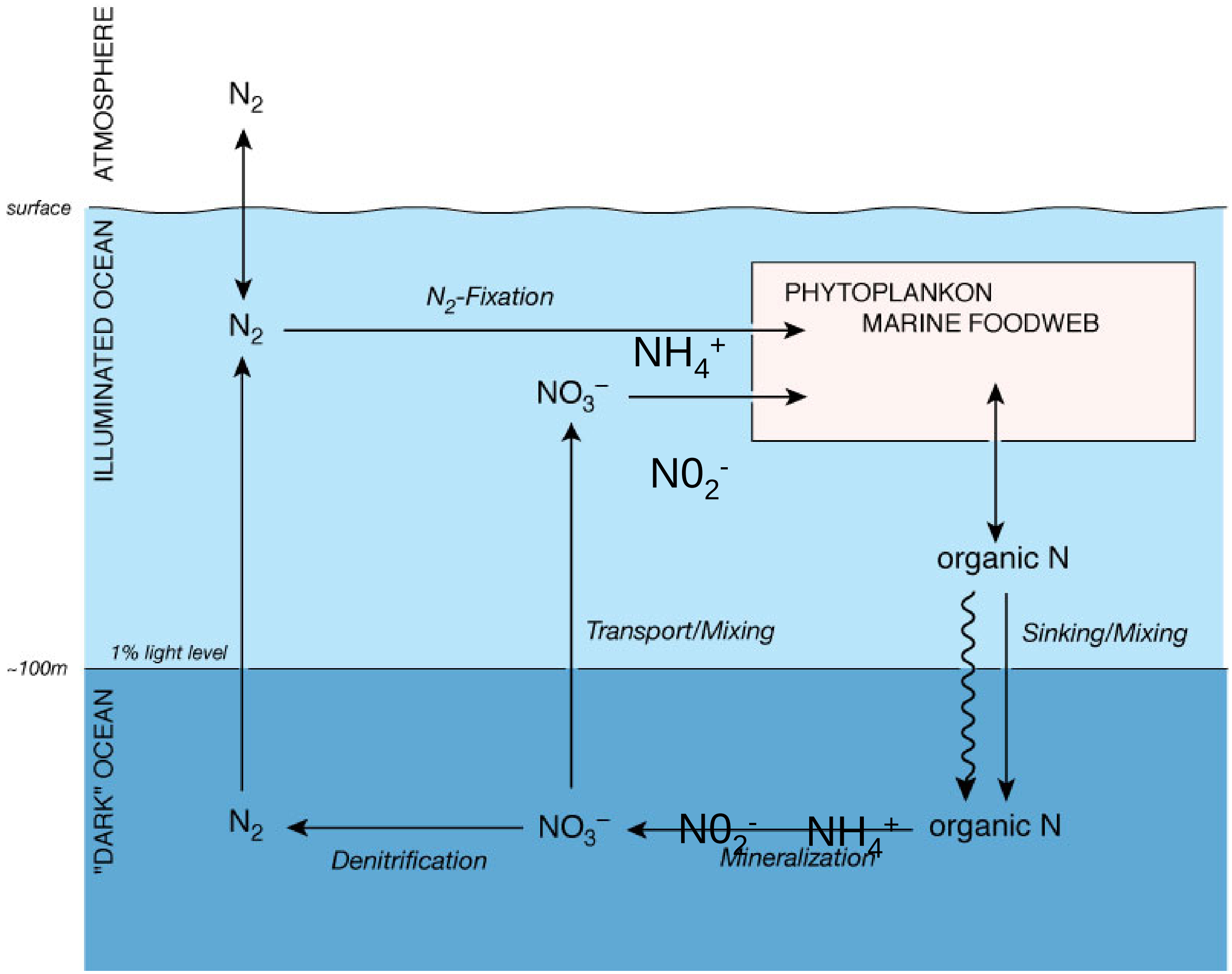
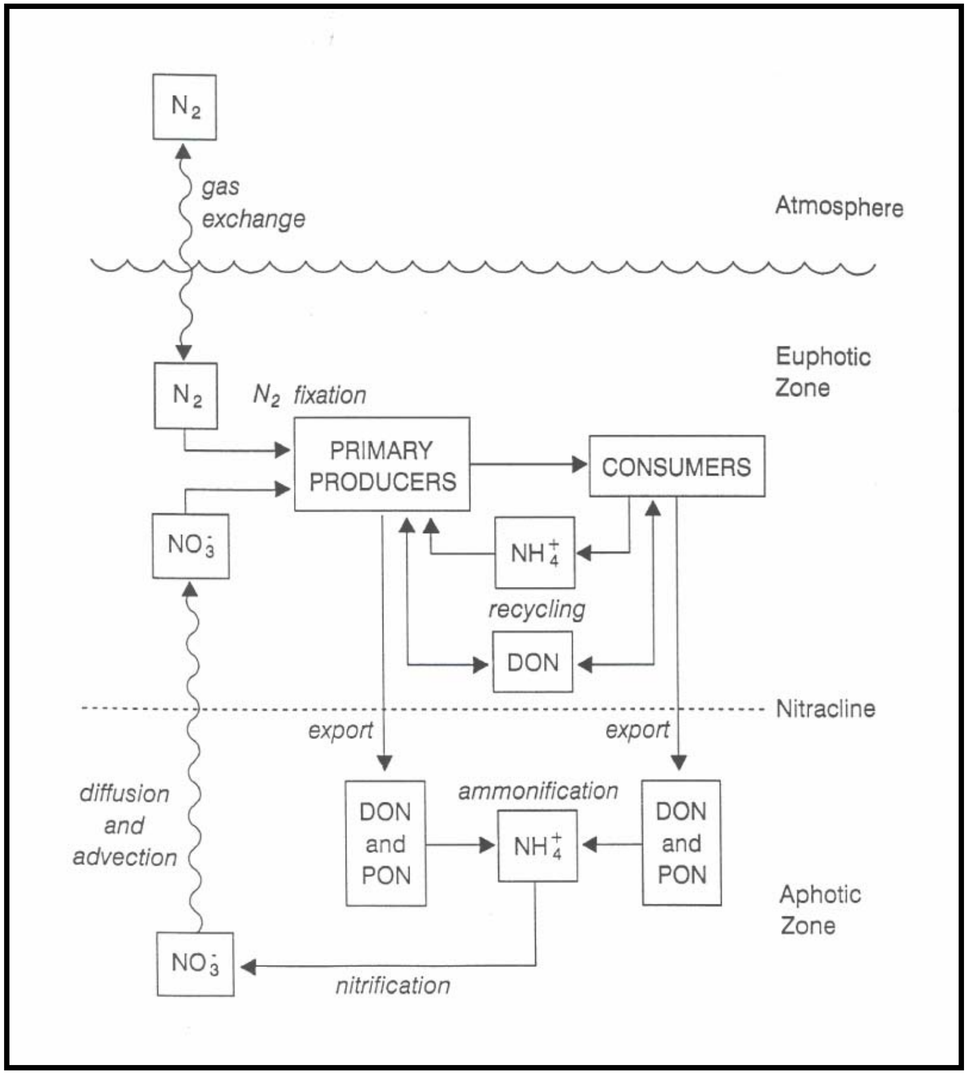
Nitrogen Cycling in the Sea



Summary

- The oxidation-reduction potential of N facilitates the role of N- containing compounds as electron donors and acceptors.
- The principal transformations of N in the ocean include both assimilatory processes (uptake and N_2 fixation), and dissimilatory processes (ammonification, nitrification, denitrification)
- Total amount of fixed nitrogen in an ecosystem depends on the balance between N_2 fixation and denitrification
- Ocean nitrogen budgets remain highly uncertain

Pools and pathways of nitrogen in the sea



Nitrogen as a nutrient (nitrogen assimilation):

