Nitrate Isotope Fractionation During Microbial Nitrate Reduction

Moritz F. Lehmann
GEOTOP-UQAM-McGill, Montréal

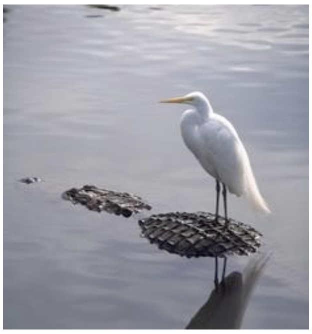
GASIR Annual Meeting
11 October, 2005, MPI Jena

Thanks to:

Daniel Sigman, Greg Cane, Princeton University

Julie Granger, UBC, Vancouver

Dan McCorkle, Woods Hole Oceanographic Institution

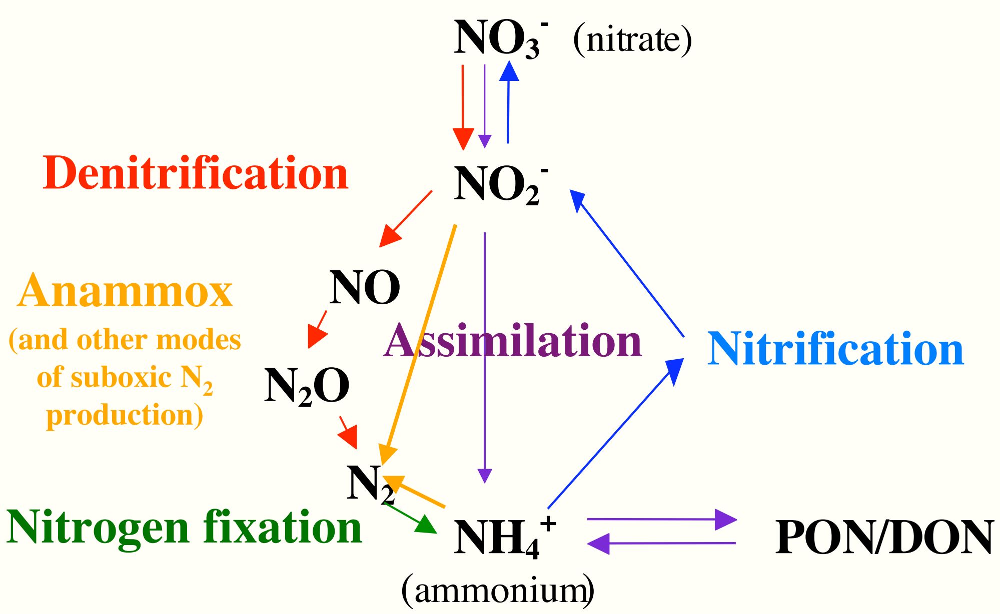


Outline:

- The marine N-cycle, the global N budget
- N and O isotopes in nitrate; the utility of dual isotope approach
- Isotope effects during microbial denitrification (laboratory, lakes, ocean water column, marine sediments)

