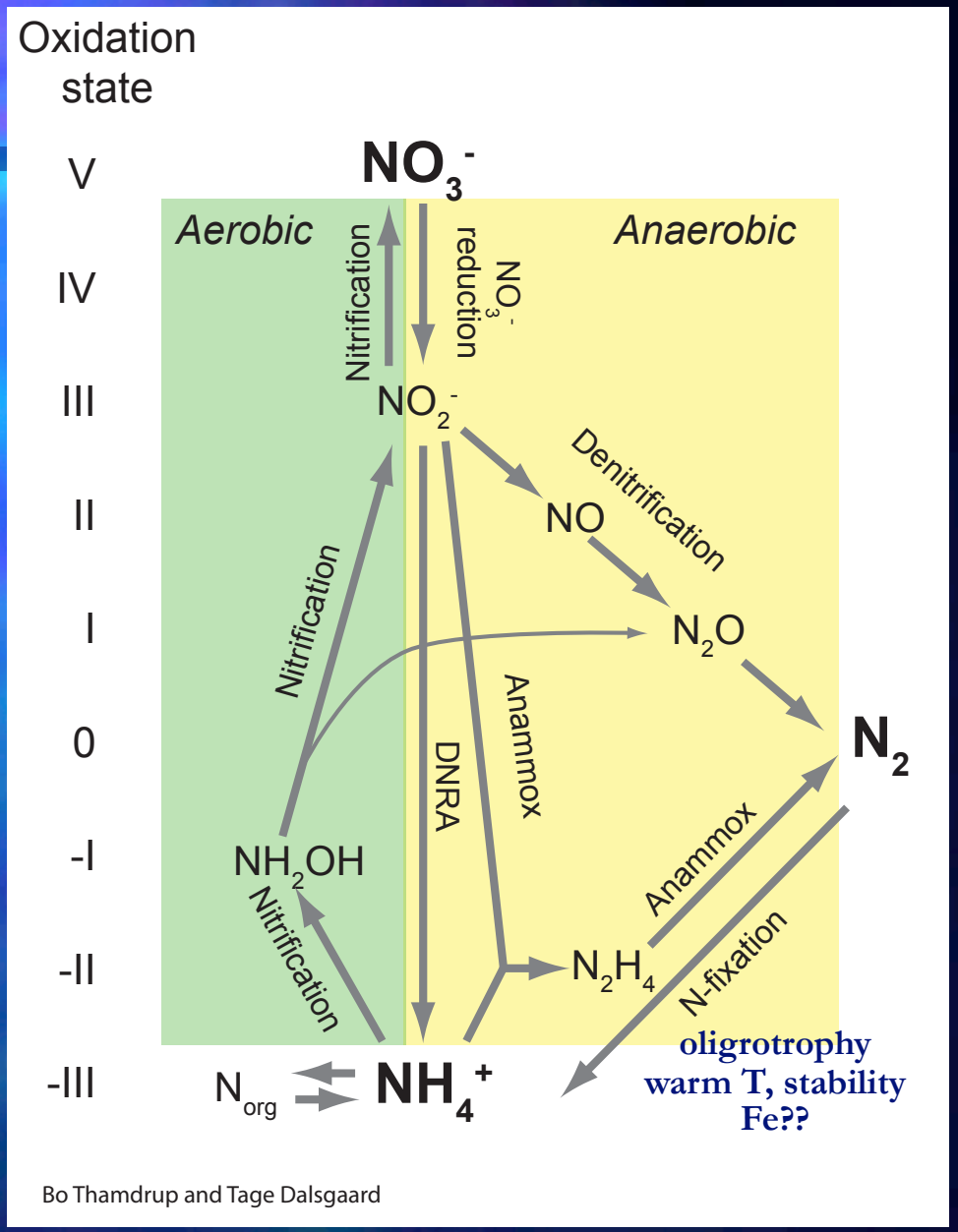
How can We Quantify Past Changes in Water Column Denitrification?

1. Background
2. Local Signal Generation
3. Regional Integration
4. Looking Toward the Future

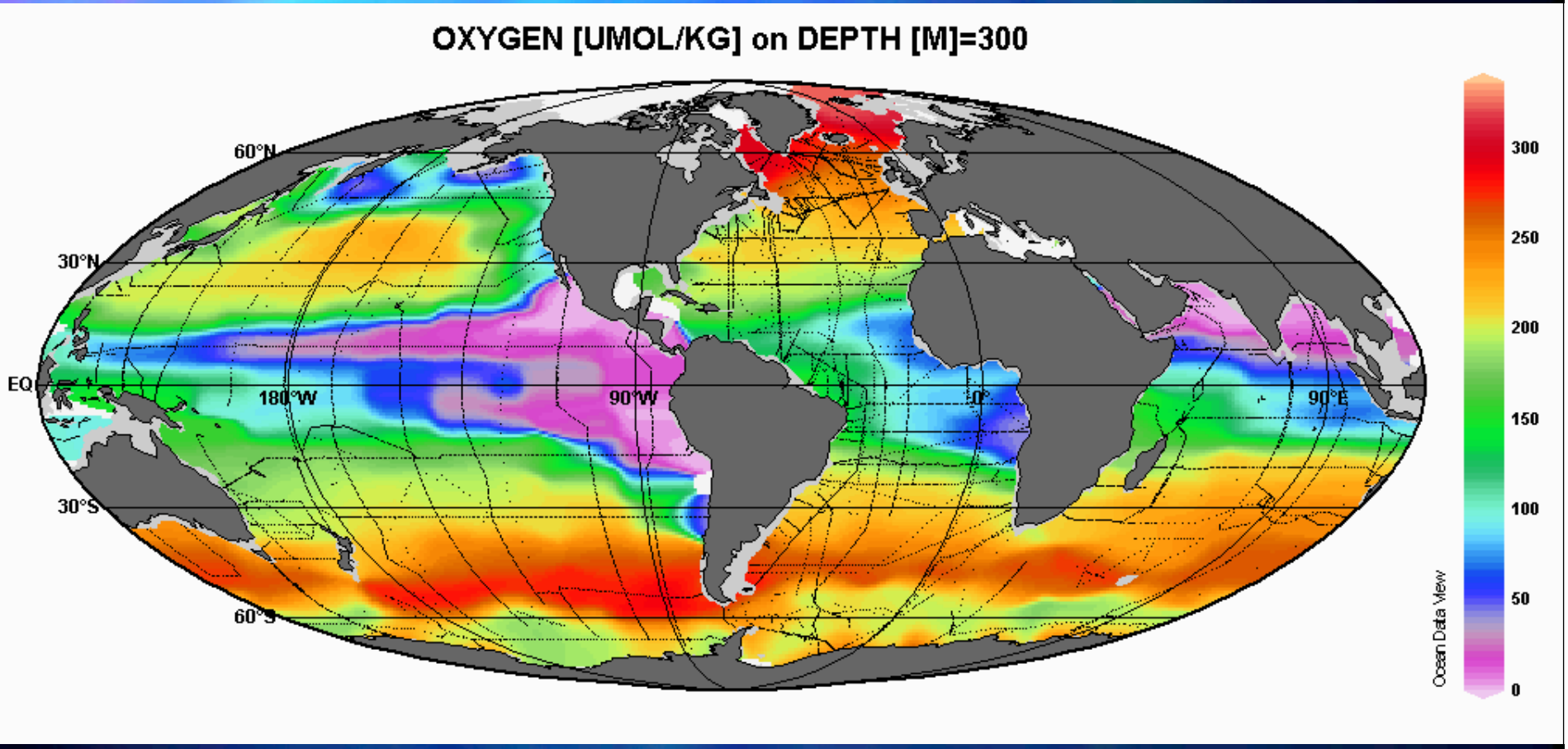
N-Cycling

Most Important Isotopic Fractionation Effects

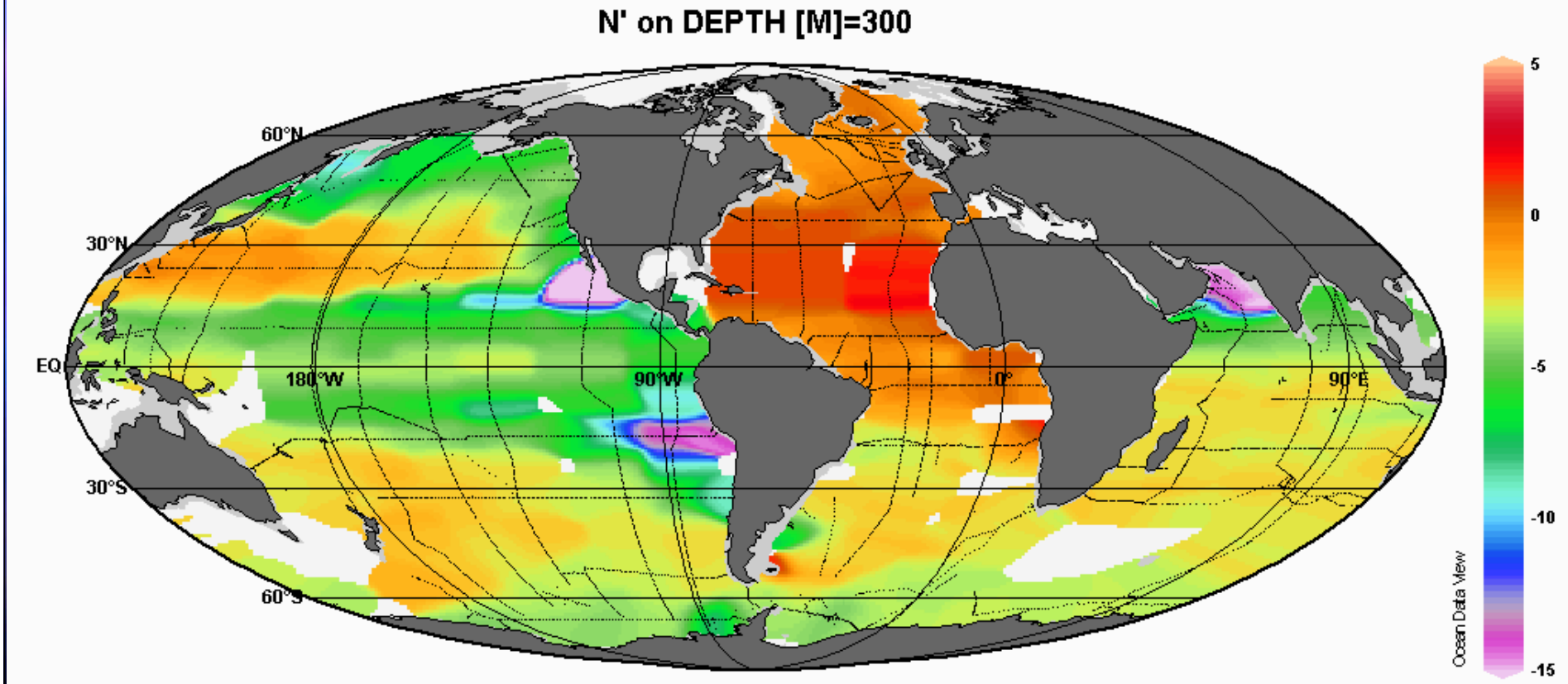
1) NO_3^- uptake by phytoplankton (diatoms; 5 to 8 per mil)
2) Trophic transfer (3 to 4 per mil)
3) OM diagenesis (up to 5 per mil)
4) Nitrification (10 to 30 per mil)
5) Denitrification (20 to 30 per mil) (in sediments, effectively nil)
6) N_2 fixation (2 per mil)



Geographic Separation (Decoupling)

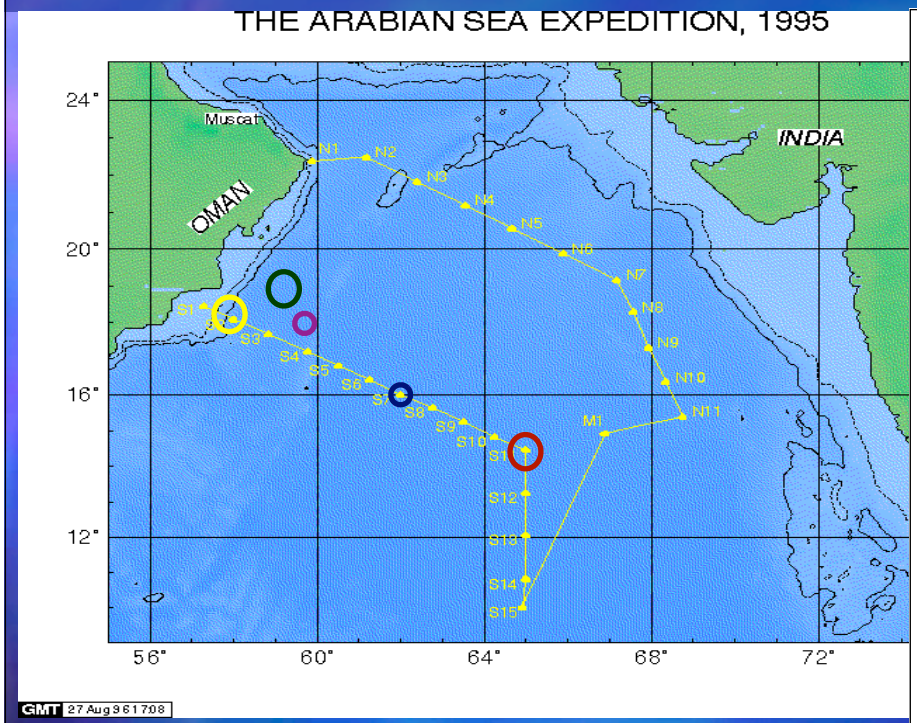


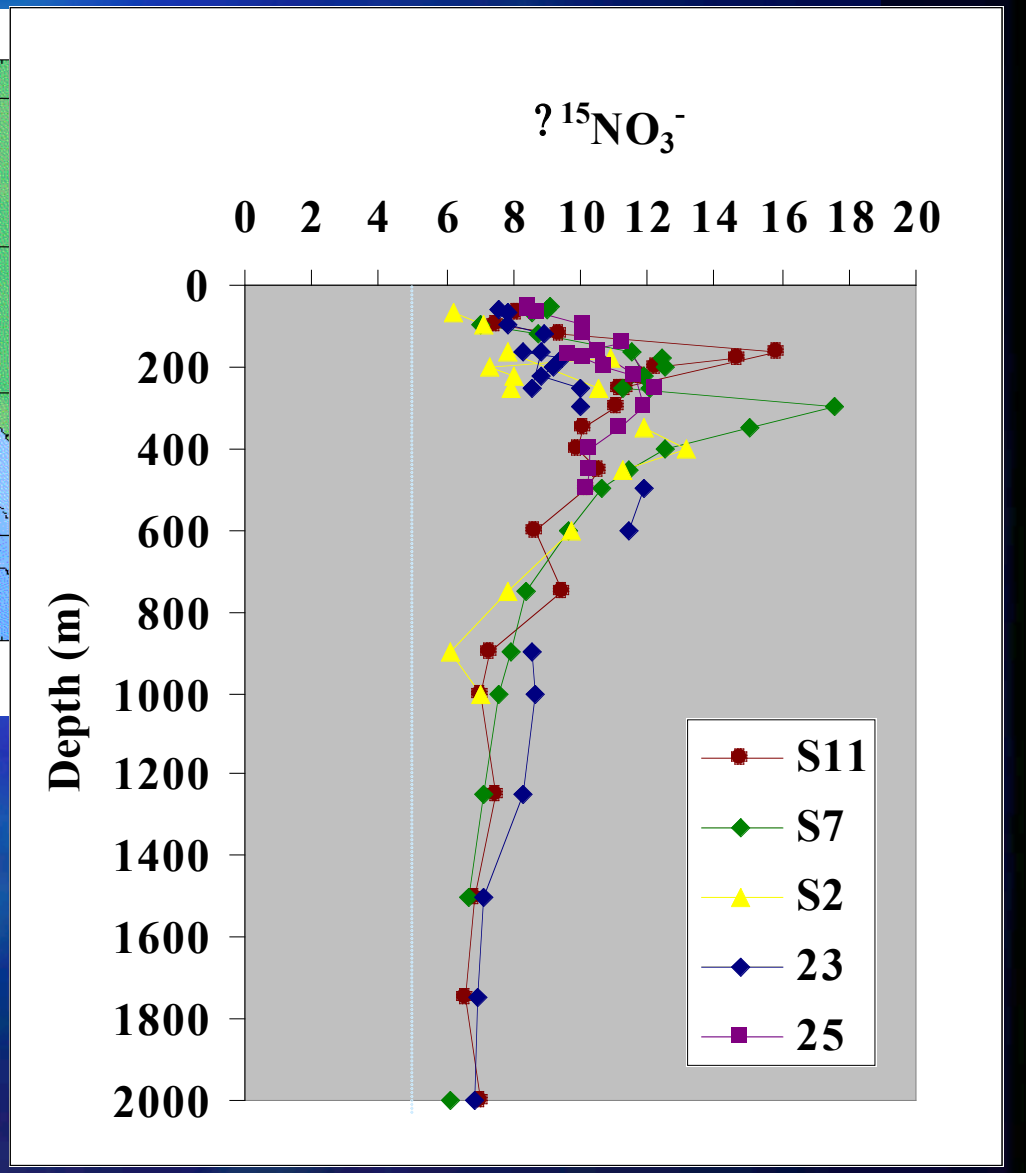
OMZ's Important Locations for Denitrification