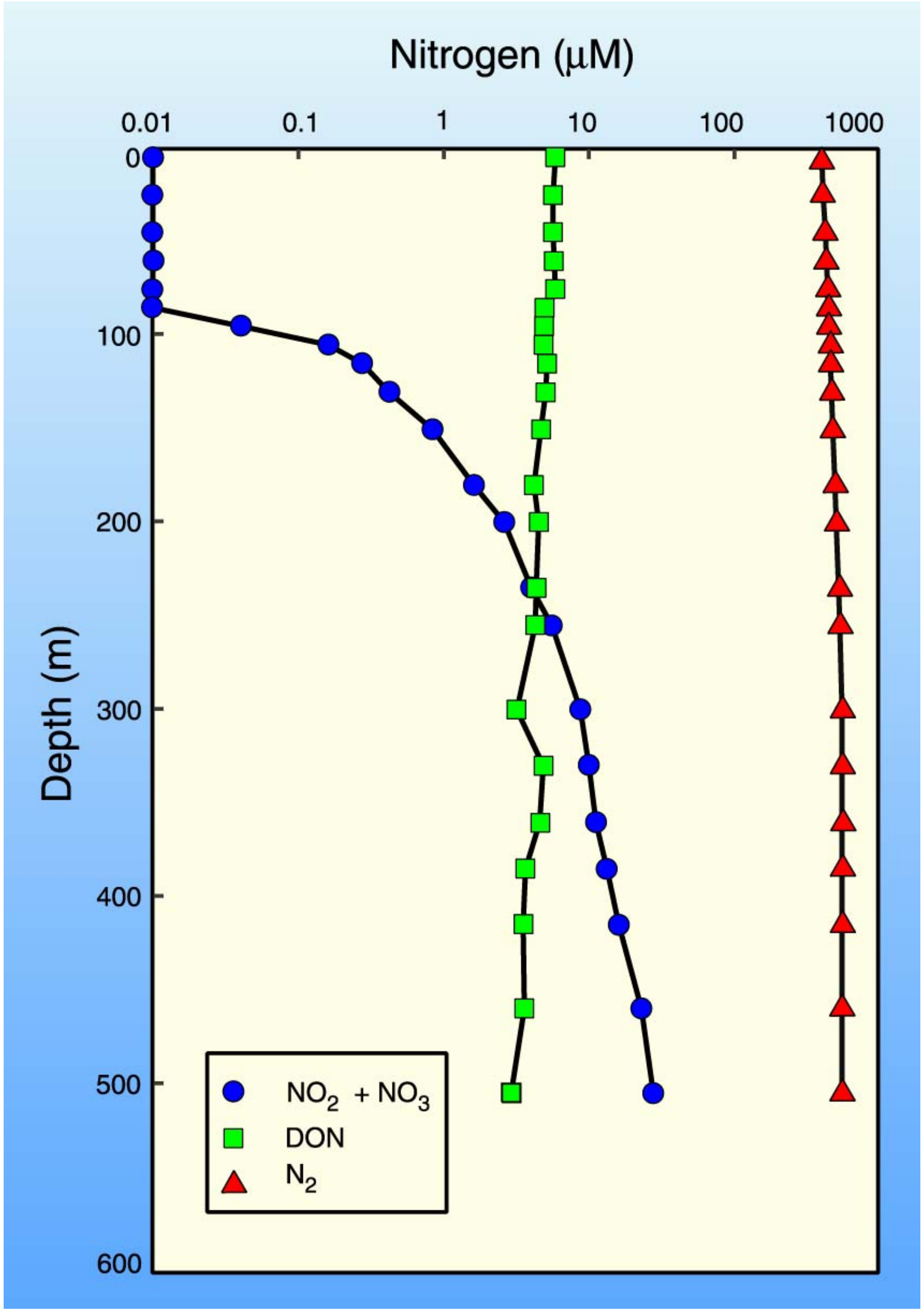
NO_3^-
NO_2^-
NH_4^+
DON
N_2--only selected groups of prokaryotes use N_2

Nitrogen as an electron donor:

NH_4^+ : ammonium oxidation/annamox
NO_2^-: nitrite oxidation
DON : heterotrophic catabolism

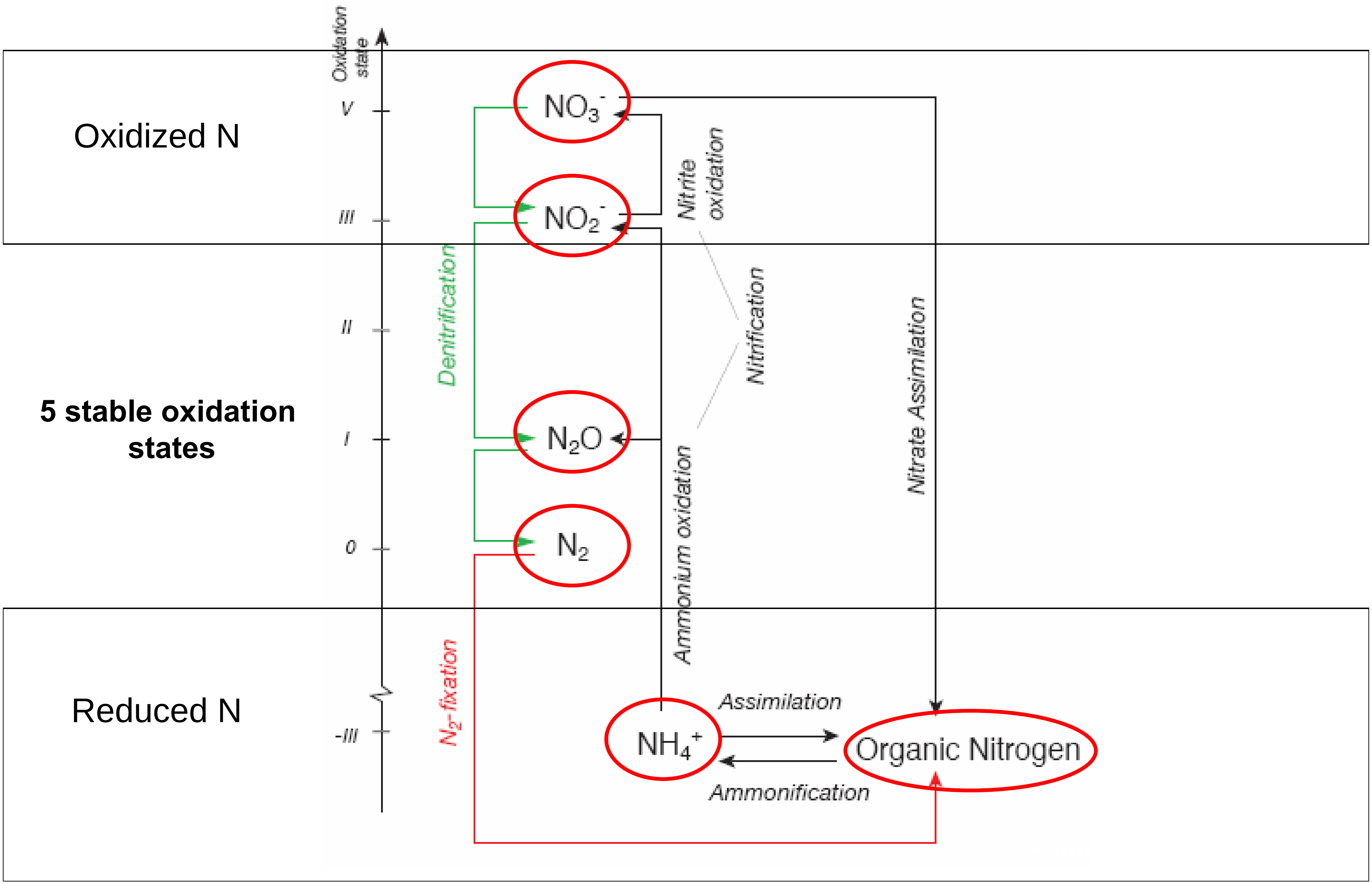
Nitrogen as an electron acceptor:

NO_3^- : denitirification
NO_2^- : denitrification, annamox
NO: denitrification
N_2O: denitrification



- NO_3^- : concentrations range nanomolar to micromolar
- N_2 : biologically inert (mostly); concentrations ~600 μmol L^{-1}
- NH_4^+ : rapidly consumed in the photic zone, concentrations typically nanomolar
- DON : concentrations typically 4-6 μmol L^{-1} but mostly unavailable for plankton growth

Redox states and chemical forms of nitrogen



Nitrogen assimilation

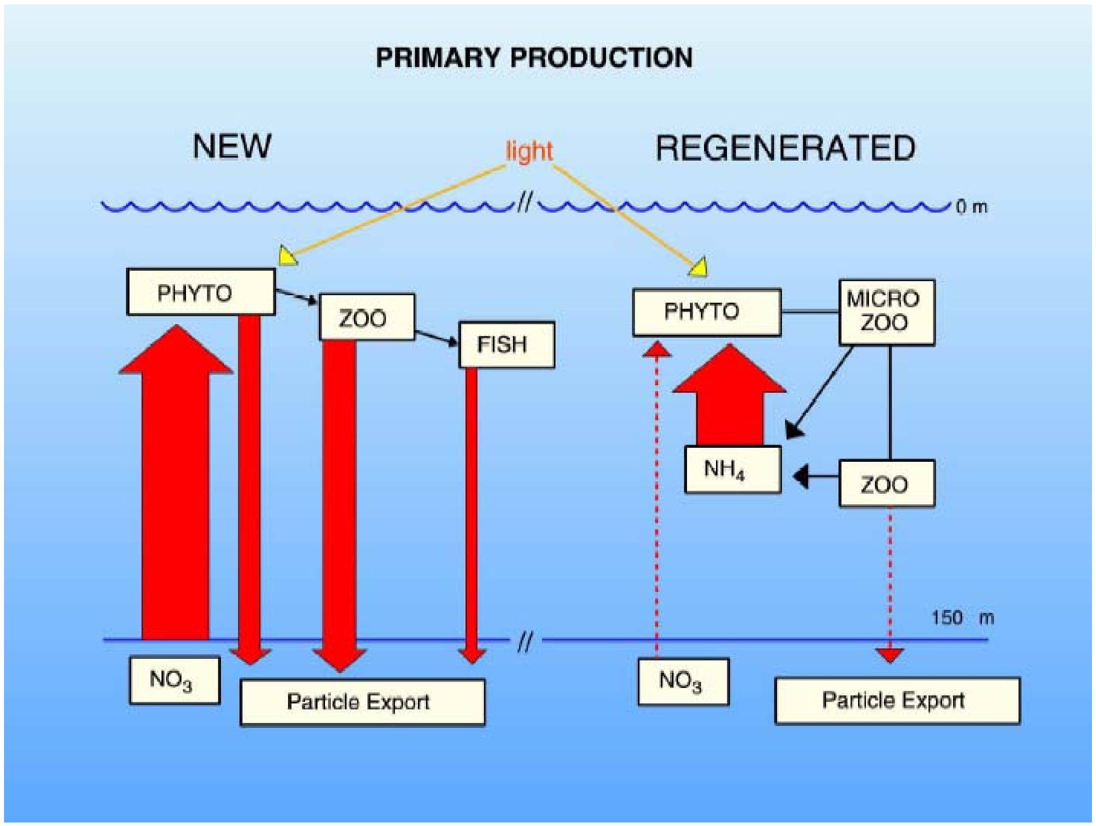
- **Nitrogen is an essential nutrient found in amino acids, protein, and nucleic acids.**
- **Nitrogen is assimilated by both autotrophs and heterotrophs.**
- **In large areas of the world's ocean, nitrogen limits primary production.**
- **Nitrogen in organic matter is reduced; however, most "fixed" nitrogen in the ocean is oxidized (nitrate) and thus requires reductant for assimilation into biomass.**

Energy and reducing power required for assimilation of various N compounds

Substrate	Enzyme	Reaction	Electrons	ATP
N_2	Nitrogenase	$N_2 \rightarrow NH_3$	8	16
NO_3^-	Nitrate reductase	$NO_3^- \rightarrow NO_2^-$	2	0
NO_2^-	Nitrite reductase	NO_2- $\rightarrow NH_3$	6	0
NH_3	Glutamine synthetase Glutamate synthetase	$NH_3 \rightarrow$ Glutamate	2	1

New and regenerated production

1) *new* production supported by external input of N (e.g. NO_3^- and N_2),
2) *recycled or regenerated* production, sustained by recycling of N.



Assumes steady state:
Input of new N is balanced by export of N.

Not all “new” nutrients are introduced from below the euphotic zone

- Atmospheric deposition (both dry and wet) can form an important source of nutrients.
- Advection: lateral input of nutrients
- N_2 fixation

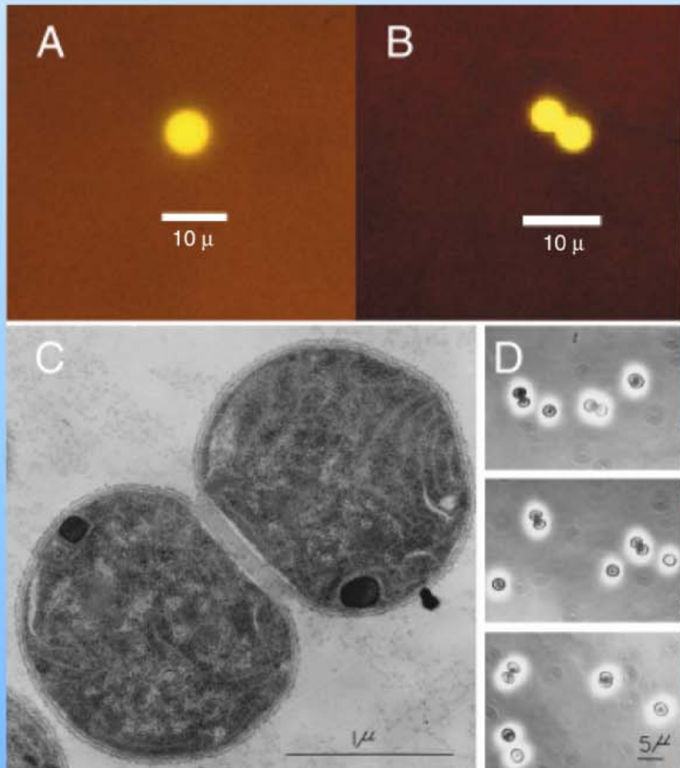
- N_2 fixation is the primary mode of introducing “fixed” nitrogen to the biosphere.

- N_2 fixation converts N_2 to NH_3; process is exclusively mediated by prokaryotes

- Energy expensive to break triple bond in N_2

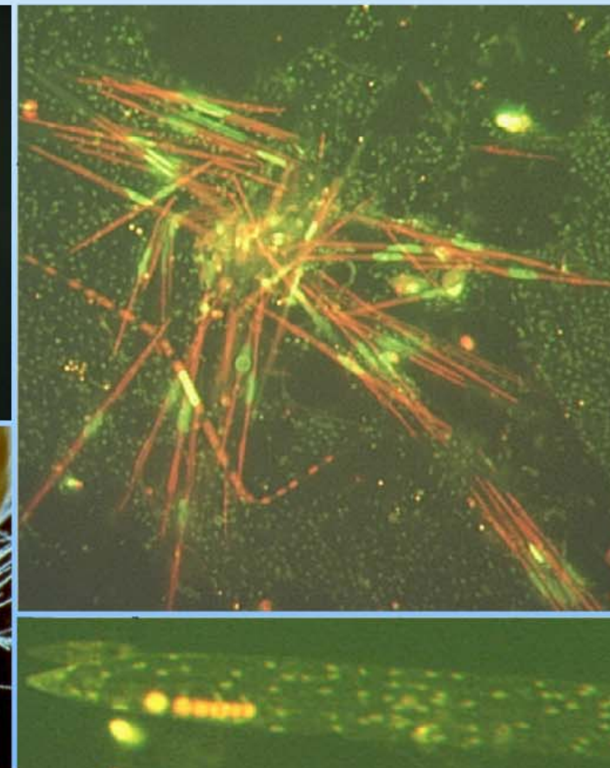
$$\mathbf{N_2 + 8H^+ + 8e^- + 16\ ATP \rightarrow 2NH_3 + H_2 + 16ADP + 16\ PO_4^{3-}}$$

