber and Sarmiento, 2002; G2004 = Gruber, 2004; C et al. 2001 = Codispoti et al., 2001; C2006 = this paper. The plus signs indicate the author's speculations about how much the fixation and denitrification terms will need to be increased as we learn more. The greater deficit in the C 2006 budget vs the C et al. 2001 budget arises from discussions at the SPOT-ON meeting that suggest that the atmospheric source term in Codispoti et al. (2001) was too large. The arrows and the value "50" indicate that with respect to isotopic fractionation ∼1/3 of water column denitrification may behave like sedimentary denitrification. The "benthic"/water column denitrication ratios are included because the isotopic budget of Brandes and Devol (2002) suggests that benthic (low fractionation) denitrification should be >3 times higher than water column (high fractionation) denitrification. These budgets include continental shelves, but exclude estuaries.

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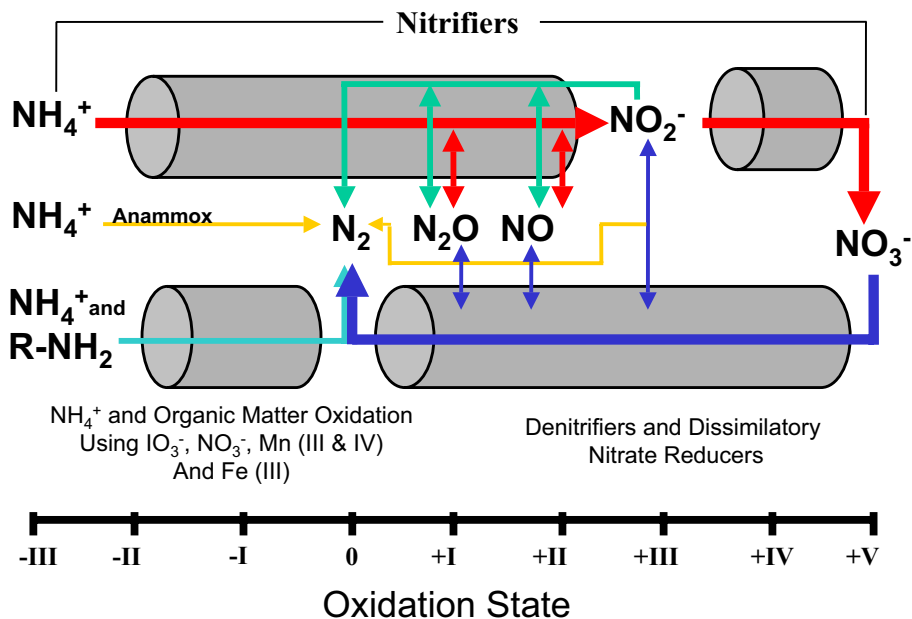Printer-friendly Version