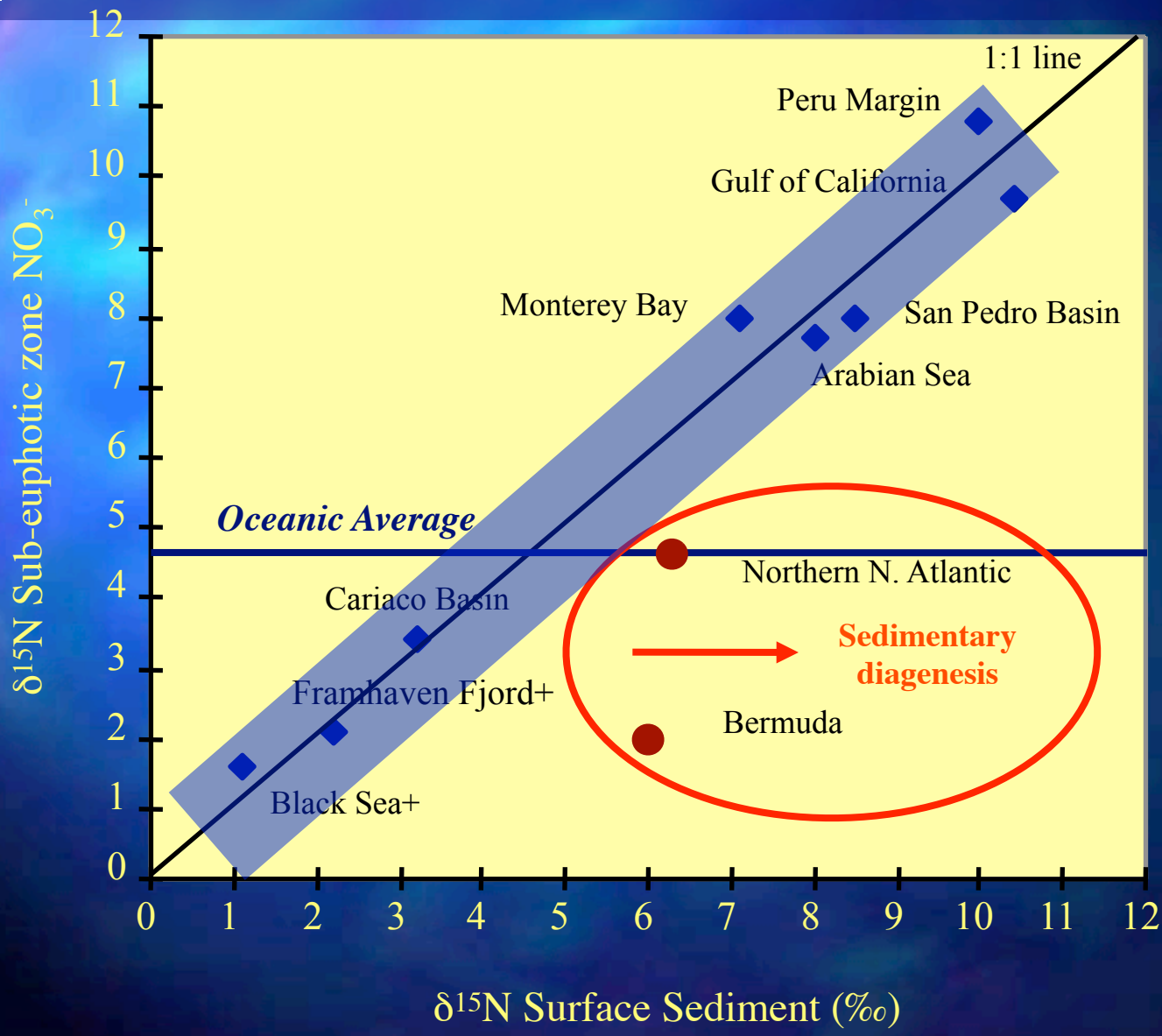
$$N' = NO_3^- + NO_2^- - 16 \times PO_4^{-3}$$

Denitrification Effects – JGOFS Results

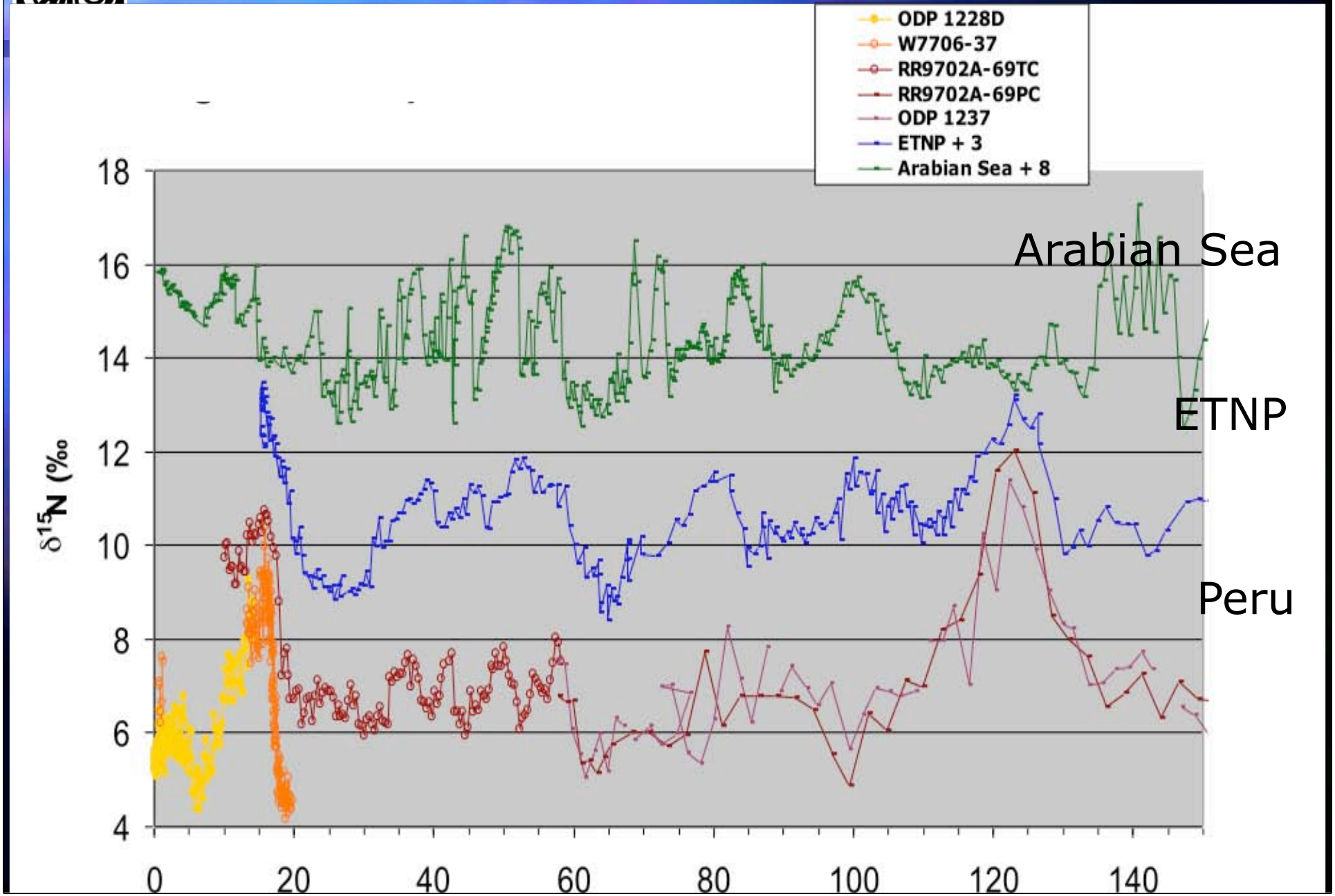


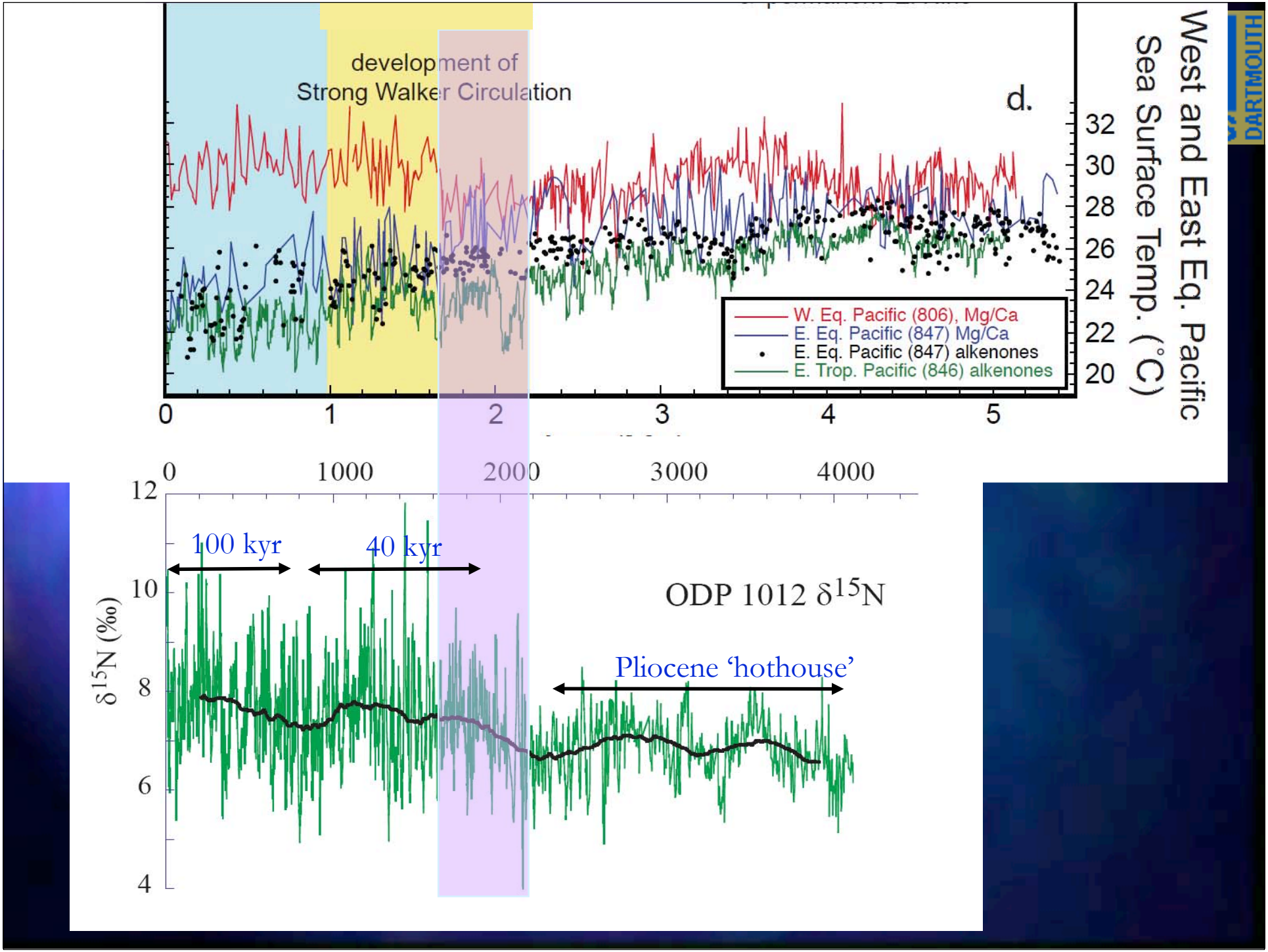


Preservation of $\delta^{15}N$ Signal in Marine Sediments



Regional comparison last glacial cycle




development of
Strong Walker Circulation
d.
West and East Eq. Pacific
Sea Surface Temp. (°C)
32
30
28
26
24
22
20
0
1
2
3
4
5
W. Eq. Pacific (806), Mg/Ca
E. Eq. Pacific (847) Mg/Ca
E. Eq. Pacific (847) alkenones
E. Trop. Pacific (846) alkenones
0
1000
2000
3000
4000
12
10
8
6
4
δ15N (‰)
100 kyr
40 kyr
ODP 1012 δ15N
Pliocene 'hothouse'

Variability in ε for denitrification (NO_3^- reduction)?