The Rogues Gallery



Pico

Tricho



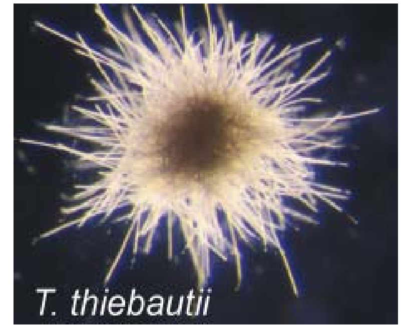
Diatomic diatom

Table 1. Annual particulate nitrogen export fluxes at Station ALOHA.

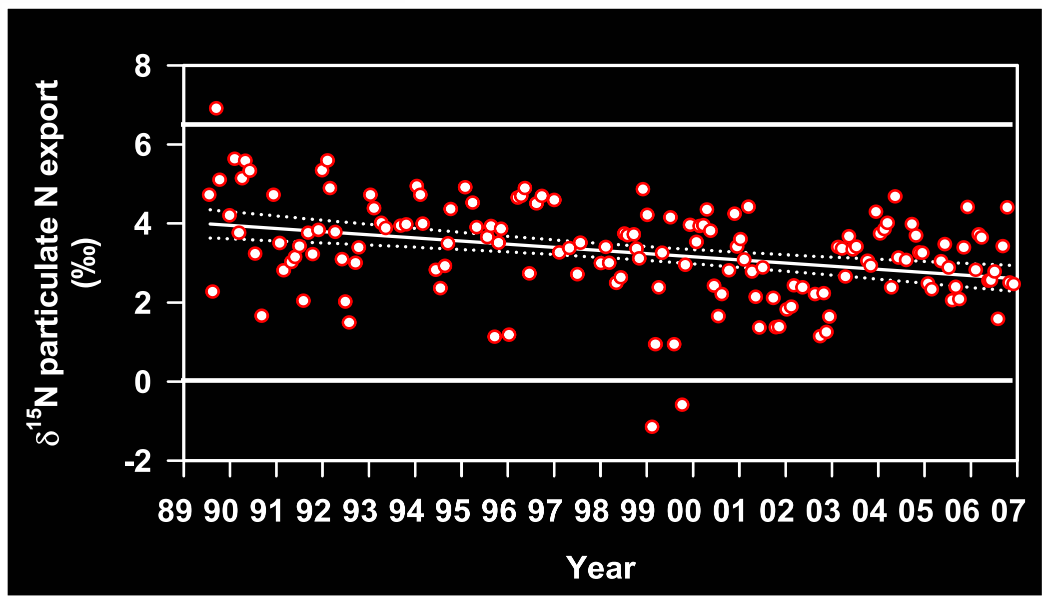
Year	Total PN flux (mmol N m^{-2} yr^{-1})	$\delta^{15}N$-F_{PN}* (‰ vs. air N_2)	N_2-supported fraction (%)	Contributions to flux (mmol N m^{-2} yr^{-1})	
				N_2	NO_3^-
1990	145	3.85	41	59	86
1991	111	3.21	51	56	55
1992	80	3.58	45	36	44
1993	86	4.15	36	31	55
1994	80	3.81	41	33	47
1995	81	3.76	42	34	47
1996	87	4.04	38	33	54
1997	113	3.29	49	56	57
1998	116	3.21	51	59	57
1999	122	2.03	69	84	38
2000	113	3.05	53	60	53

* Flux-weighted annual average.

Dore et al. (2002)

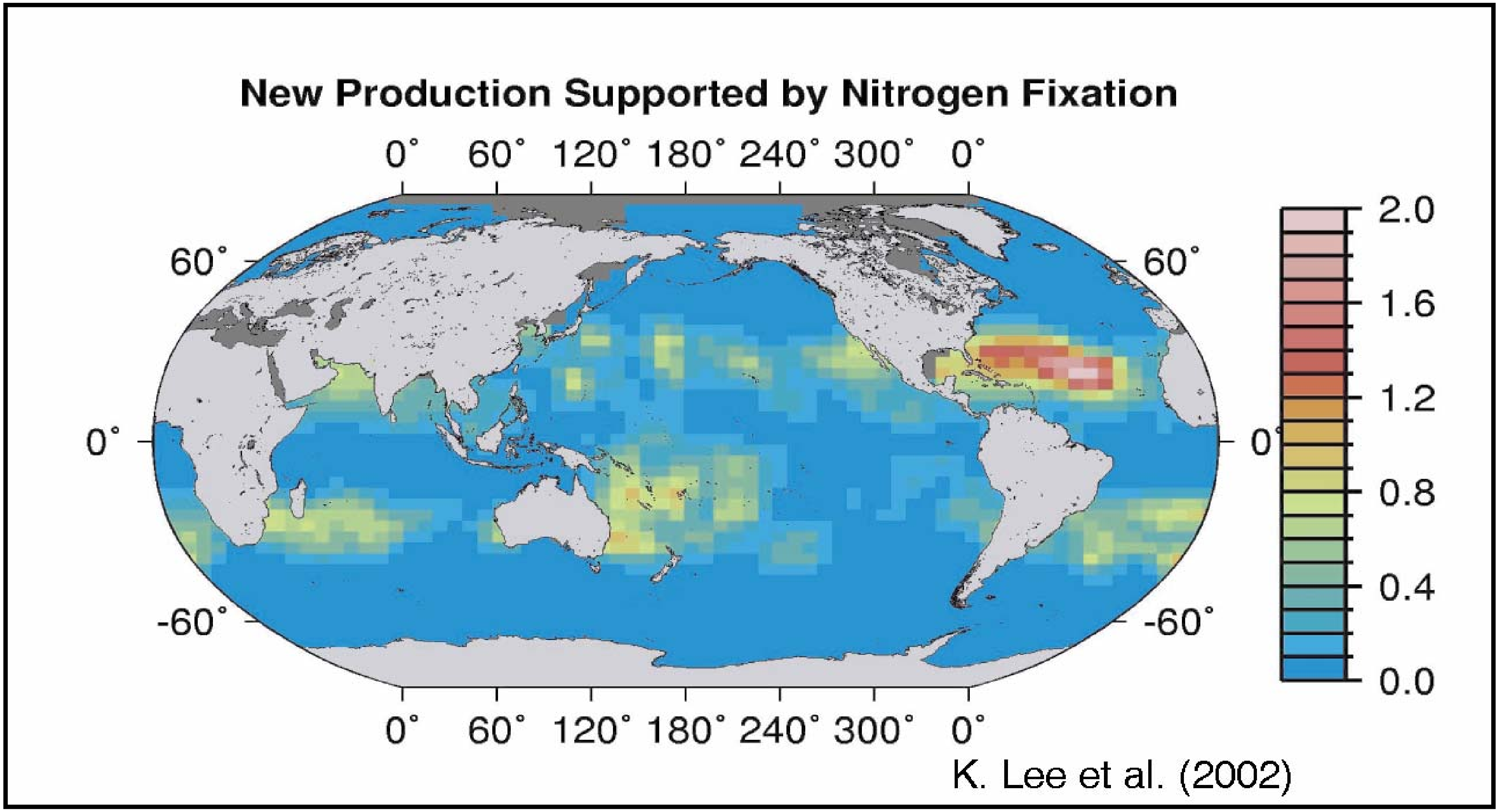


At Station ALOHA, N_2 fixation appears to contribute ~30-84% of new production-note that this is <5% of total production