Interactive Discussion

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Fig. 1. This figure is re-drawn and updated from Codispoti et al. (2005). The suite of reactions supporting canonical denitrification are shown by the broad red (nitrification) and blue (canonical denitrification) arrows. The green line indicates a denitrification process that is enhanced at low oxygen concentrations during the first stage of nitrification and that is associated with enhanced N_2O production. This process might also produce N_2. During these three processes, the intermediates, N_2O, NO, and NO_2^- can leave the cell and be exchanged between nitrifiers and denitrifiers. The NO_2^- produced can also support the anammox pathway (yellow arrows) in which NH_4^+ is oxidized to N_2 and NO_2^- is reduced to N_2. A review of the literature also suggests that oxidation of organic-N or NH_4^+ by NO_3^-, iodate (IO_3^-), oxidized metals such as Mn (III&IV), Fe (III) and various oxidized trace metals can also produce N_2 (light blue arrow). Not shown is the possibility that the oxidation of Mn (II) by NO_3^- may also produce N_2 (Luther et al., 1997).
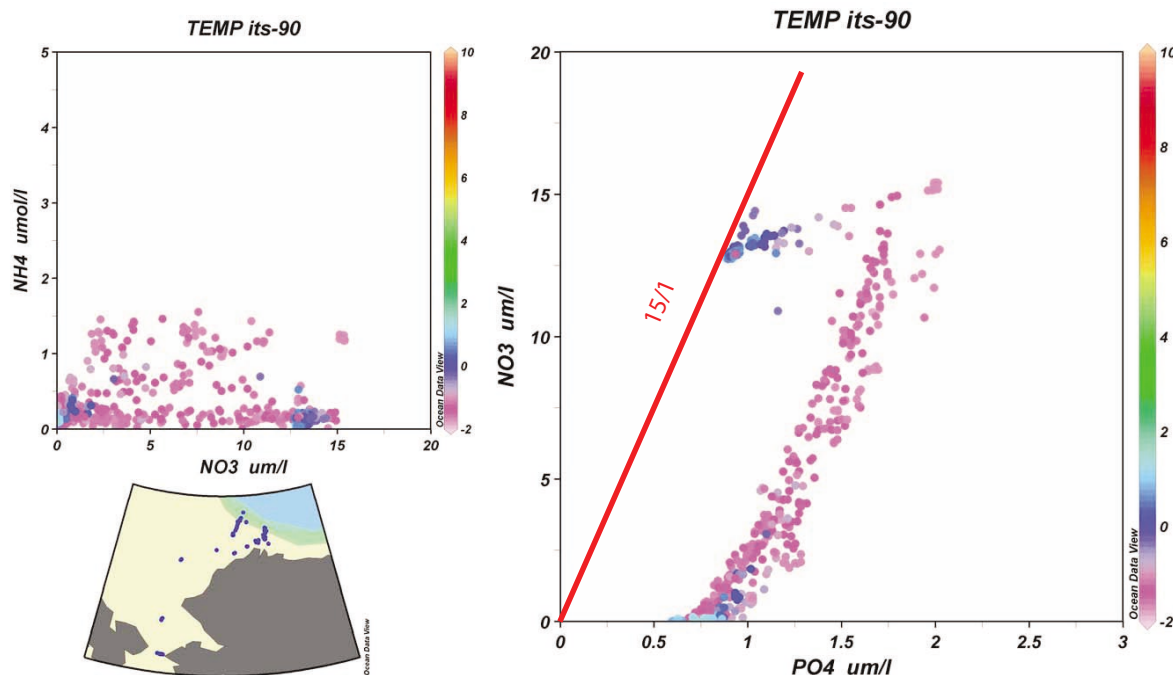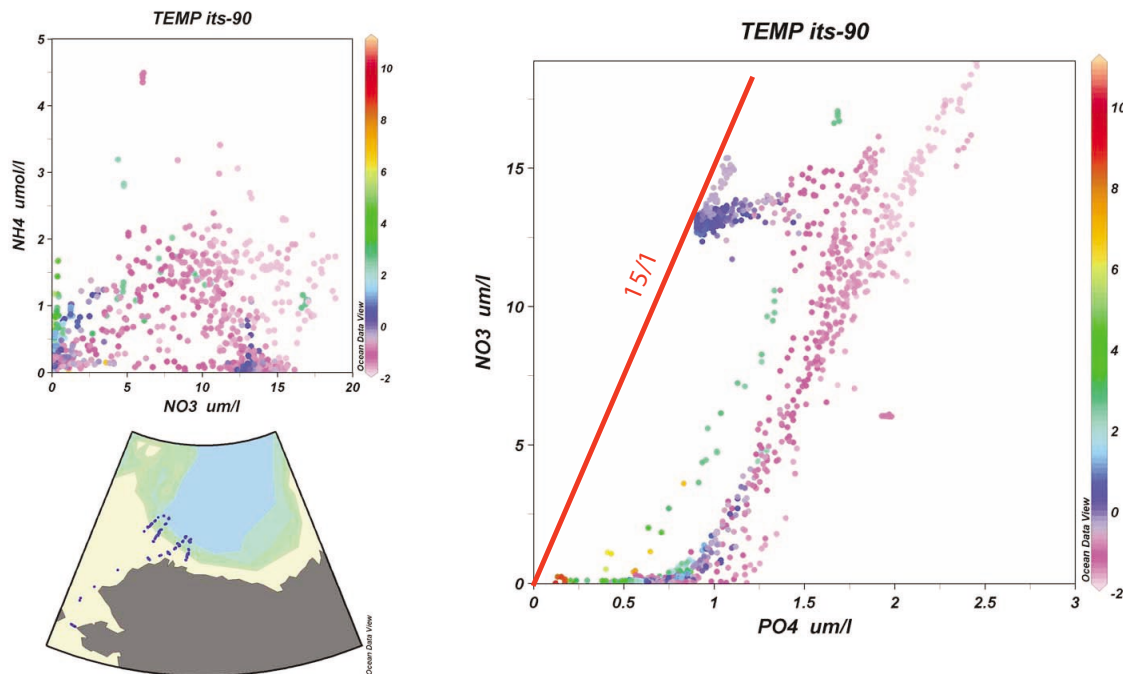
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Fig. 2a. Nitrate-ammonium and nitrate-phosphate scatter diagrams (concentrations in μM) from data collected in the Chukchi Sea during May–June 2004 (U.S.C.G.C. Healy, cruise HLY 04-02). Station locations are shown in inset chart. Water temperature color scale is on the right.

Fig. 2b. Nitrate-ammonium and nitrate-phosphate scatter diagrams (concentrations in μM) from data collected in the Chukchi Sea during July–August 2004 (U.S.C.G.C. Healy, cruise HLY 04-03). Station locations are shown in inset chart. Water temperature color scale is on the right.