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Nitrogen and oxygen isotope fractionation during dissimilatory nitrate reduction by denitrifying bacteria

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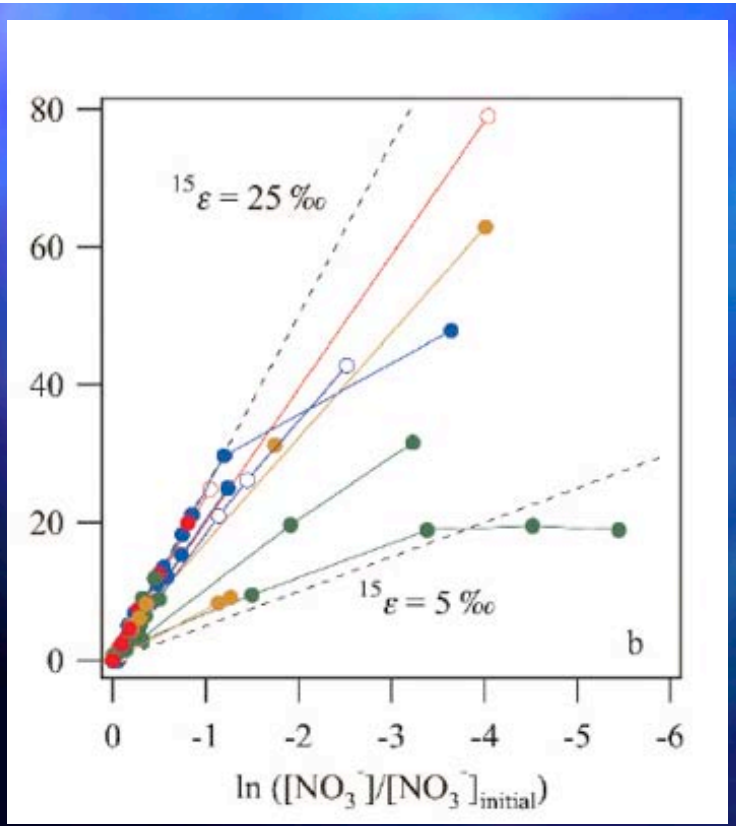


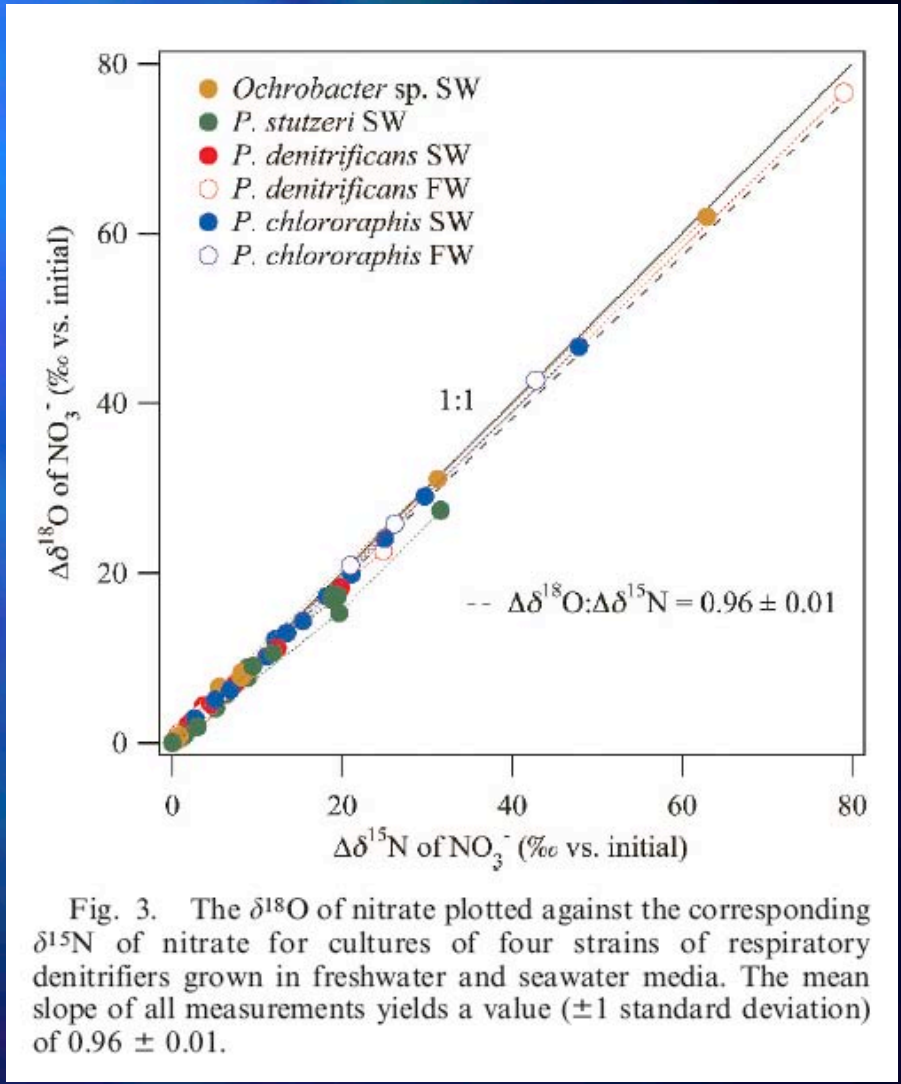
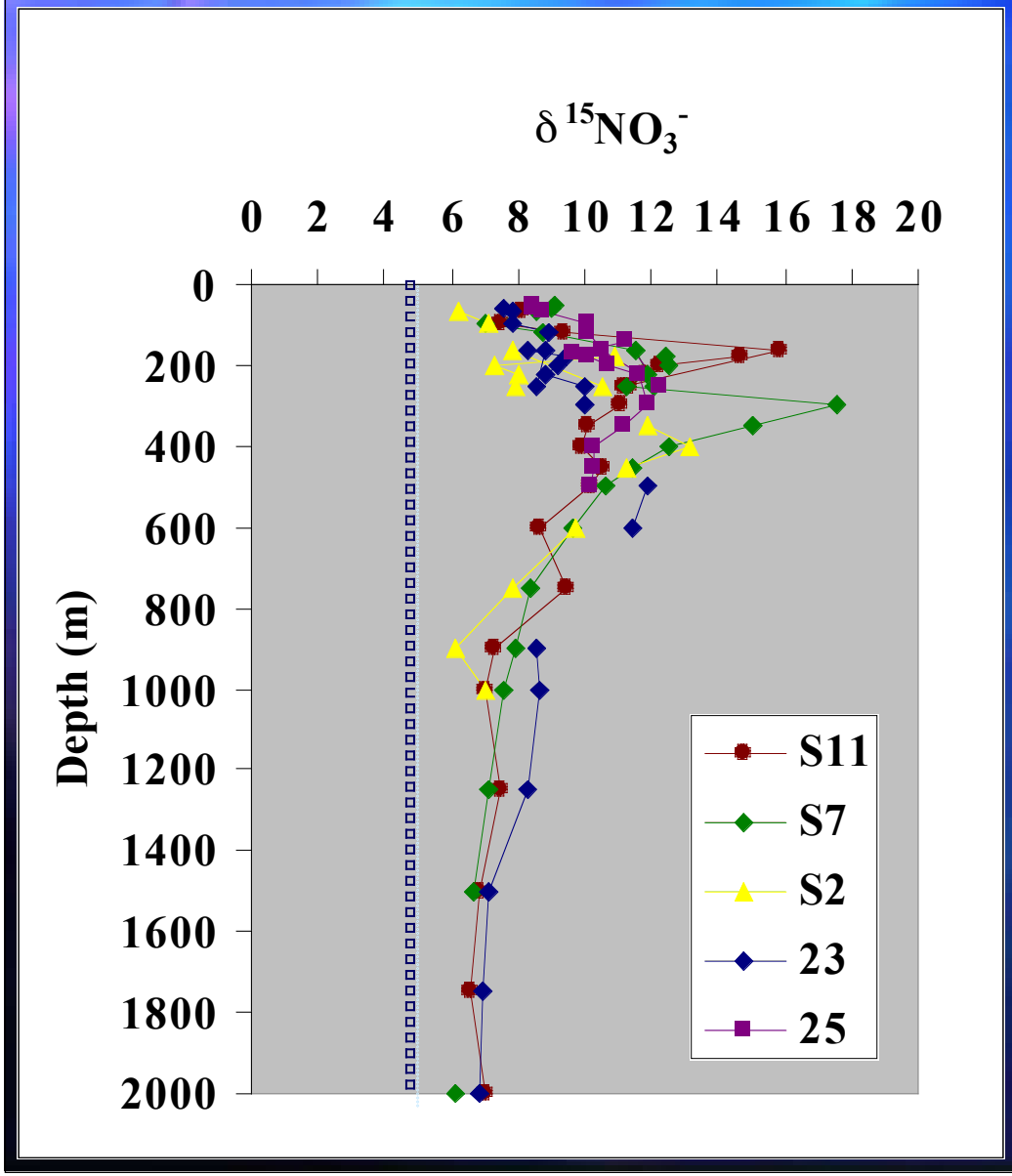


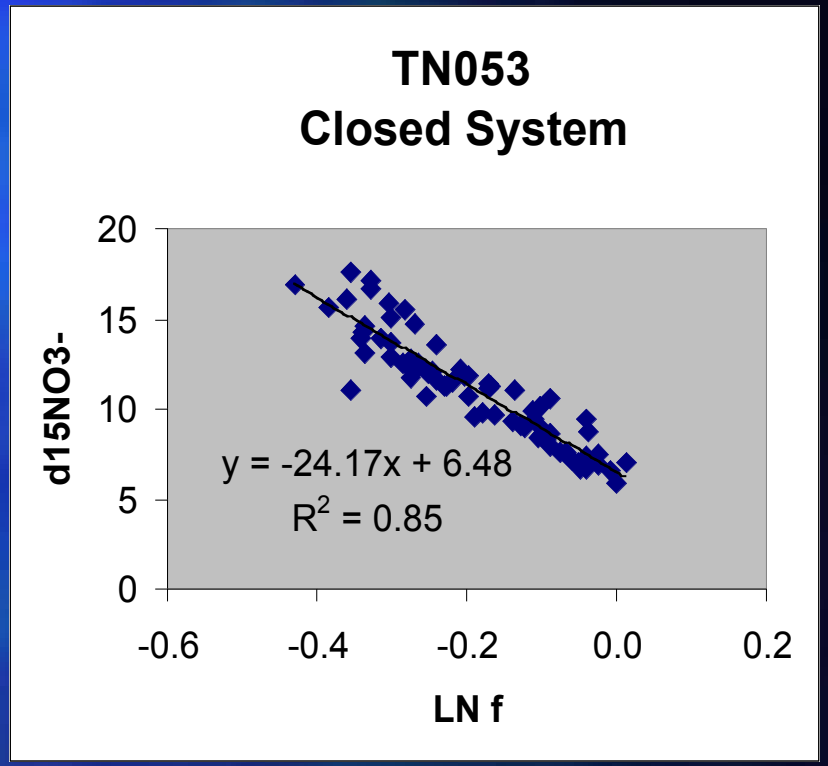
Fig. 3. The $\delta^{18}O$ of nitrate plotted against the corresponding $\delta^{15}N$ of nitrate for cultures of four strains of respiratory denitrifiers grown in freshwater and seawater media. The mean slope of all measurements yields a value (±1 standard deviation) of 0.96 ± 0.01.

Table 1. Estimates of nitrogen (ε_N) and oxygen (ε_O) isotope enrichment factors for denitrification in culture experiments and natural environments.

Setting	ε_N (‰)	ε_O (‰)	Reference
Culture	−28.6		Barford et al. (1999)
Culture	−12.3 to −13.3		Blackmer and Bremner (1977)
Culture	−13.4 to −20.8		Delwiche and Steyn (1970)
Culture	−24.6 to −29.4		Mariotti et al. (1981)
Culture	−20		Myake and Wada (1971)
Culture	−30	−15	Olleros (1983)
Culture	−2 to −12		Wada (1980)
Culture	−19 to −20		Wellman et al. (1968)
Groundwater	−22.9		Aravena and Robertson (1998)
Groundwater	−15.9	−8	Böttcher et al. (1990)
Groundwater	−4.7 to −5		Mariotti et al. (1988)
Groundwater	−27.6	−18.3	Mengis et al. (1999)
Groundwater	−13.9		Smith et al. (1991)
Groundwater	−30 ± 6		Vogel et al. (1981)
River (sediments in stagnant annex)	−1.5		Sebilo et al. (2003)
Coastal marine sediments	±0		Brandes and Devol (1997)
Continental margin sediments	0 to −3		Brandes and Devol (2002)
Central Arabian Sea	−22 to −25		Brandes et al. (1998)
Eastern tropical North Pacific	−25 to −30		Brandes et al. (1998)
Eastern tropical North Pacific	−30 to −40		Cline and Kaplan (1975)
Eastern tropical North Pacific	−30 ± 7.5		Voss et al. (2001)

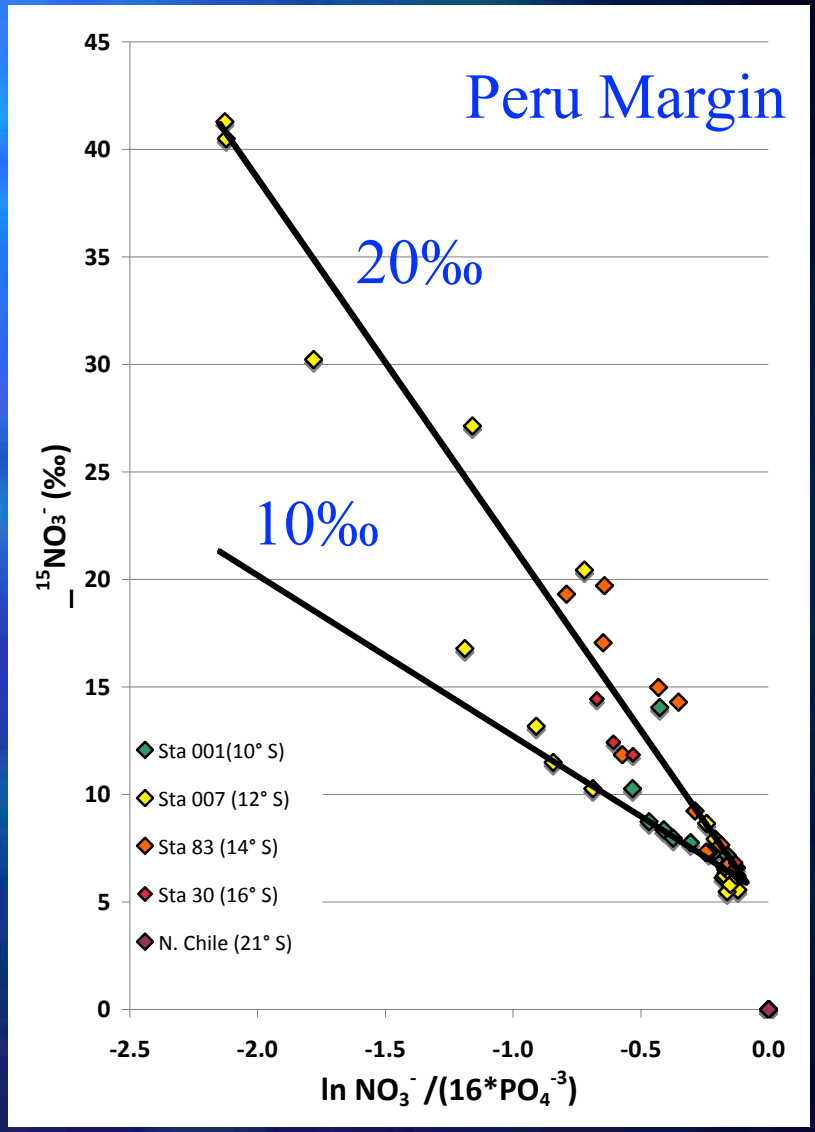
Denitrification ^{15}N Effects – Arabian Sea