NO_{3-}

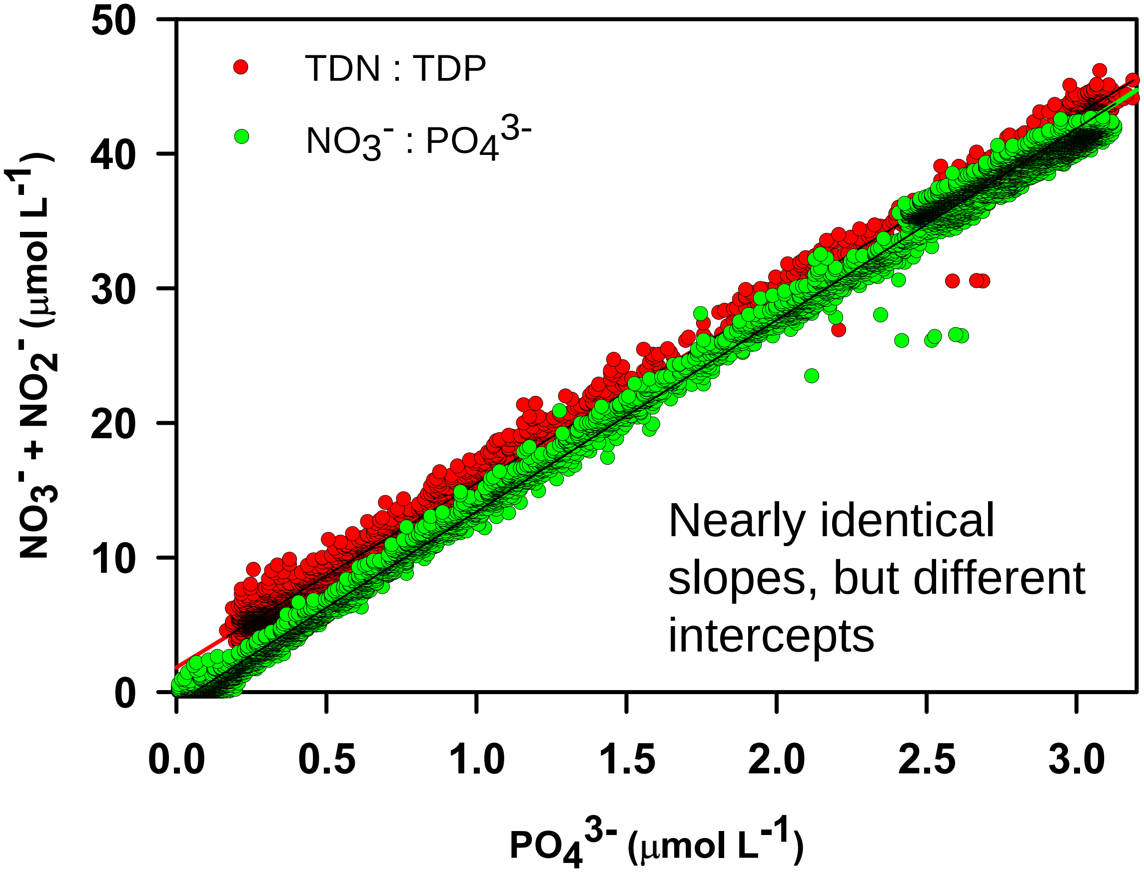
N_2



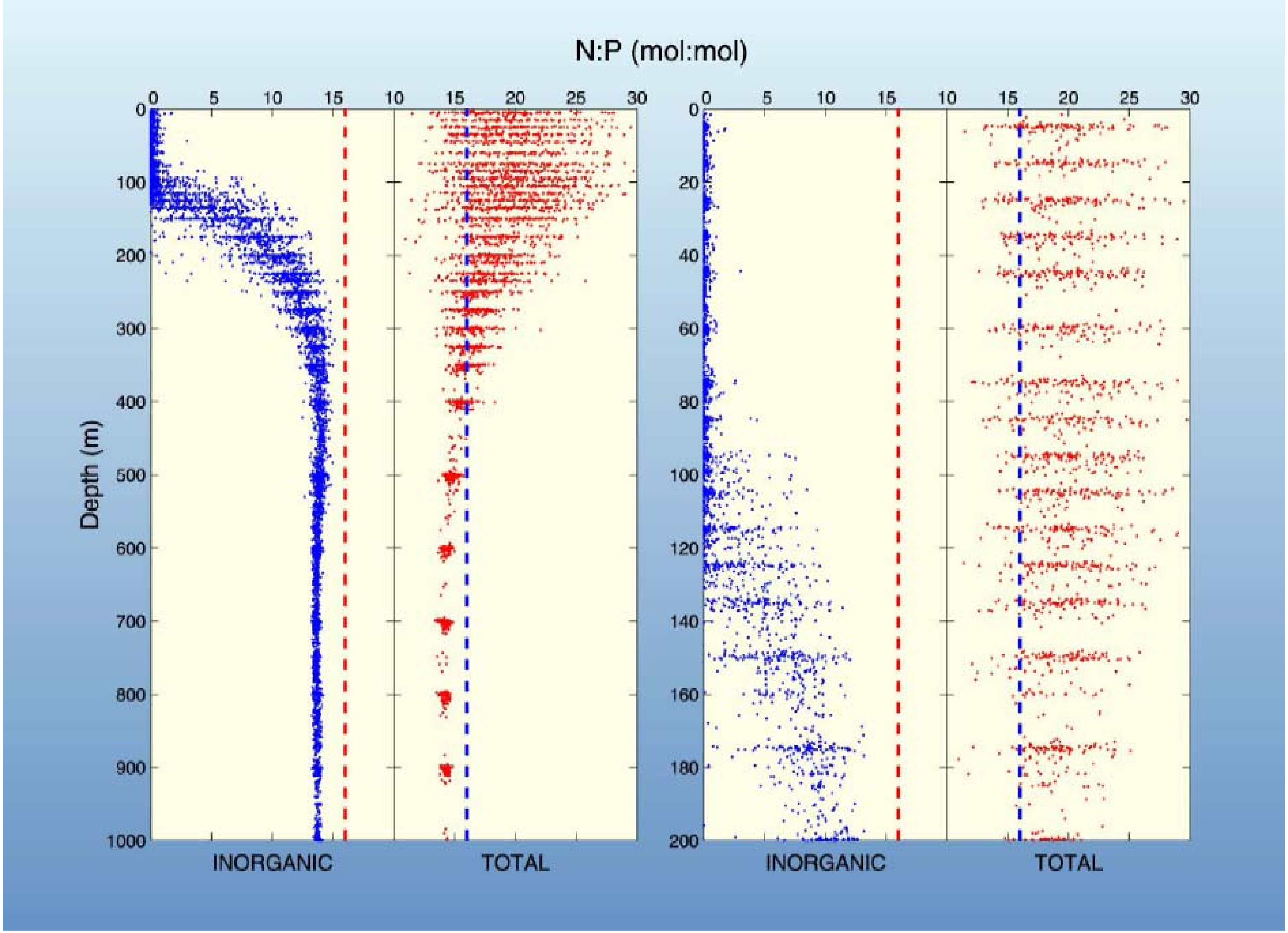
Global estimate of N_2 fixation based on DIC drawdown in NO_3-depleted waters averages 0.8 ±0.3 Pg C yr^{-1}

N_2 fixation may also play an important role in controlling nutrient stoichiometry in the sea

$TDN = 14.57(TDP) + 1.5$



$NO_3^- = 14.62\ (PO_4^{3-}) - 1.08$



N:P (mol:mol)
0 5 10 15 10 15 20 25 30
0 5 10 15 10 15 20 25 30
Depth (m)
0 100 200 300 400 500 600 700 800 900 1000
0 20 40 60 80 100 120 140 160 180 200
INORGANIC
TOTAL
INORGANIC
TOTAL