The marine N-cycle

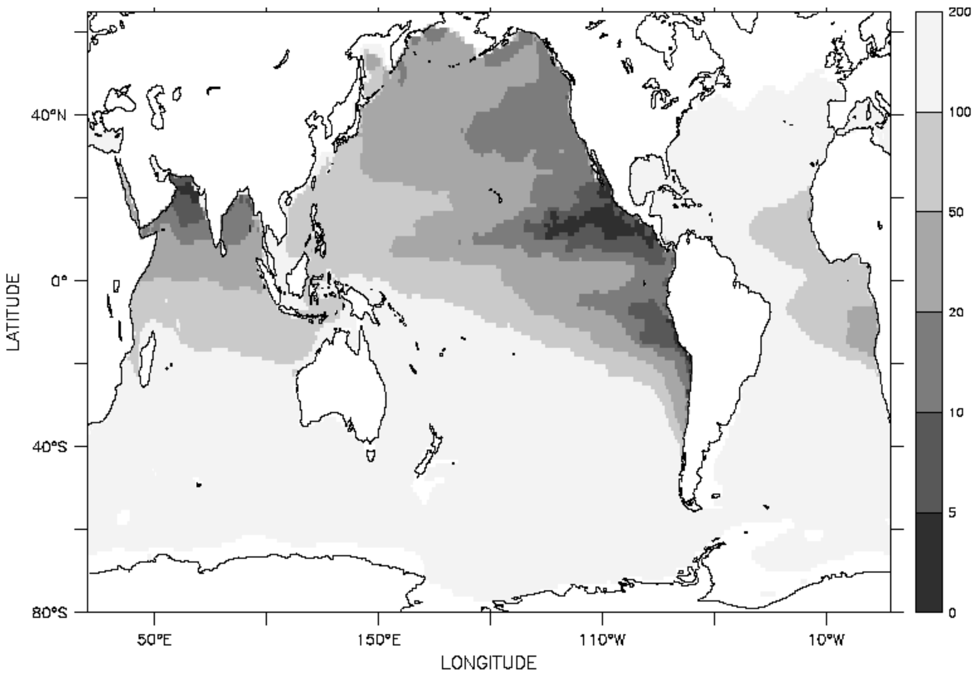
The Nitrogen Cycle



Ecological Significance of Nitrogen/Denitrification

- Primary nutrient in freshwater systems
- Control on eutrophication in lakes and reservoirs, as well as coastal and estuarine environments
- The ocean and lakes are significant sources of atmospheric N_2O
- N is limiting nutrient in the ocean ("biological pump")

Denitrification in the Pacific

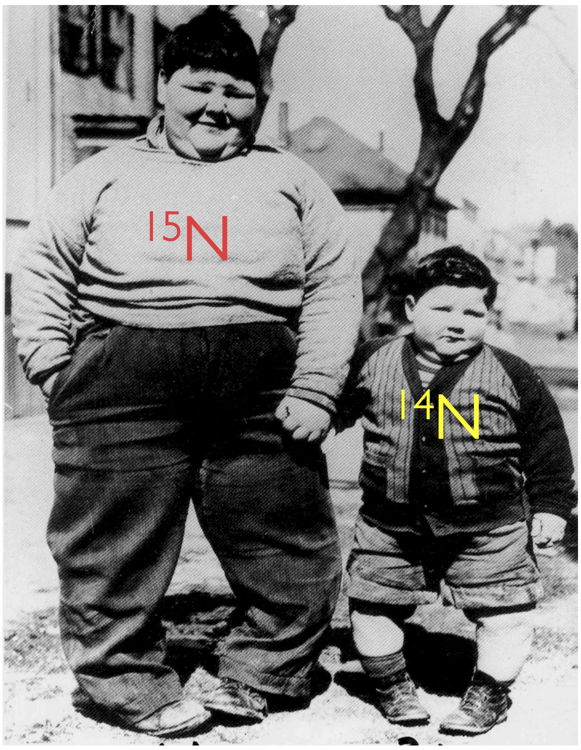


Oxygen at annual mean OMZ

The Oceanic fixed N Budget

Flux TgN/yr	Codispoti and Christensen 1985	Gruber and Sarmiento 1997	Brandes and Devol 2002
N_2 Fixation	25	125	110-330
Rivers	25	42	25
Atmosphere	25	15	25
Inputs Total	75	231	160-380
Benthic Denit.	60	95	200-280
W.C. Denit.	60	80	75
Sedimentation	21	25	25
Outputs Total	142	204	300-380
Imbalance	-70	0 +/- 50	0 or -200
Residence time	> 5000 yr	~ 3500 yr	< 2000 yr

With courtesy from C. Deutsch



Isotope definitions

N isotopes in nature: $^{14}N = 99.64\%$
$^{15}N = 0.36\%$

$$\delta^{15}N\ (‰\ \text{vs. air}) = \left(\frac{(^{15}N/^{14}N)_{sample}}{(^{15}N/^{14}N)_{air}} - 1 \right) * 1000$$

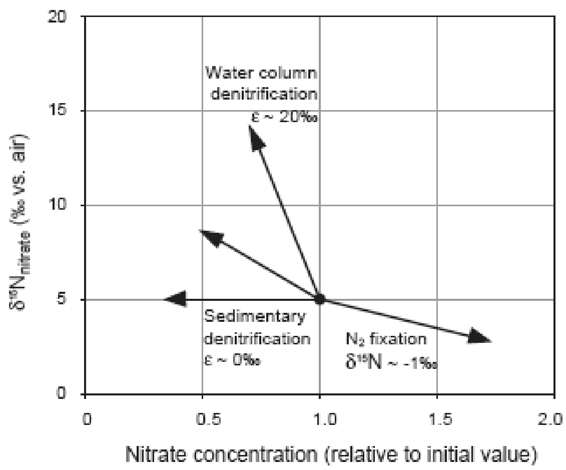
Isotope effect: $\varepsilon \sim \delta^{15}N_{react} - \delta^{15}N_{prod(inst)}$