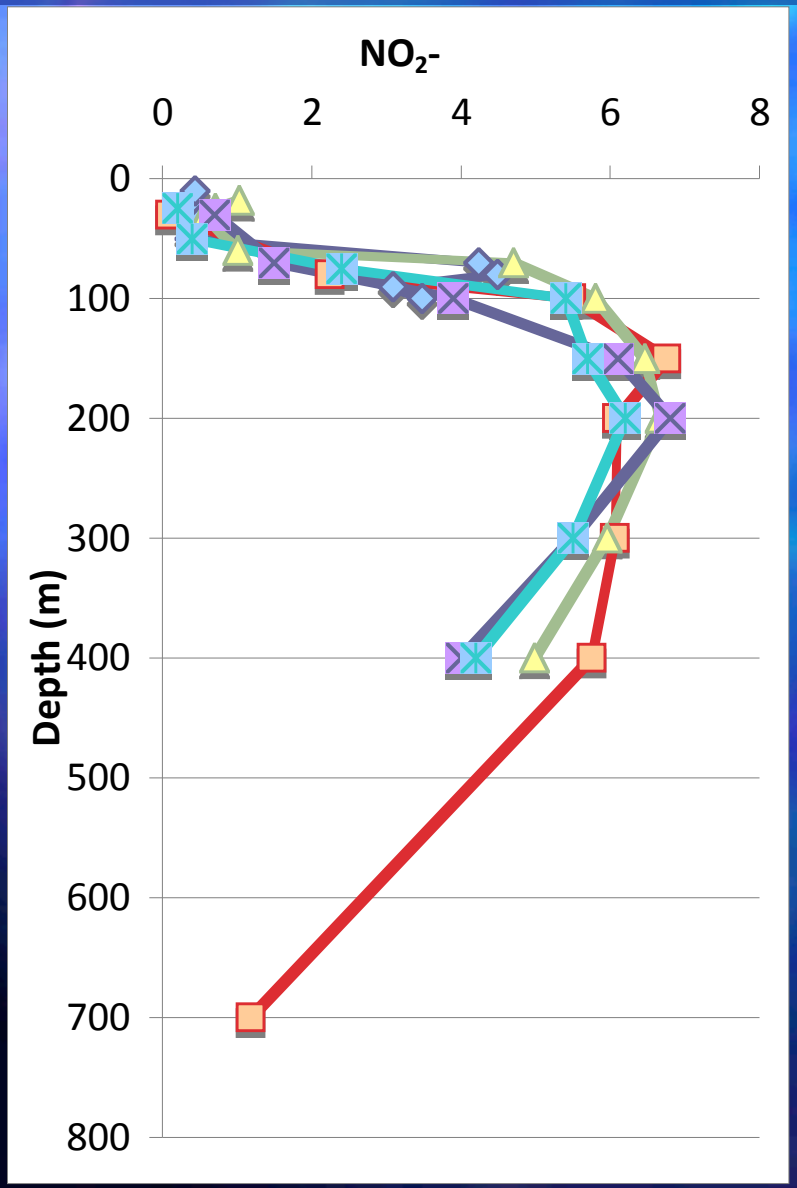


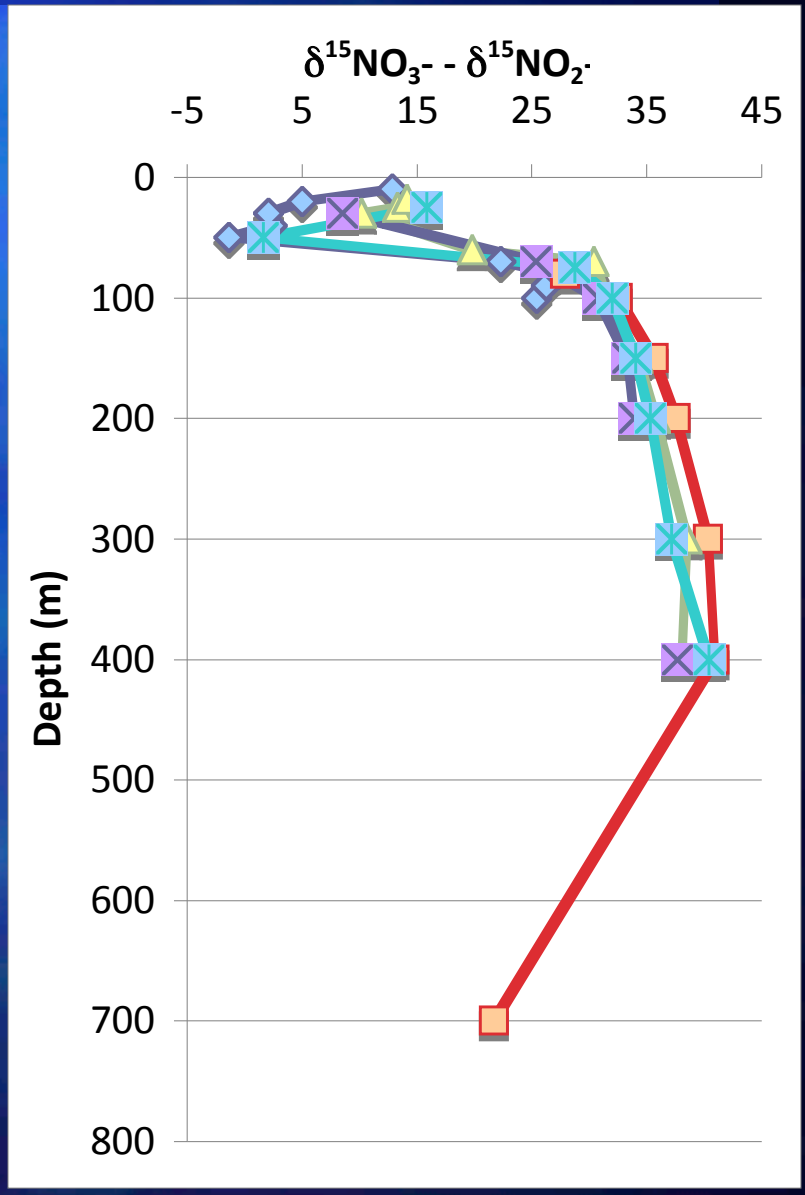
$$\Delta\delta^{15}N = -\varepsilon \times \ln f$$

Peru different?



Northern Coastal Chile (off Iquique)
Isolating NO_3^- reduction?

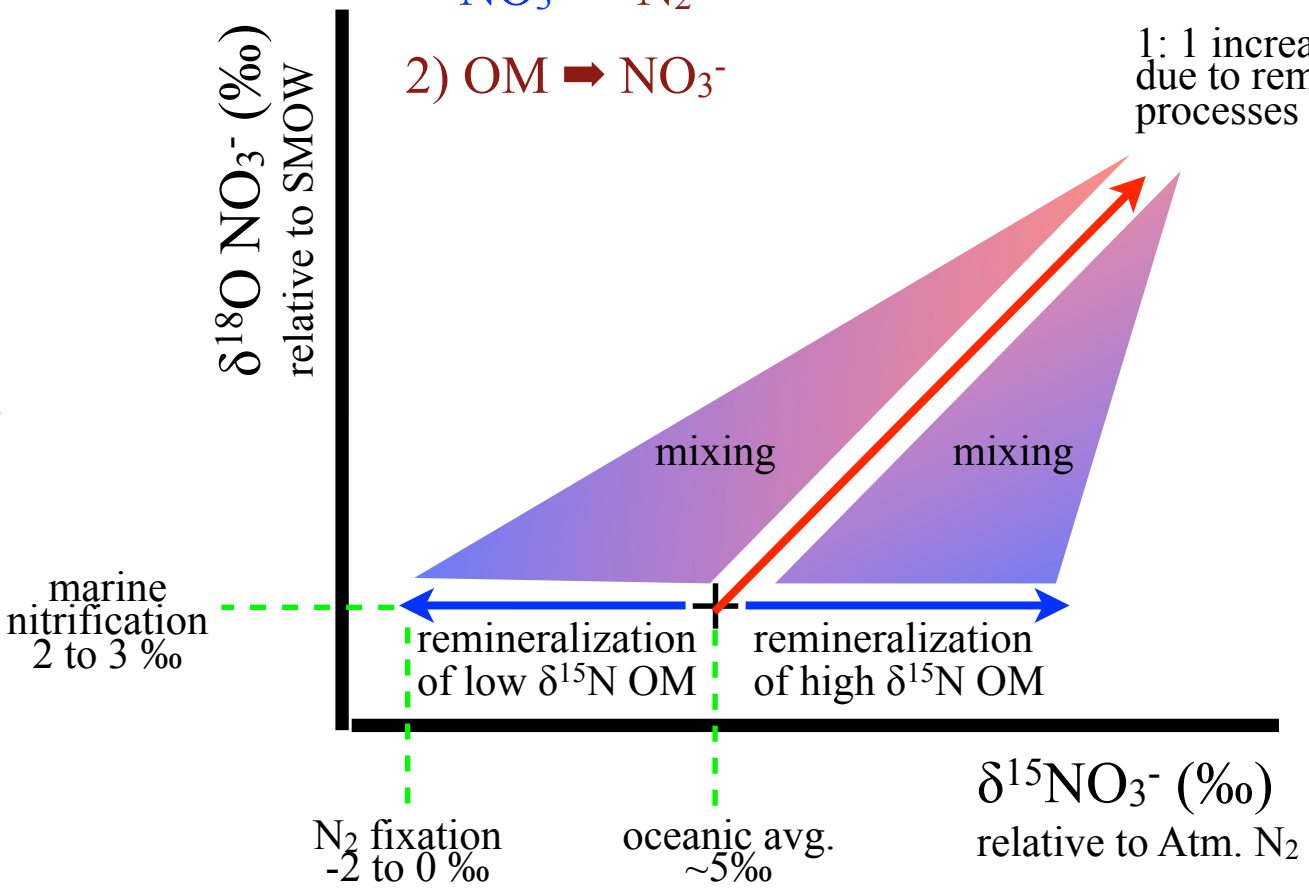




Other influences on $\delta^{15}NO_3^-$?

1) NO_3^- ➡ OM or
NO_3^- ➡ N_2

2) OM ➡ NO_3^-



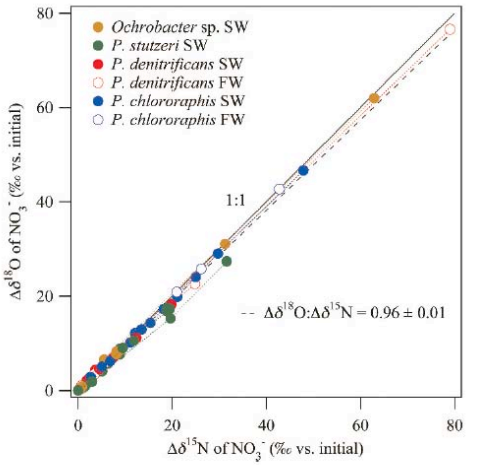
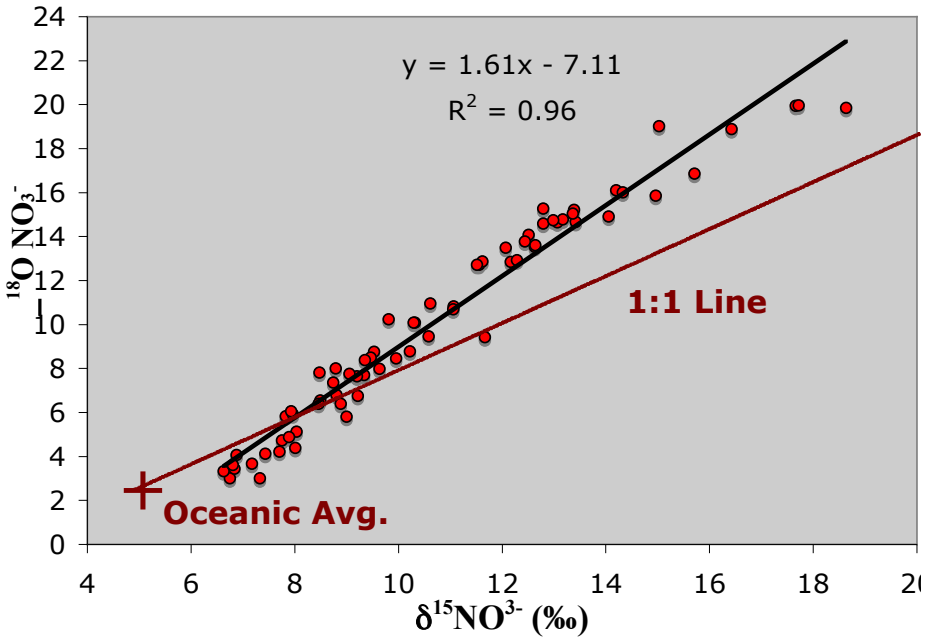
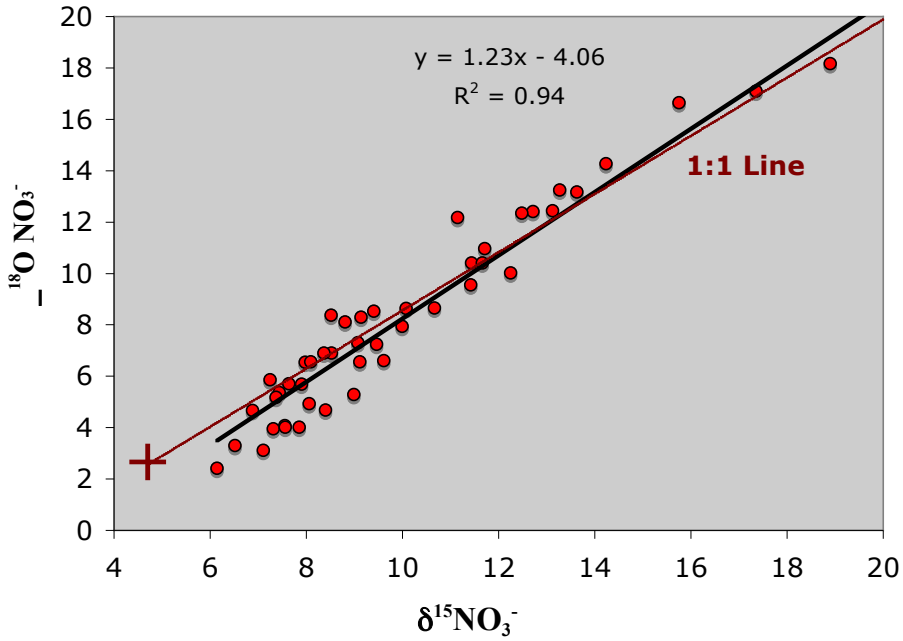


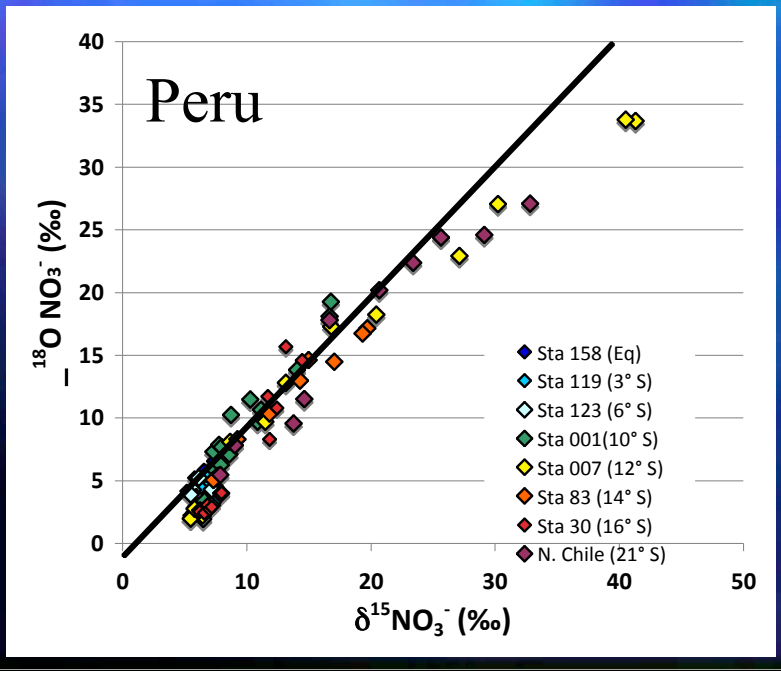
Fig. 3. The $\delta^{18}O$ of nitrate plotted against the corresponding $\delta^{15}N$ of nitrate for cultures of four strains of respiratory denitrifiers grown in freshwater and seawater media. The mean slope of all measurements yields a value (±1 standard deviation) of 0.96 ± 0.01.