Dissimilatory nitrogen transformations

$$NH_2OH \rightarrow NO \rightarrow N_2O$$

Nitrification: $NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$

Denitrification: $NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$

Anammox: $NO_2 + NH_4^+ \rightarrow N_2 + 2H_2O$

Aerobic remineralization of organic matter:

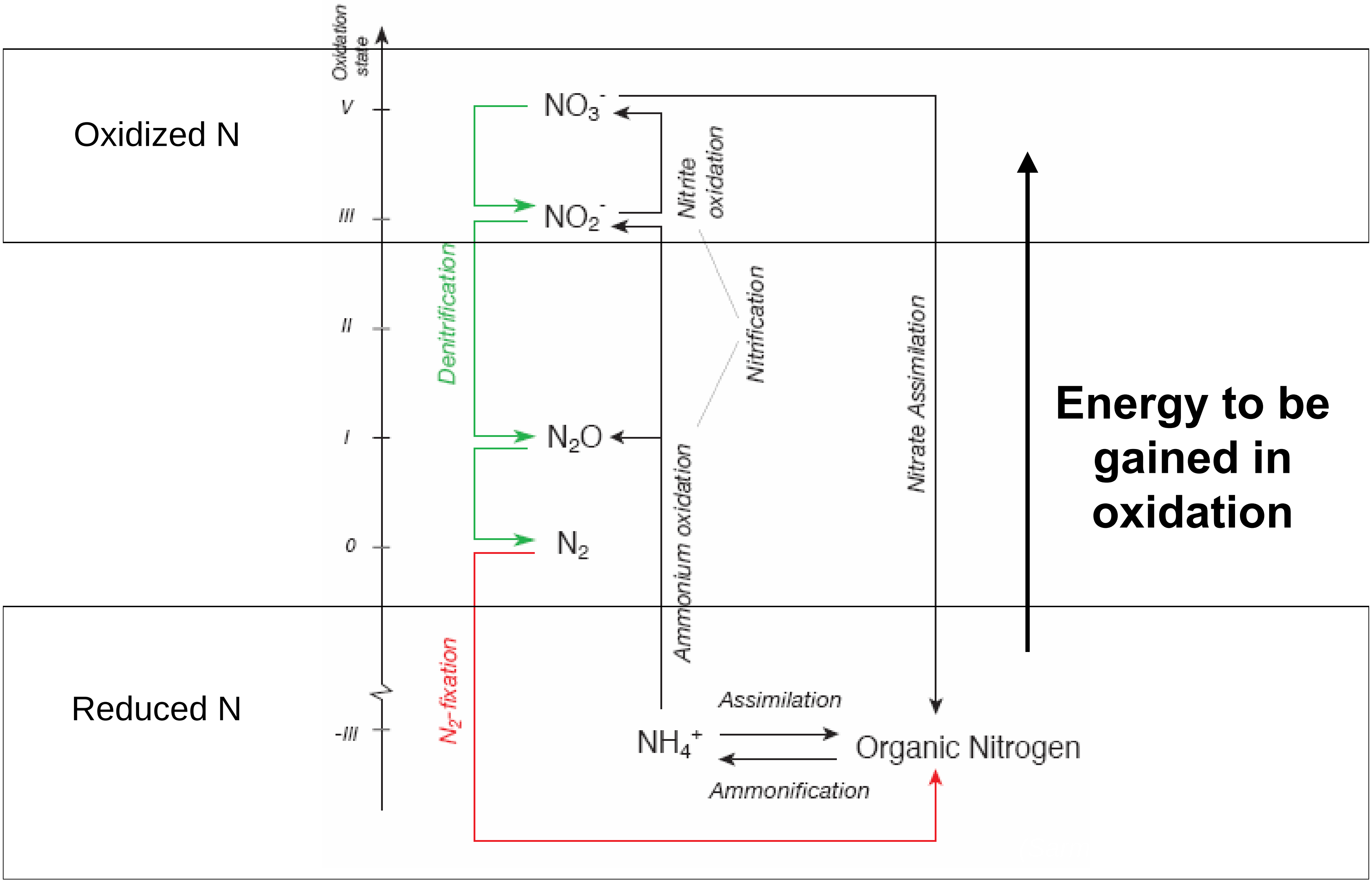
$$(CH_2O)_{106}(NH_3)16H_3PO_4 + 138O_2 \Rightarrow 106CO_2 + 122H_2O + 16HNO_3 + H_3PO_4$$

Consumes O_2 Produces CO_2 Produces nutrients

This reaction does not show the complex series of reactions required to transform organic nitrogen to nitrate (ammonification, ammonium oxidation, nitrite oxidation)

$$DON \rightarrow NH_4^+$$
$$NH_4^+ \rightarrow NO_2^-$$
$$NO_2^- \rightarrow NO_3^-$$

Redox states and chemical forms of nitrogen



Nitrification

$$NH_2OH \rightarrow NO \rightarrow N_2O$$

Nitrification: $NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$

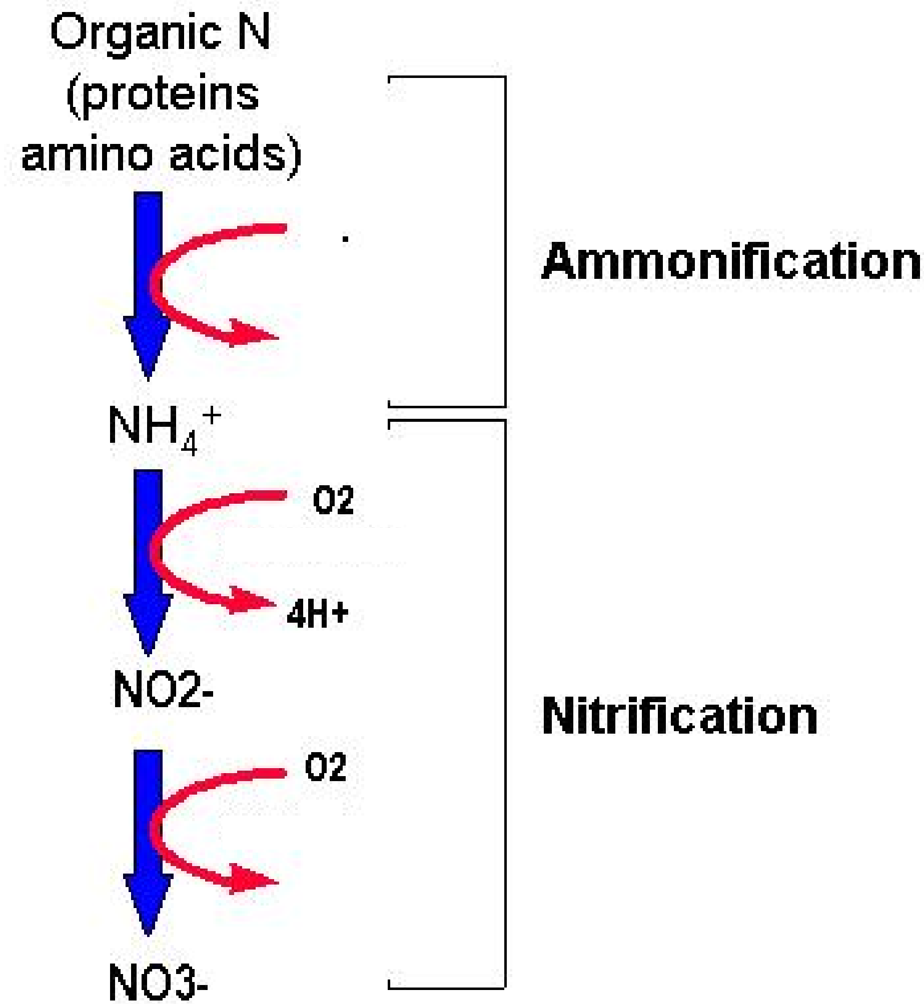
•Biological oxidation of NH_3 to NO_3^- using oxygen as terminal electron acceptor.