Kinetic isotope fractionation: Organisms preferentially utilize ^{14}N-bearing molecules → substrate becomes enriched in ^{15}N

Use of Nitrate isotopes:

- Nitrate source indicator
- **Biogeochemical tracer**
  (e.g., sedimentary vs. water column denitrification; nitrification/N_2 fixation vs denitrification)

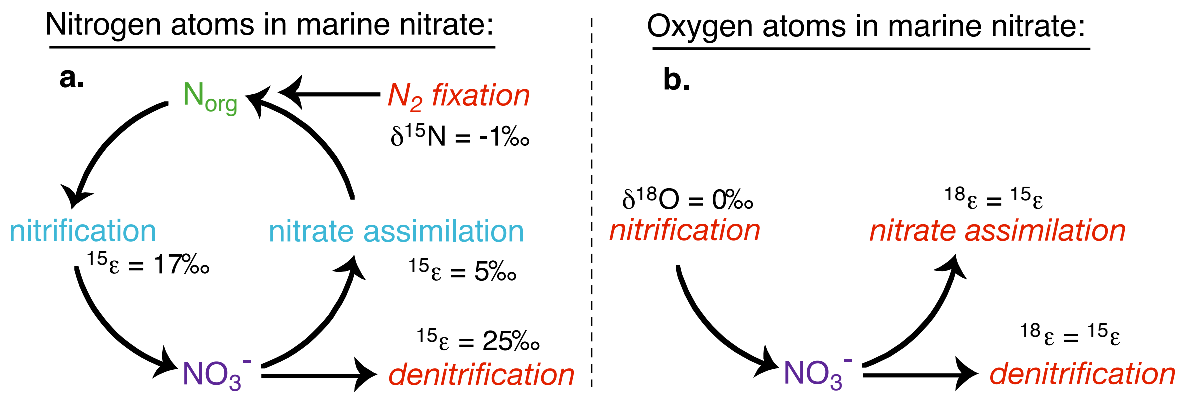
Isotope effects: major fluxes



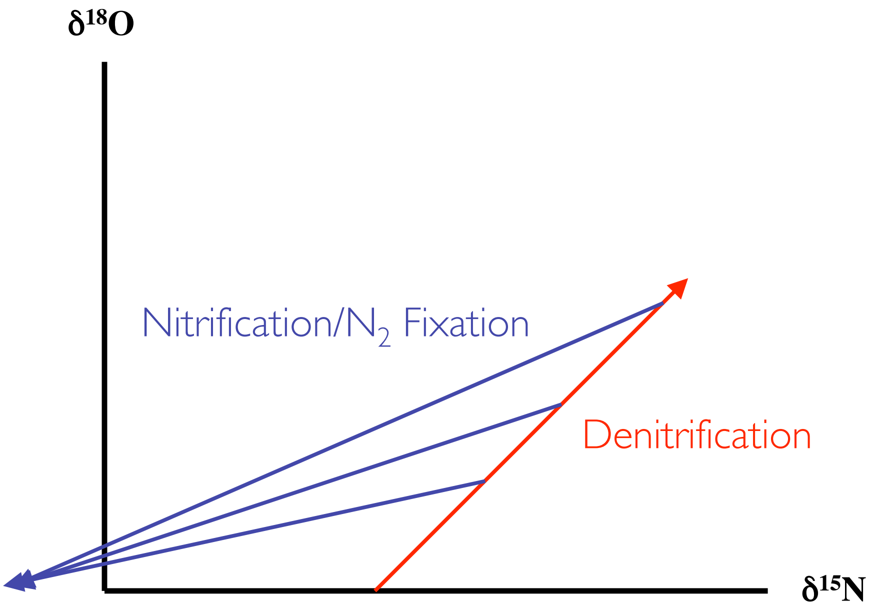
Galbreith et al. submitted

Two-endmember approach: Constraints on the relative importance of sedimentary vs. water column denitrification

The dual isotope approach: The O isotopes are useful because of what they do not record



Sigman et al. 2005



The denitrifier method:

Sigman et al. 2001 and Casciotti et al. 2002

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \not\rightarrow N_2$$

advantages of the denitrifier method:

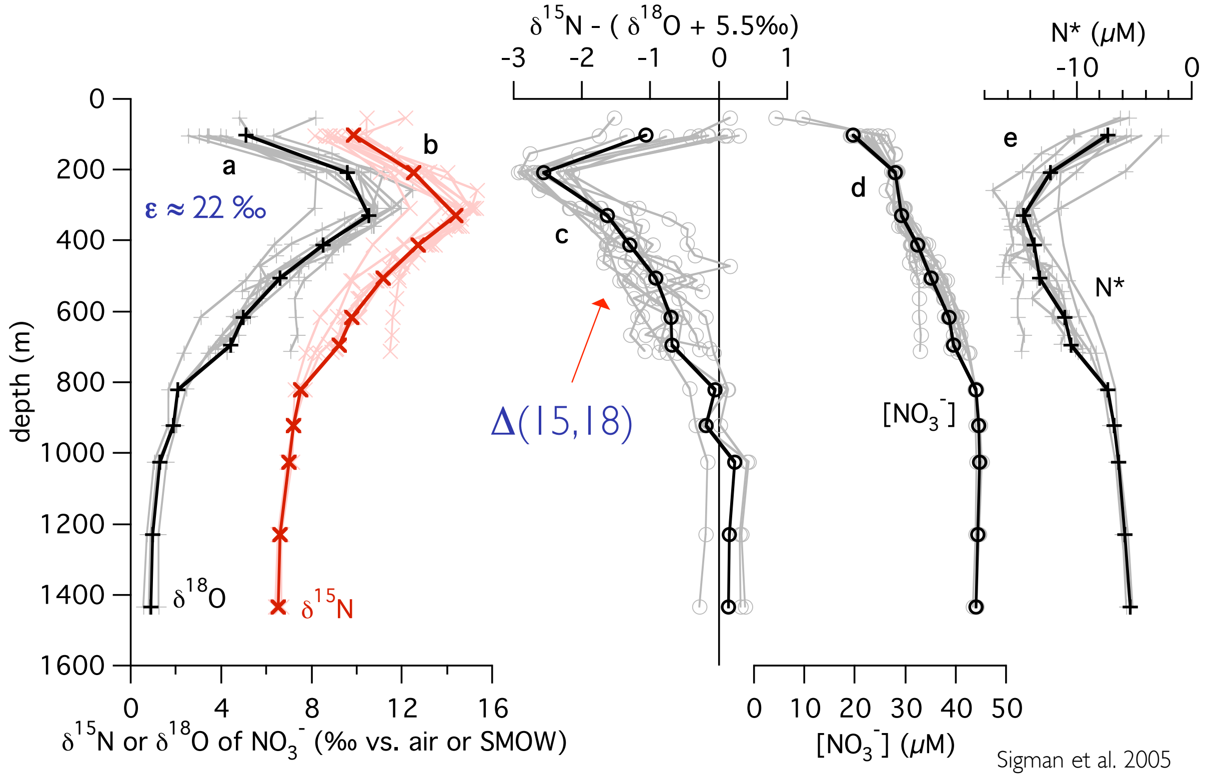
- simultaneous analysis of N and O isotopes of NO_3
- orders of magnitude smaller sample size requirement ammonium-based methods (~1 μmol)

- detection limit currently 1 μM NO_3
- precision for $\delta^{15}N$ is ± 0.2 ‰
- precision for $\delta^{18}O$ is ± 0.3 ‰