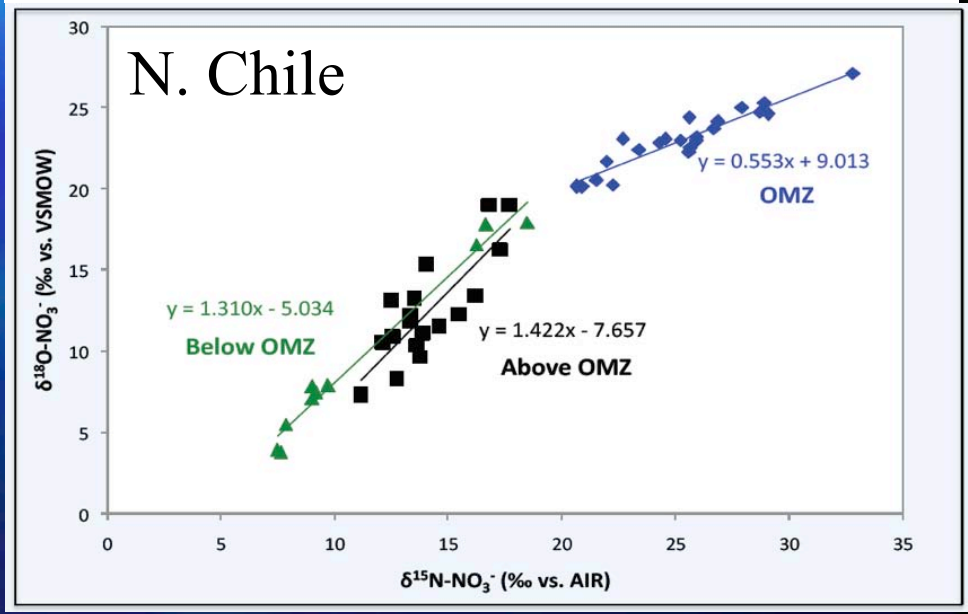
Arabian Sea Denitrification



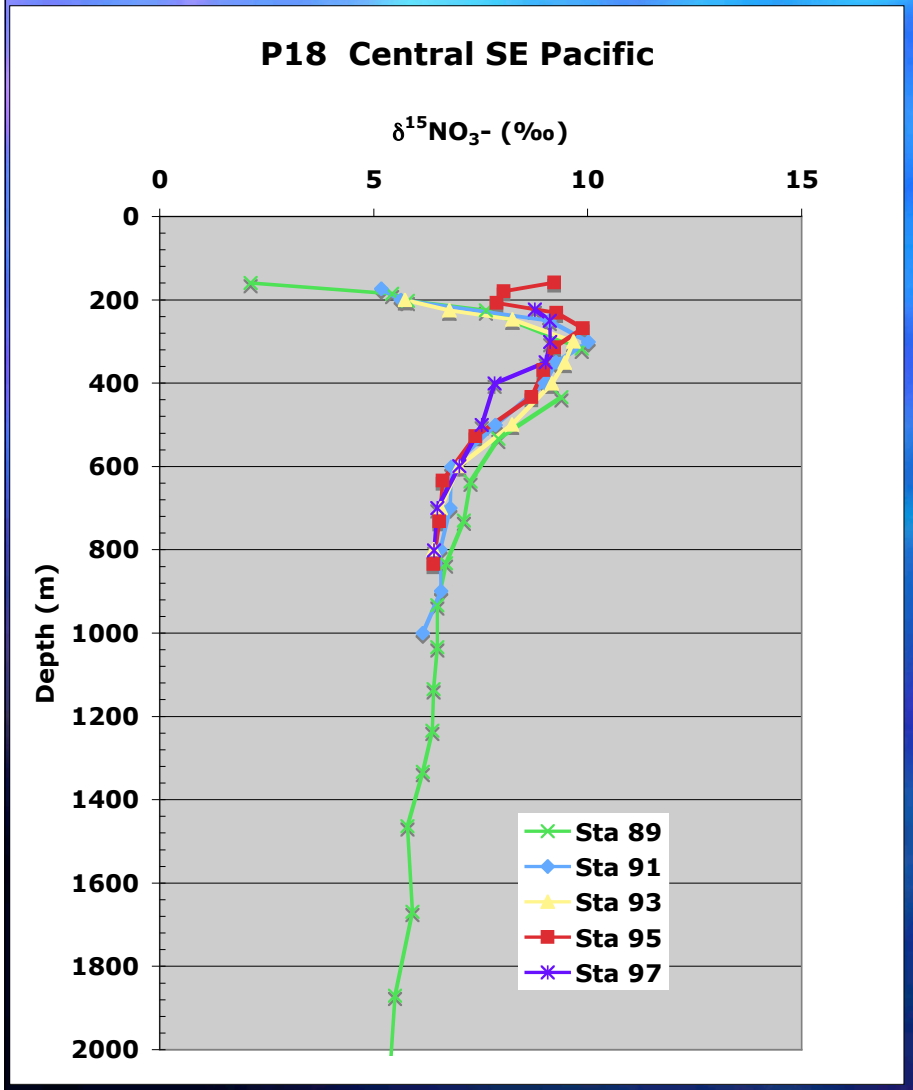
ETNP Denitrification

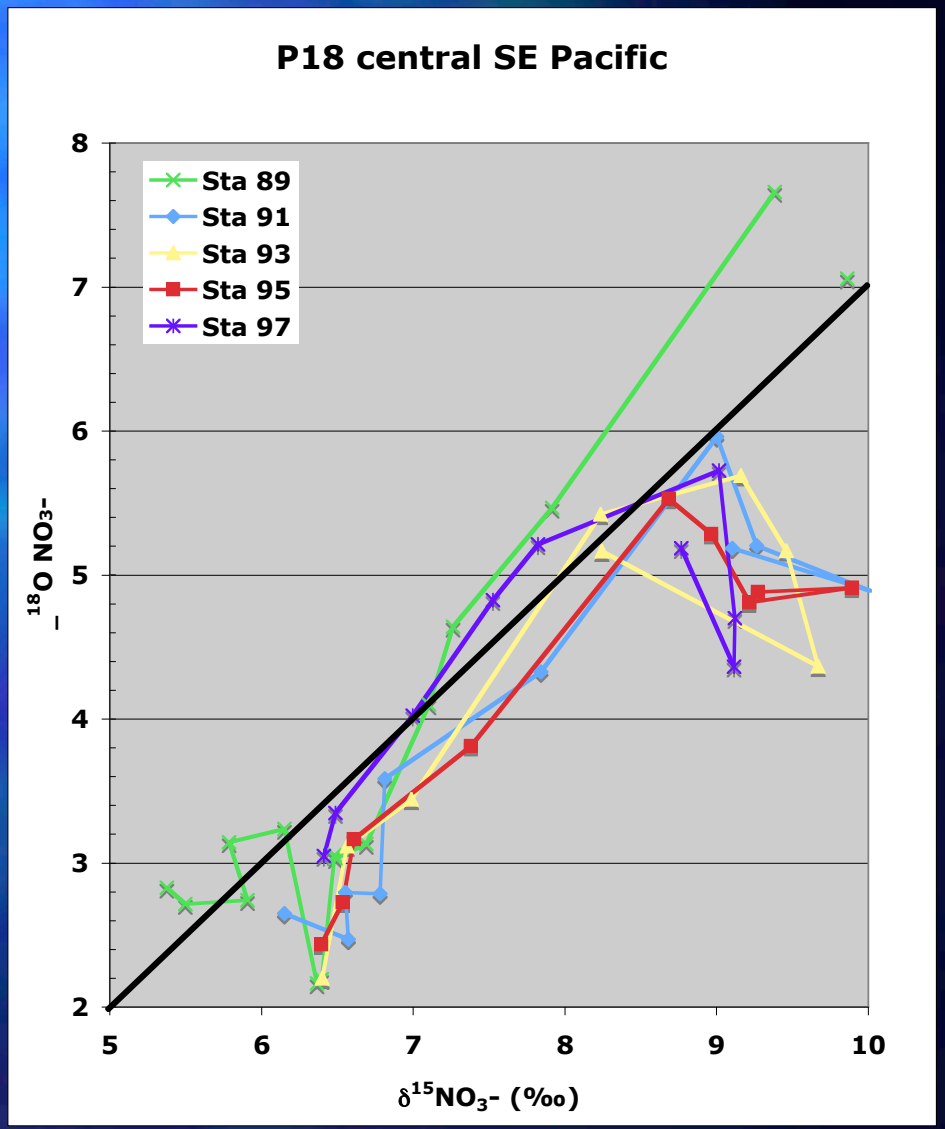




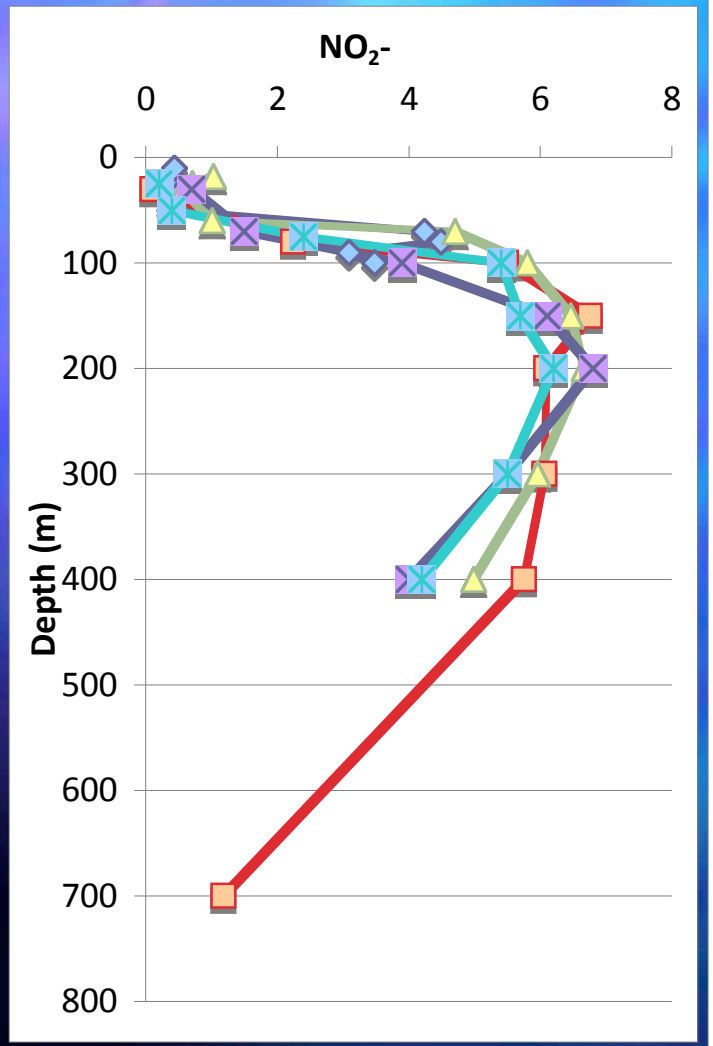


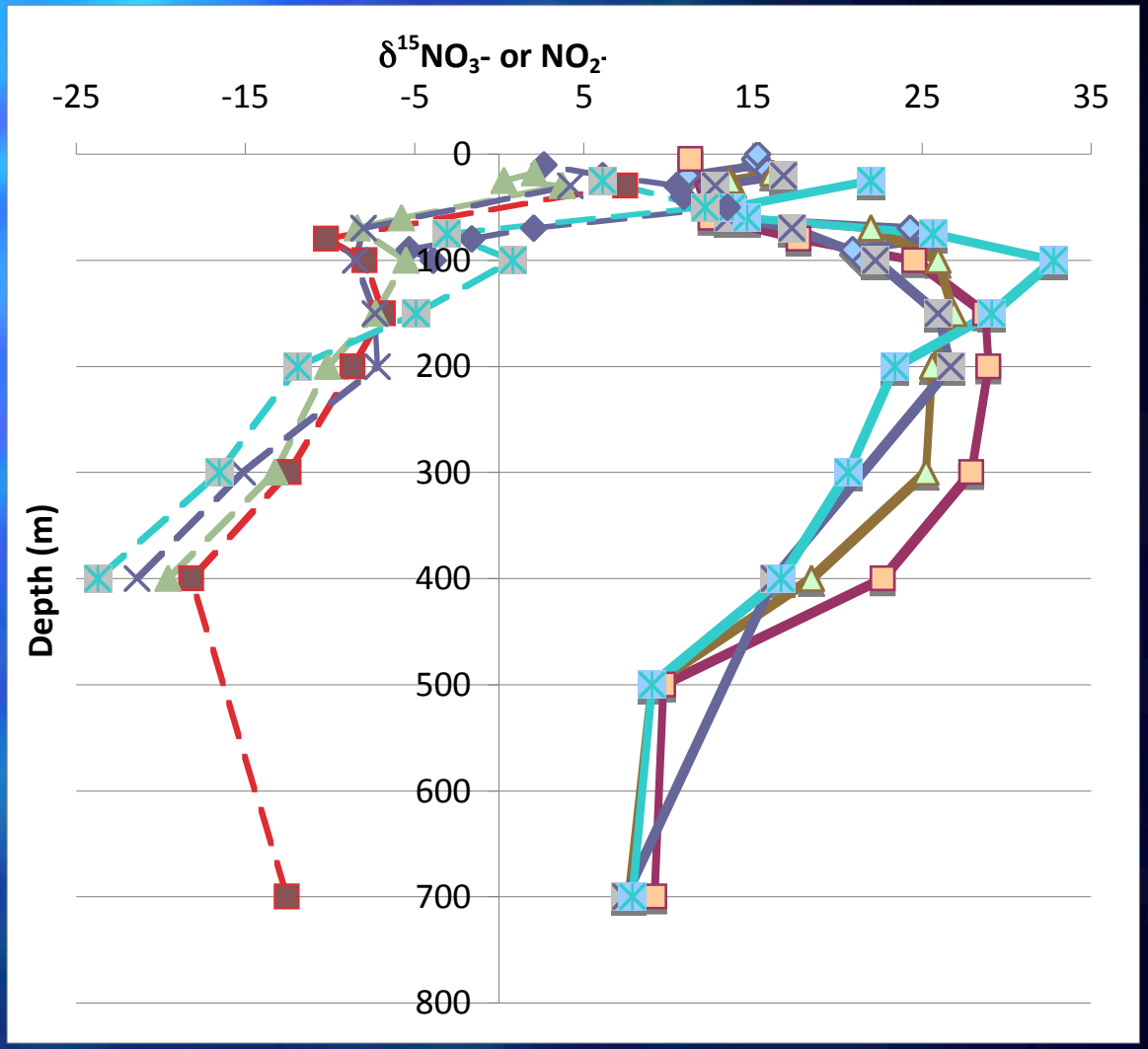
Oligotrophic region adjacent to Peru Chile OMZ