•Two step process; ammonia oxidation followed by nitrite oxidation; both reactions yield energy.

•NO_2^- serves as an important intermediate; incomplete nitrification also yields N_2O.

$$NH_2OH \rightarrow NO \rightarrow N_2O$$

Nitrification: $NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$



Degradation of organic N to ammonium occurs during heterotrophic metabolism.

Nitrification is a 2 step process that is mediated by different groups of microbes. The first step (termed ammonium oxidation) oxidizes NH_4^+ to NO_2^-, and the second step converts NO_2^- to NO_3^-.

Aerobic regeneration of nitrogen

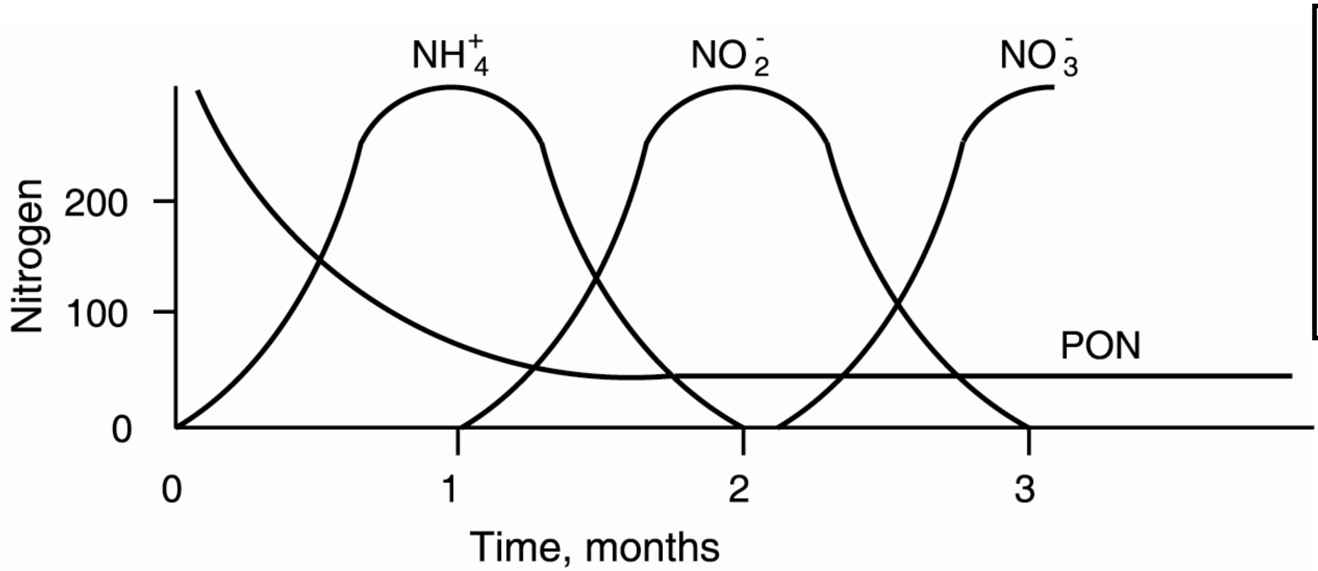
Complete decomposition of organic matter

$$(CH_2O)_{106}(NH_3)16H_3PO_4 + 138O_2 \Rightarrow 106CO_2 + 122H_2O + 16HNO_3 + H_3PO_4$$

$$2NH_4^+ + 3O_2 \Rightarrow 2NO_2^- + 4H^+ + 2H_2O$$

$$2NO_2^- + O_2 \Rightarrow 2NO_3^-$$

These reactions yield energy (but not much…)



Most nitrifying microbes are chemoautotrophic (best studied are *Nitrosomonas* and *Nitrobacter*)

Recent isolation and cultivation of an abundant archaeal ammonium oxidizer

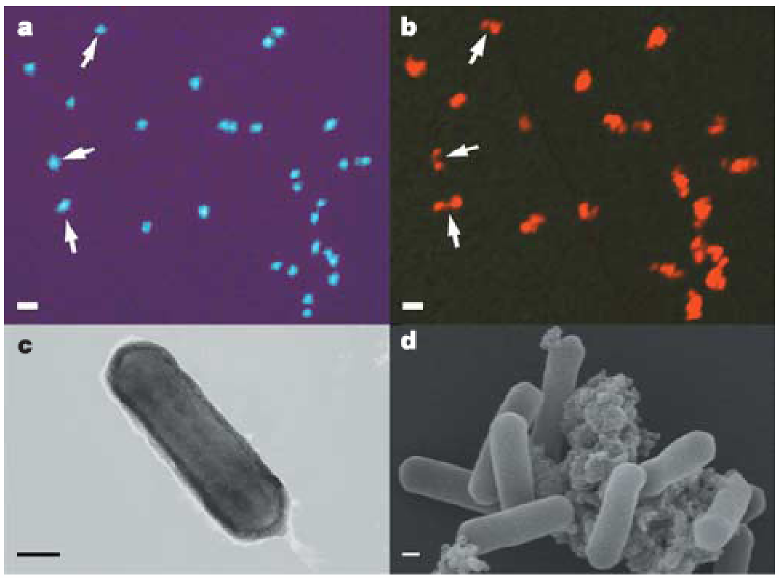


Figure 2 | Photomicrographs of SCM1. **a**, **b**, Fluorescence image of cells in identical fields of view stained with DAPI (**a**) and after hybridization with nucleotide polyprobes targeting SCM1 cells (**b**). Arrows indicate cells showing the characteristic peanut-like shape of marine Crenarchaeota[12,15]. Scale bars represent 1 μm. **c**, Transmission electron micrograph of negative-stained cells. Scale bar represents 0.1 μm. **d**, Scanning electron micrograph of Au/Pd-sputtered cells. Scale bar represents 0.1 μm.

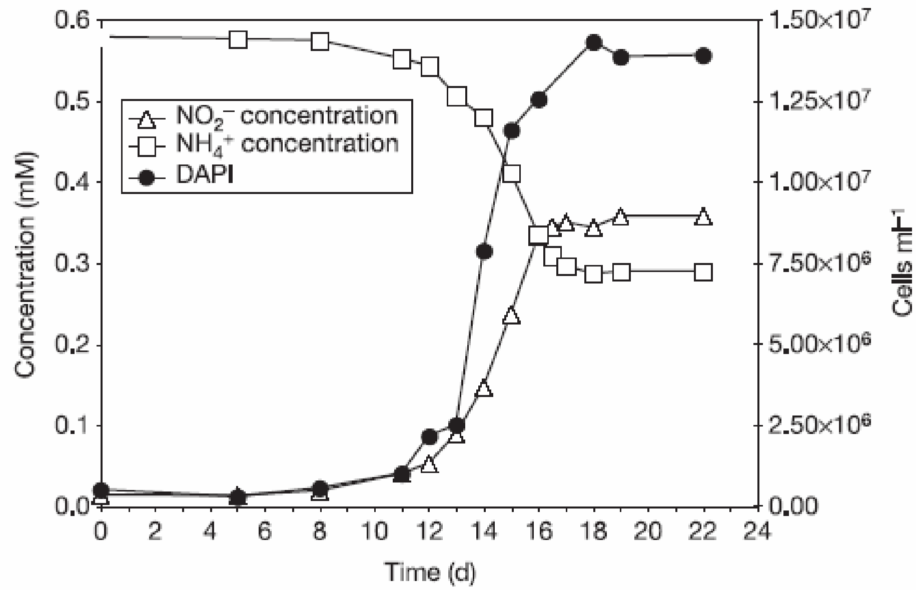


Figure 3 | Near-stoichiometric conversion of ammonia to nitrite by SCM1. Growth of SCM1 in Synthetic Crenarchaeota Media containing ammonium chloride and bicarbonate as sole energy and carbon sources, respectively. DAPI-stained cells were directly counted on filters by fluorescence microscopy. Ammonium consumption and nitrite production were determined in triplicate as described previously[27].