Pseudomonas chlororaphis

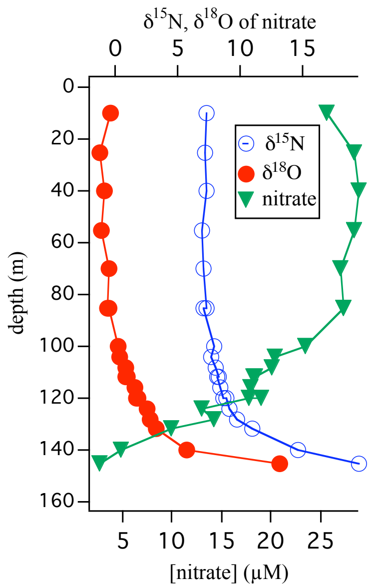
Isotope effects during denitrification

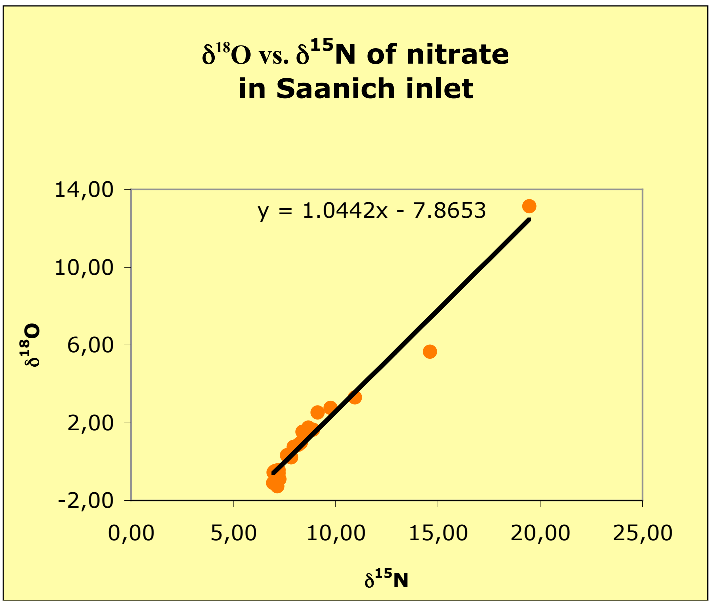
Nitrate isotopes near southern tip of Baja