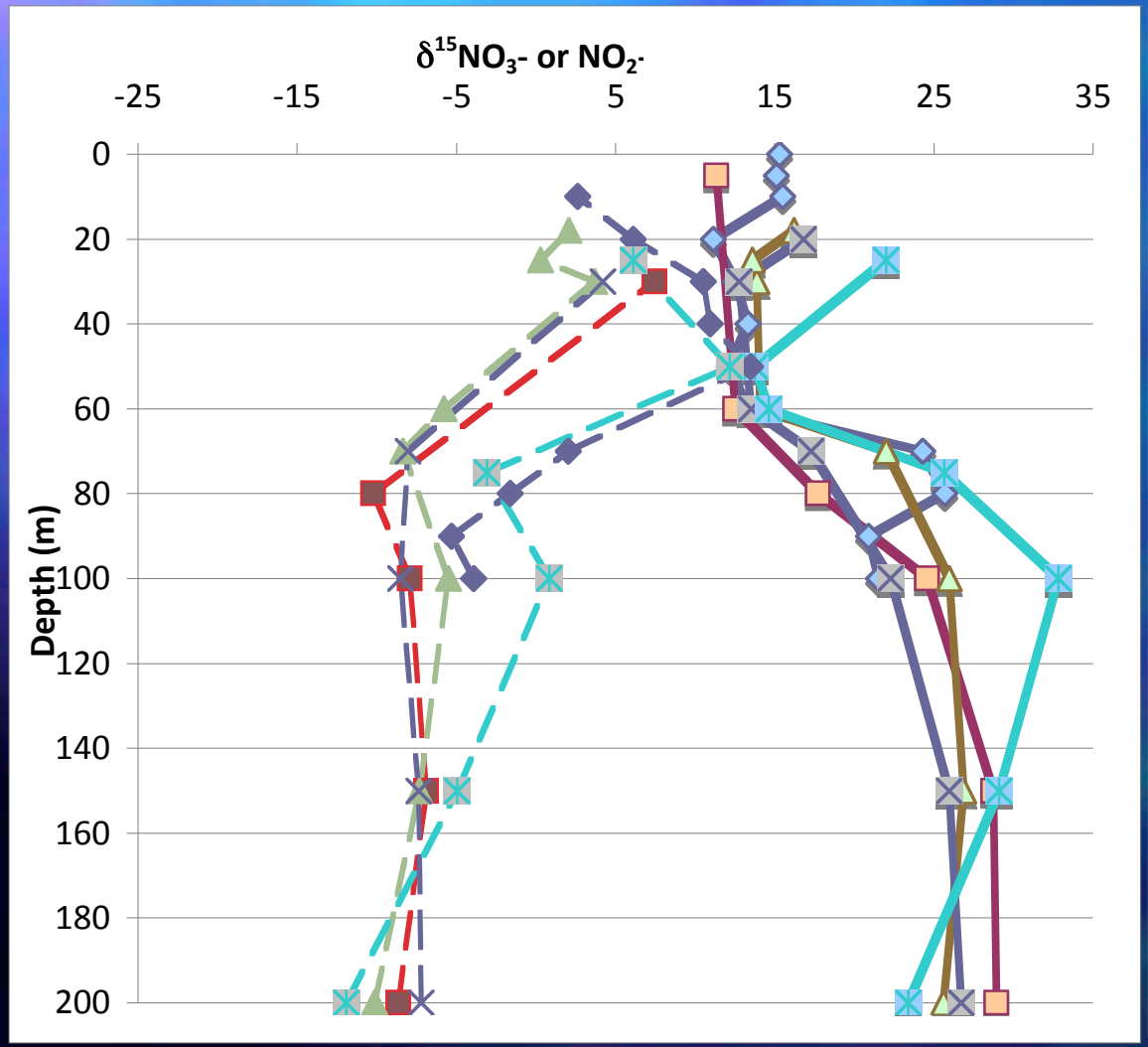


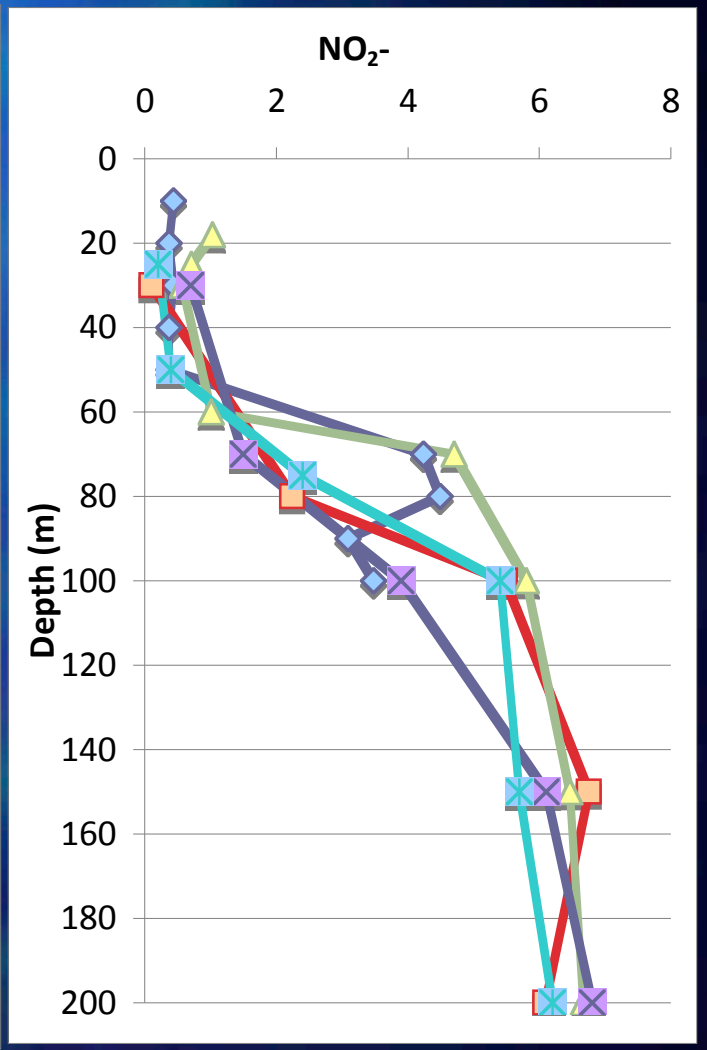


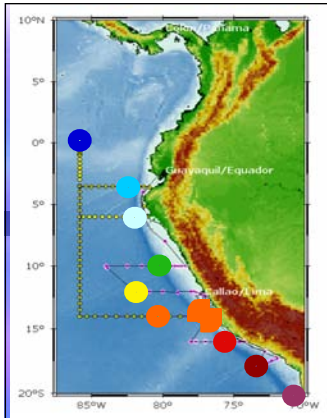
What determines the $\delta^{15}N$ of upwelled NO_3^-?



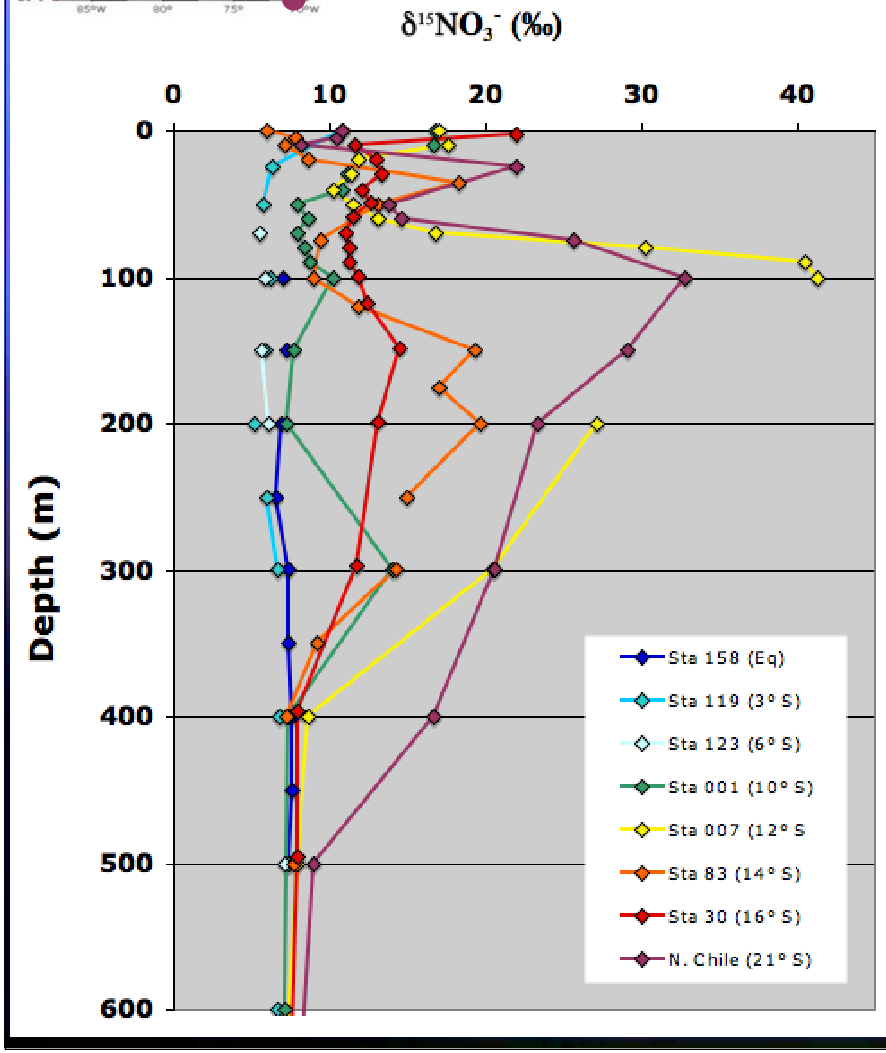


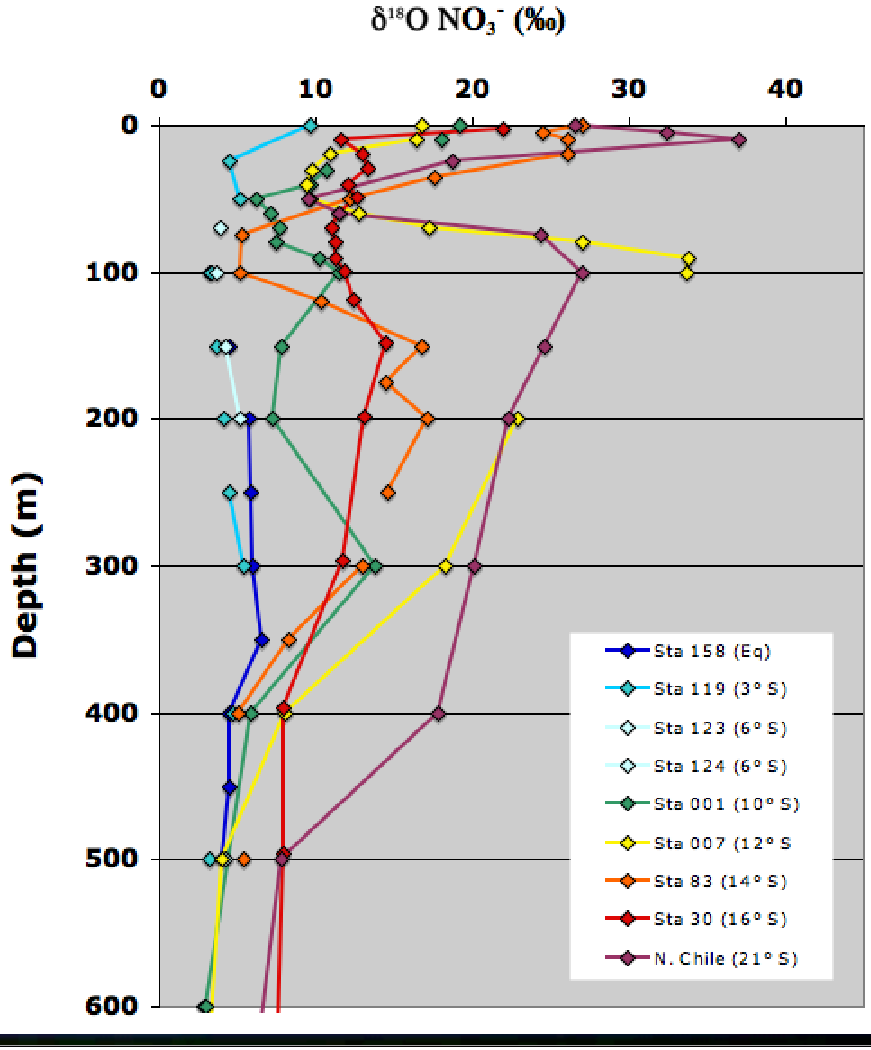

$\delta^{15}NO_3$- or NO_2-
-25
-15
-5
5
15
25
35
Depth (m)
0
20
40
60
80
100
120
140
160
180
200


NO_2-
0
2
4
6
8
Depth (m)
0
20
40
60
80
100
120
140
160
180
200

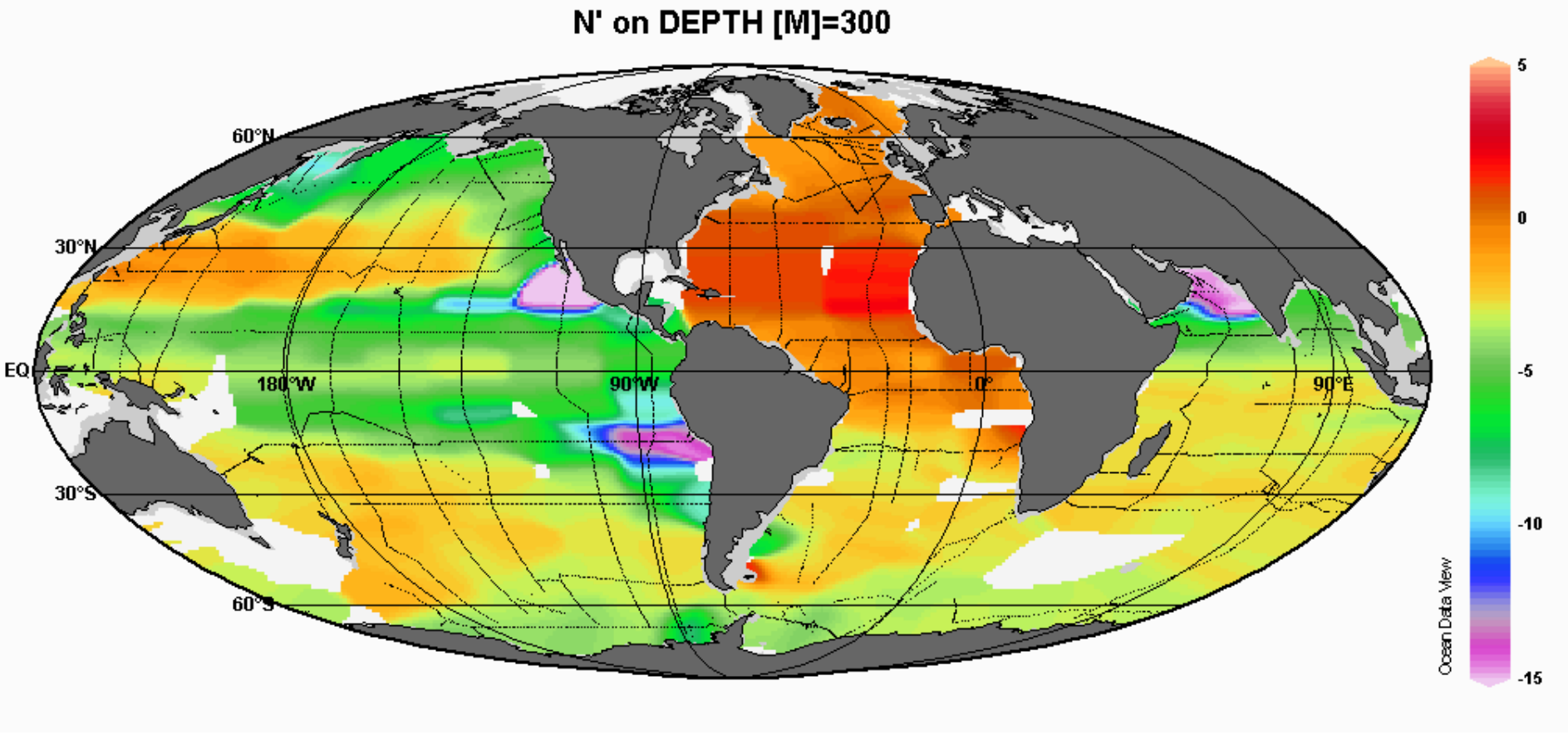


Need to know regional initial $\delta^{15}NO_3^-$ values!