Denitrification

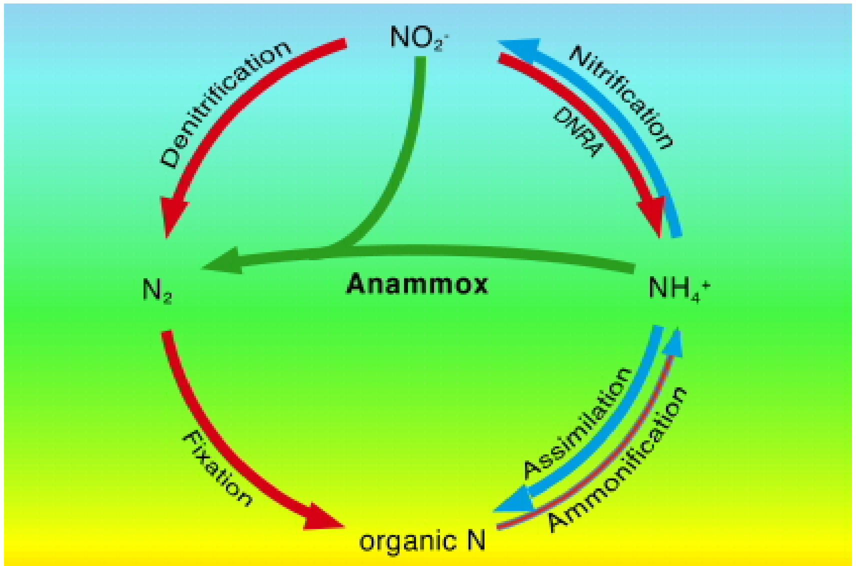
The reduction of NO_3^- and NO_2^- to N_2 during heterotrophic respiration of organic matter. Denitrification implies N is lost from the ecosystem as a gaseous bi-product. Occurs predominately in anaerobic or suboxic environments.

$$C_{106}H_{175}O_{42}N_{16}P + 104\ NO_3^- \Rightarrow 106CO_2 + 60N_2 + H_3PO_4 + 138\ H_2O$$

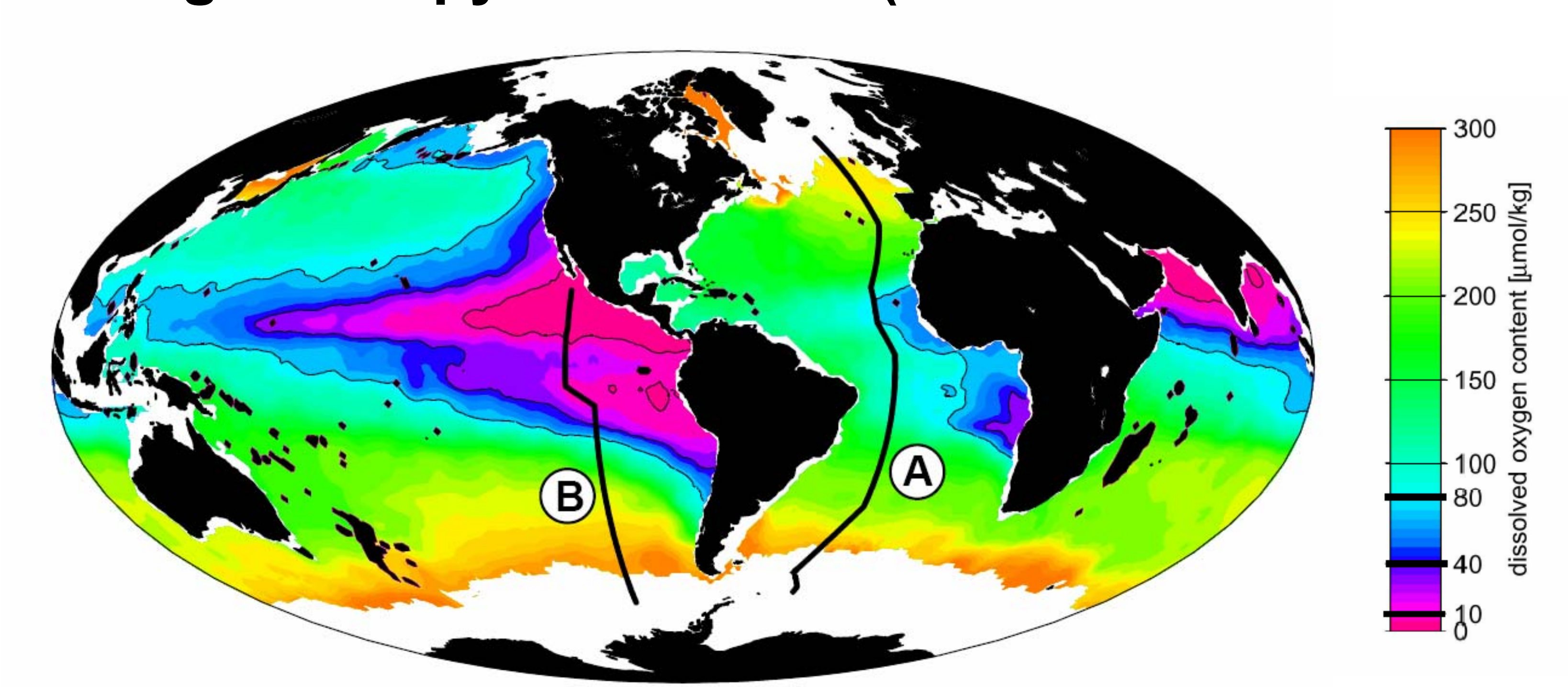
Serves as the major sink for fixed nitrogen from aquatic environments.

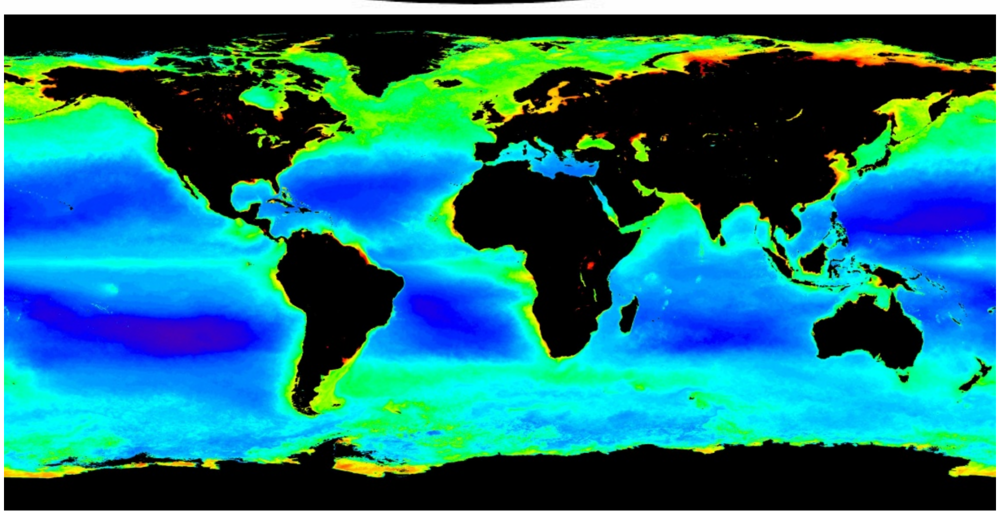
Anaerobic ammonium oxidation (anammox)

- $NH_4^+ + NO_2^- \Rightarrow 2N_2 + 2H_2O$
- Anaerobic ammonium oxidation
- Major source of N_2 gas (along with denitrification)
- Anoxic sediments, marine water column, and sewage wastewater
- Mediated by *Planctomyces*



Oxygen concentrations along the 26.9 kg m^{-3} isopycnal surface (~500 m in the N. Pacific)





Chlorophyll distributions