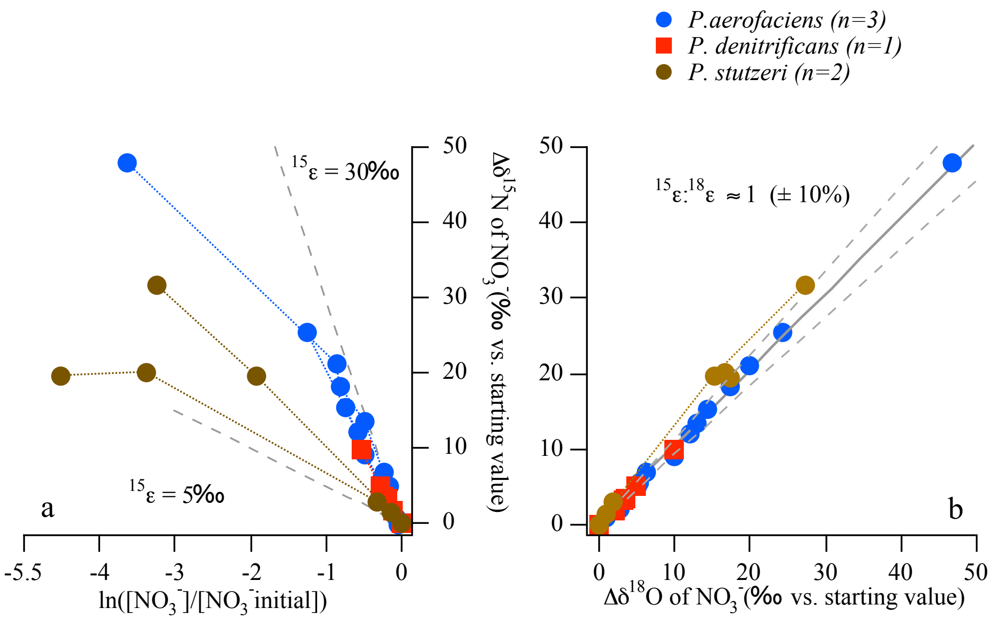
Sigman et al. 2005

Isotope effects during denitrification





NO_3^- Reduction by Denitrifiers in Seawater



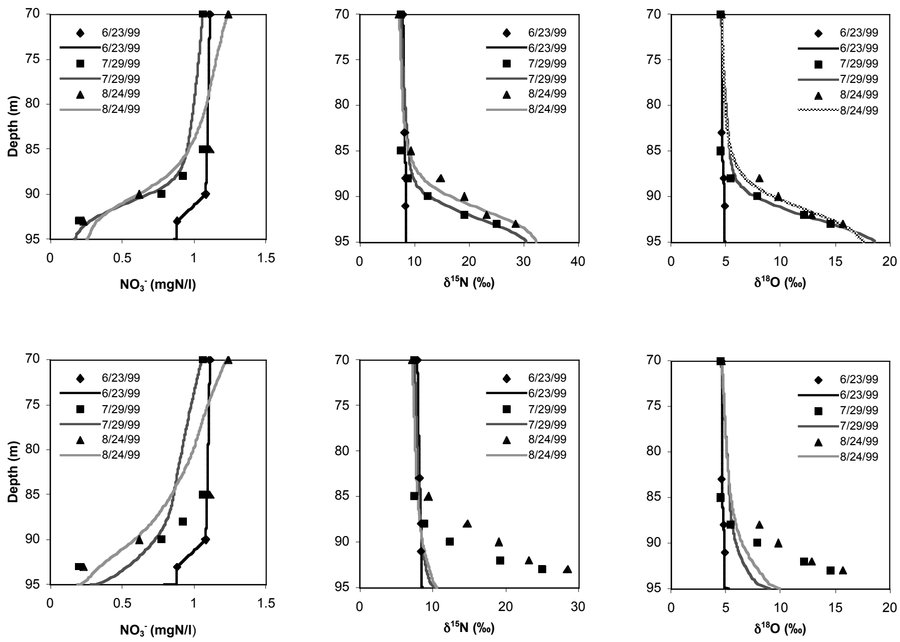
Granger et al. in prep.

Isotope effects during denitrification

Denitrification in a eutrophic lake

Water column denitrification:

Benthic denitrification only:



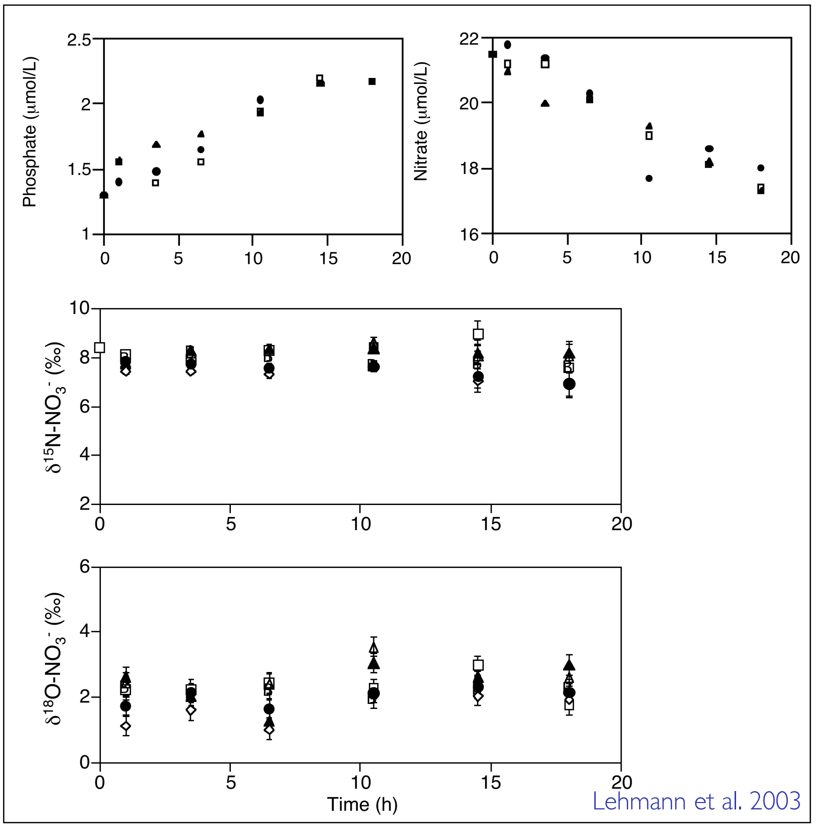
- ε variable?
- $\varepsilon_{18}/\varepsilon_{15} \approx 0.5$