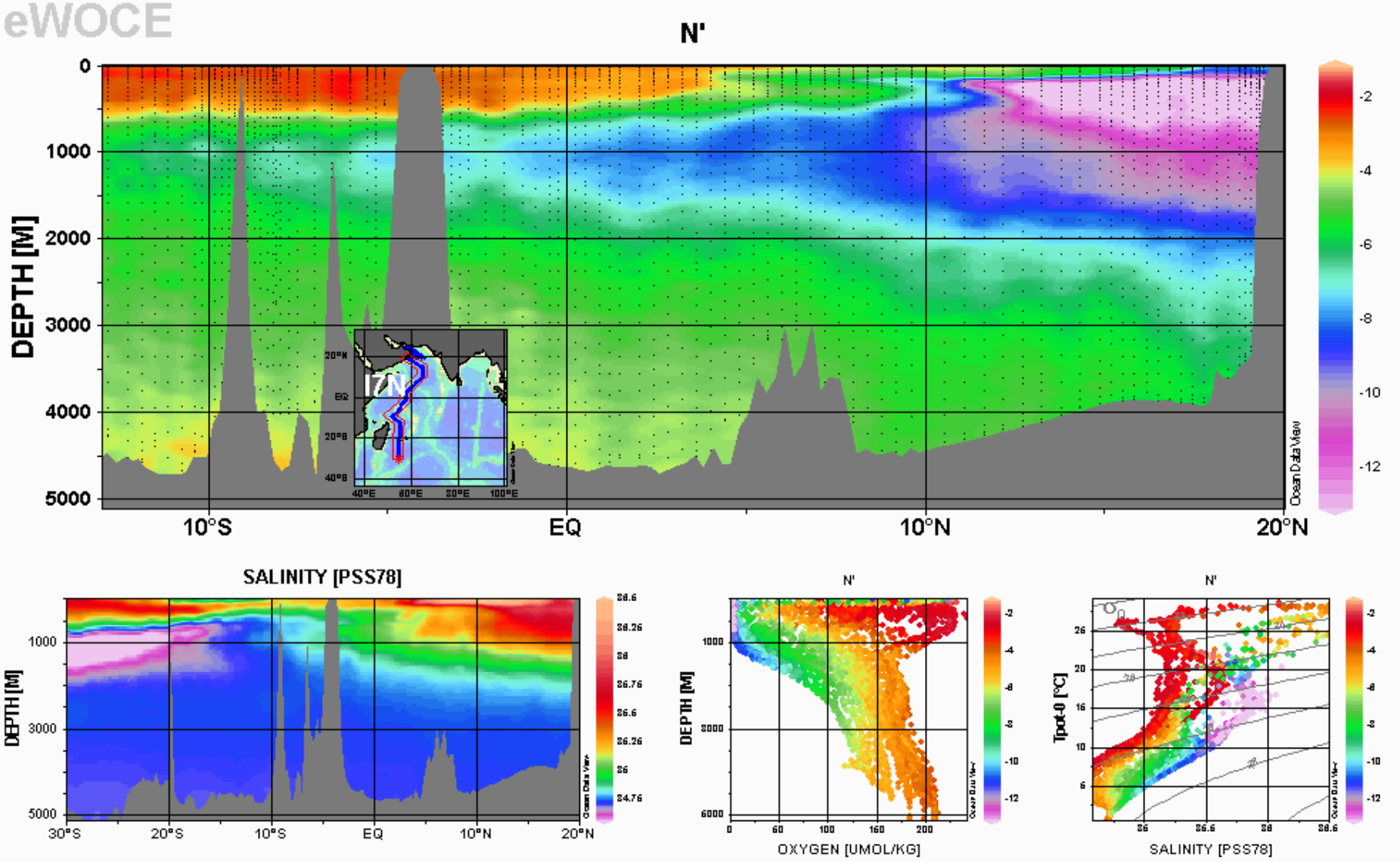


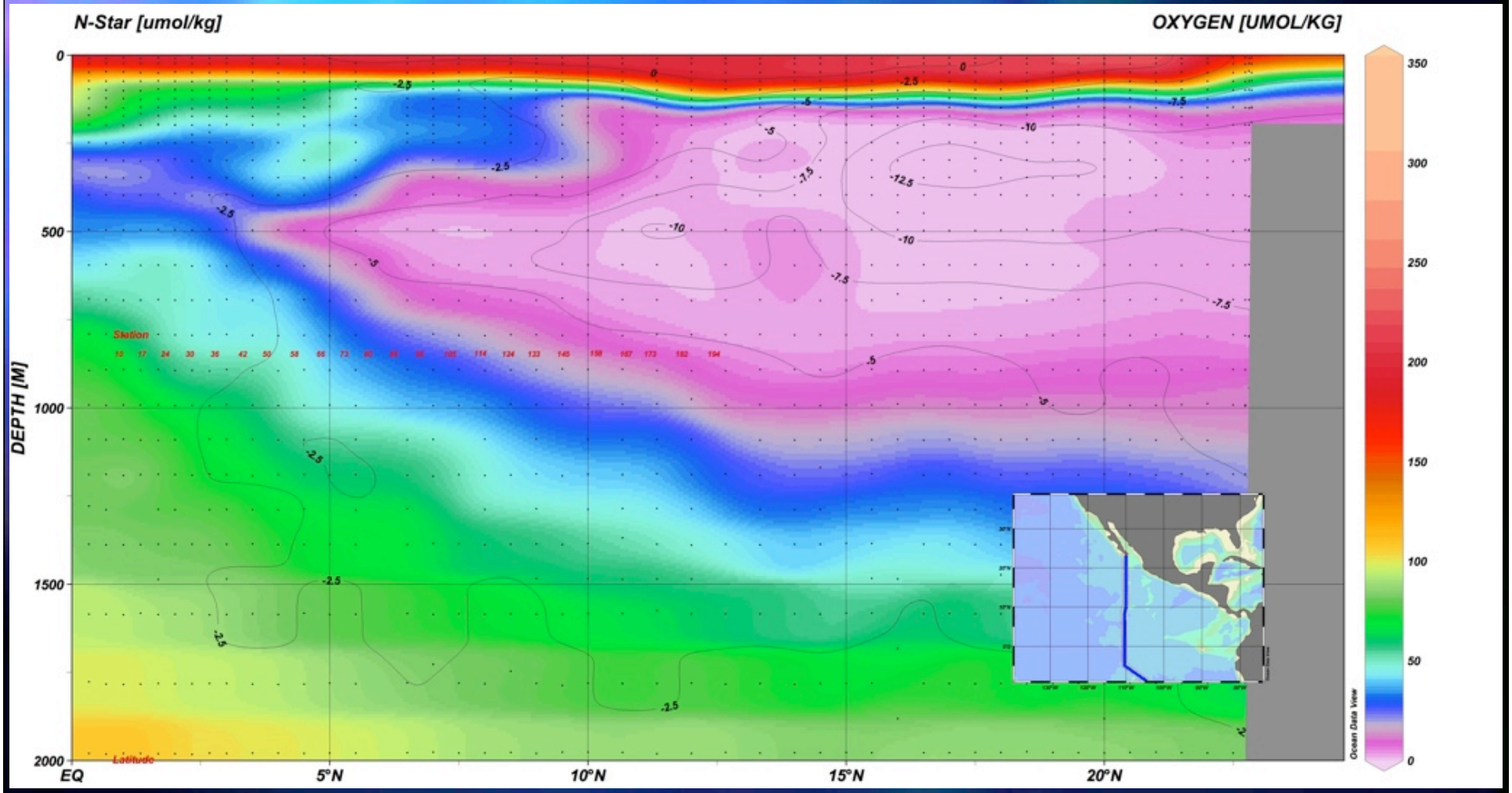
Horizontal and vertical extent for regional integration



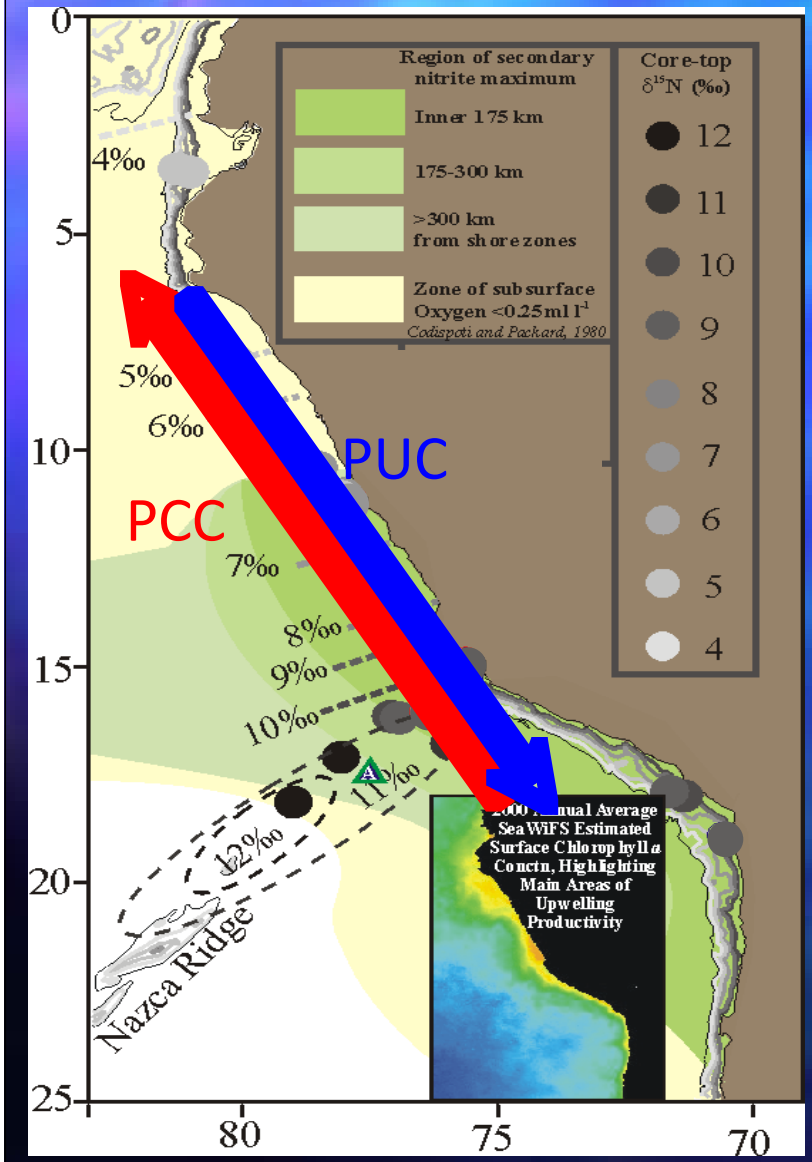
$$N' = NO_3^- + NO_2^- - 16 \times PO_4^{-3}$$

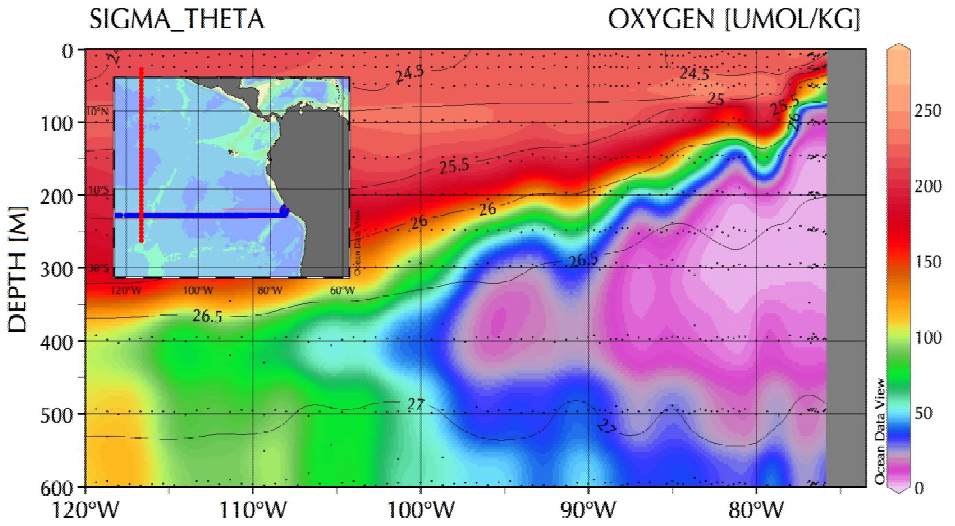
Water Column Denitrification Effects
(N' down, δ15N up)

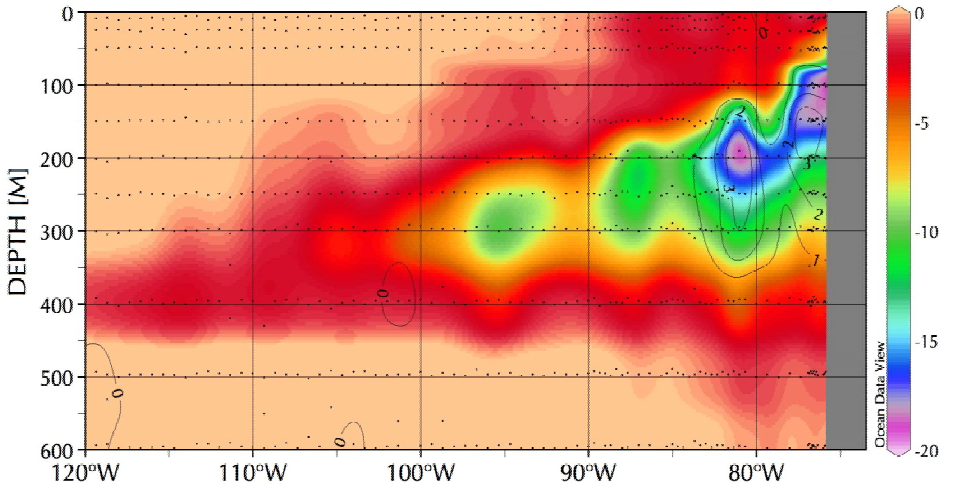



N-Star [umol/kg]
OXYGEN [UMOL/KG]
DEPTH [M]
0
500
1000
1500
2000
EQ
5°N
10°N
15°N
20°N
Station
Latitude
350
300
250
200
150
100
50
0
Ocean Data View

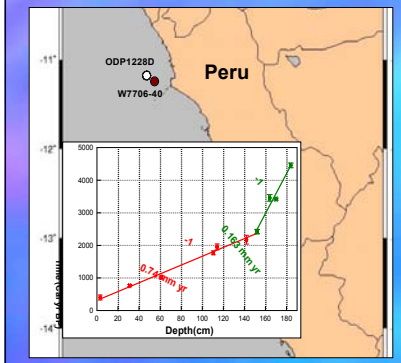
The Peru OMZ/Denitrification Region

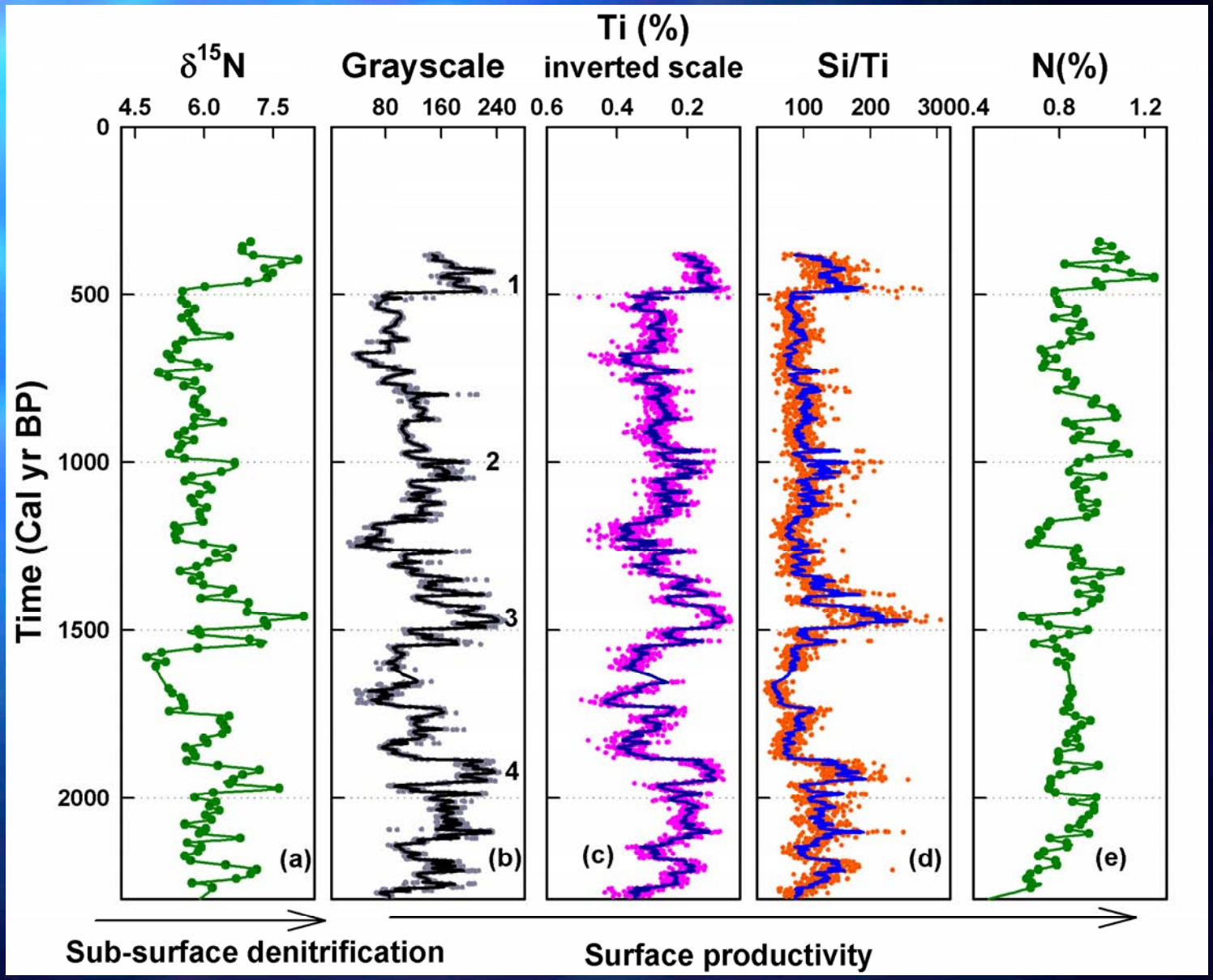






Late Holocene Variations Linked to Productivity?





GCM's can simulate the major low O_2 zones, but are too coarse for getting the detailed circulation right!

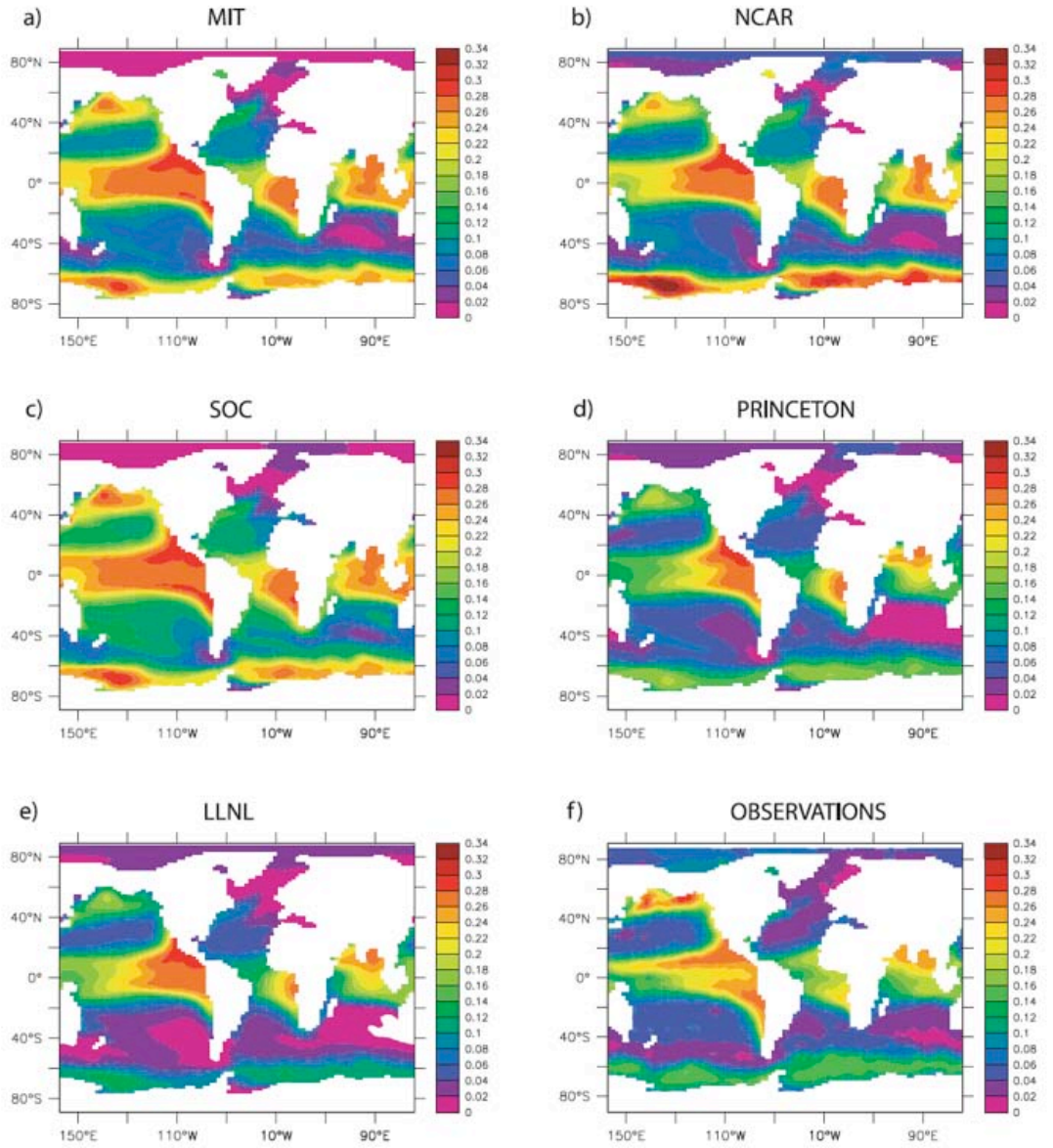
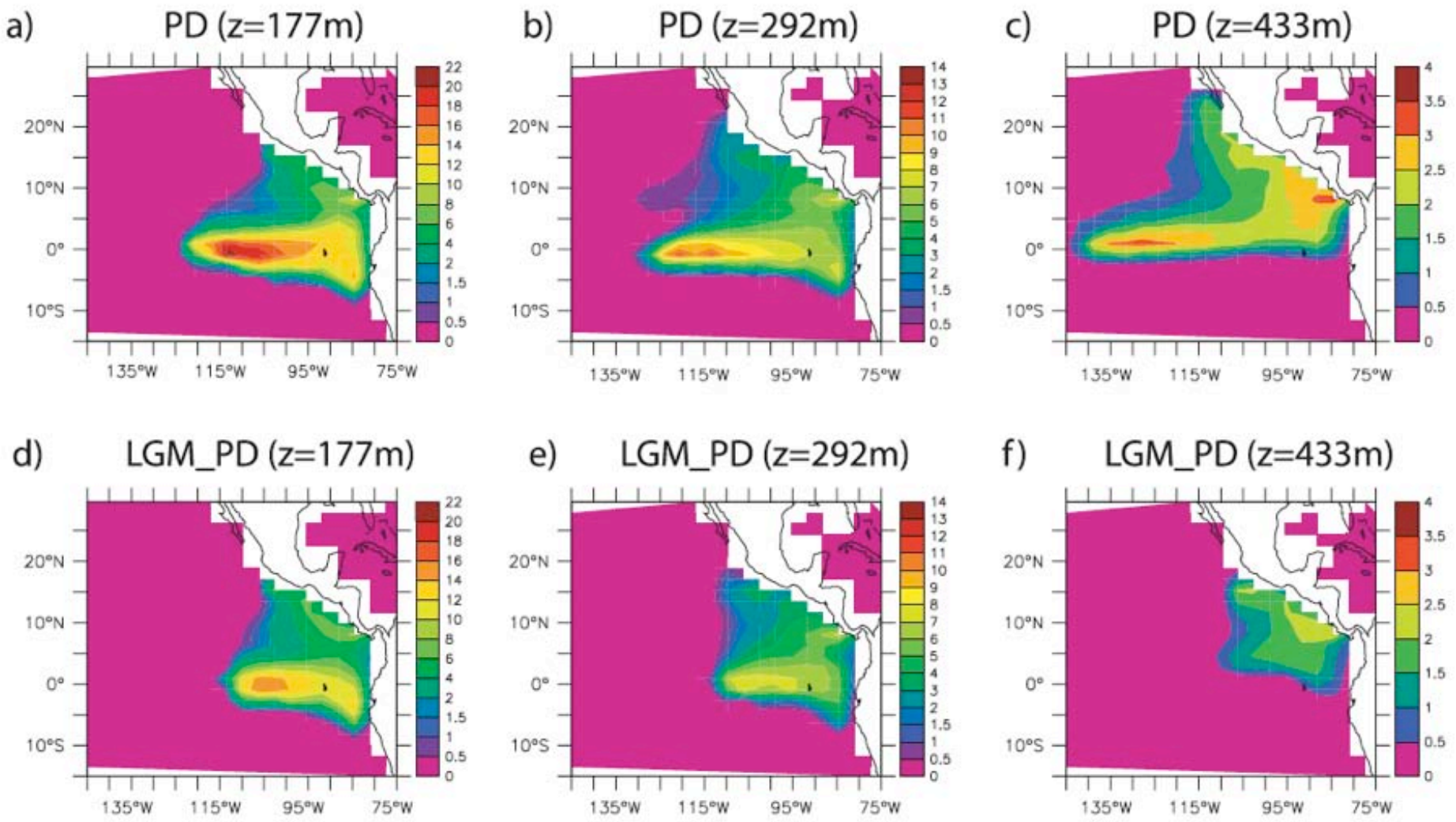
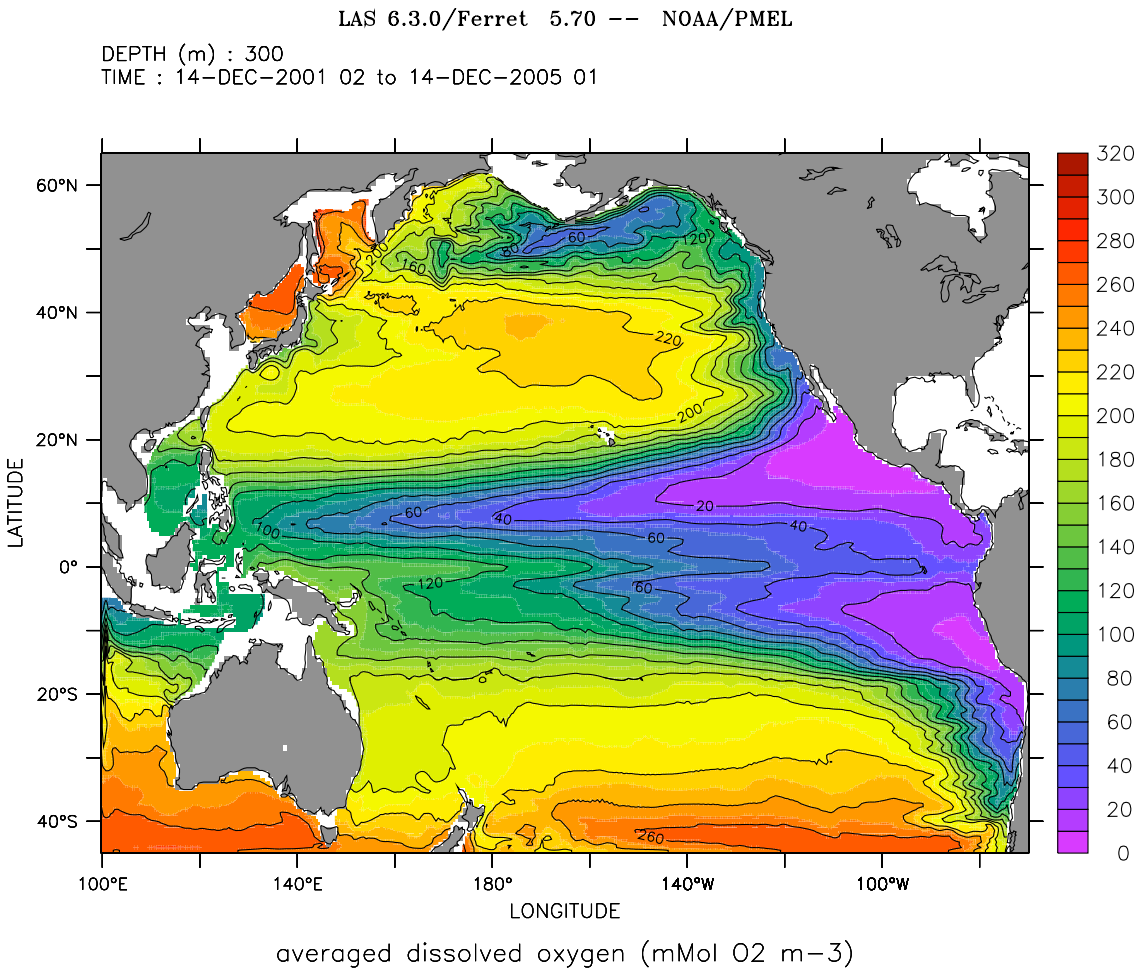
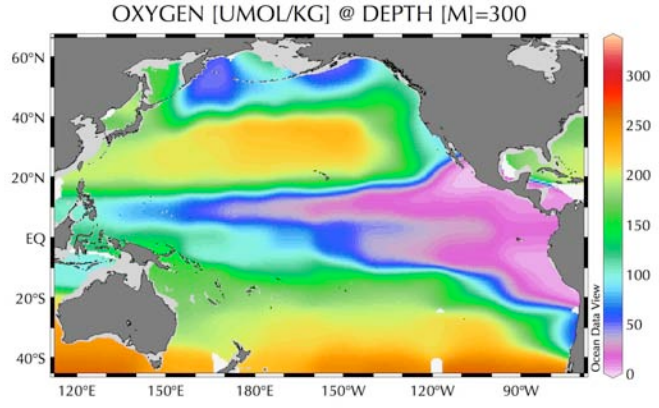


Figure 1. Annually averaged apparent oxygen utilization (AOU) at 300 m depth under present-day conditions for experiments run with data from (a) MIT, (b) NCAR, (c) SOC, (d) PRINCETON, (e) LLNL, and (f) observations [*Conkright et al.*, 2002]. Units are in mol m^{-3}.

Citation: Meissner, K. J., E. D. Galbraith, and C. Völker (2005), Denitrification under glacial and interglacial conditions: A physical approach, *Paleoceanography*, *20*, PA3001, doi:10.1029/2004PA001083.



A 50-year modern simulation using the Pacific ROMS-CoSine