Lehmann et al. 2003

Isotope effects during denitrification

NO_3^- Reduction by Denitrifiers in sediments

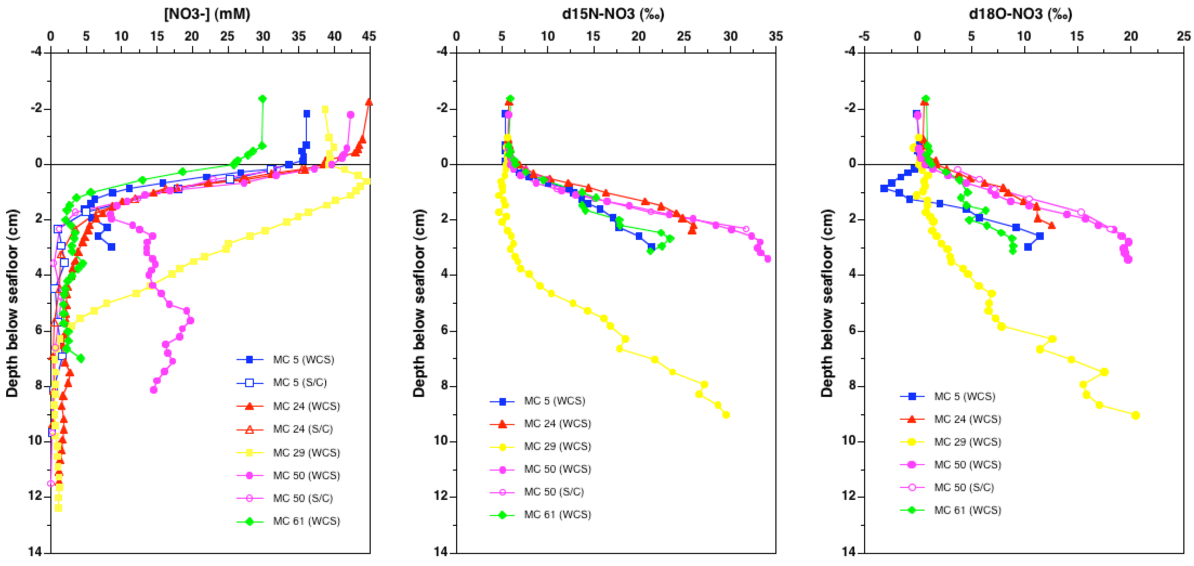
BC experiments on the southern Californan Shelf)



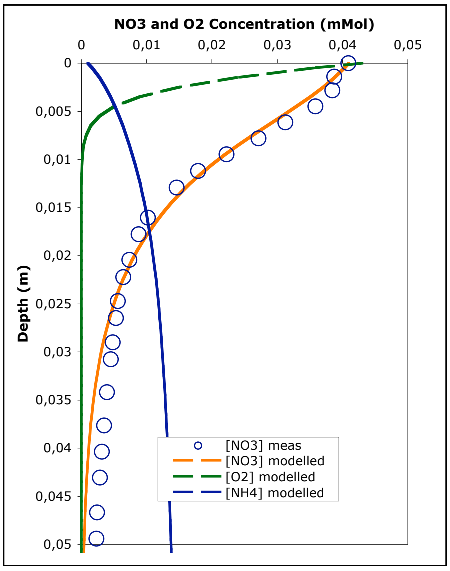
Lehmann et al. 2003

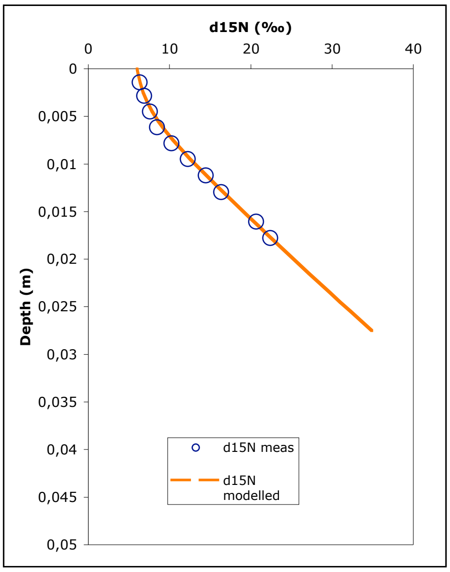
Isotope effects during denitrification

Bering Sea porewater nitrate:



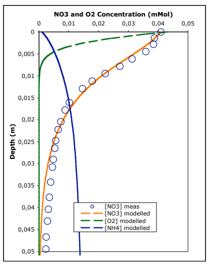
Benthic denitrification: Porewater nitrate isotope effect

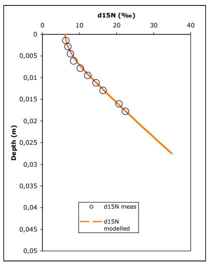




$\varepsilon_{biol} = 28\pm3‰$

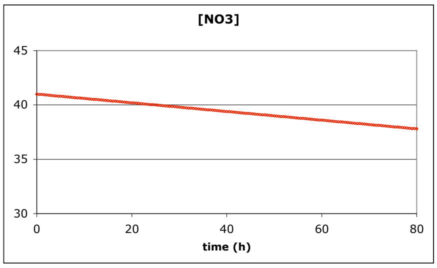
Simulated Benthic chamber experiment

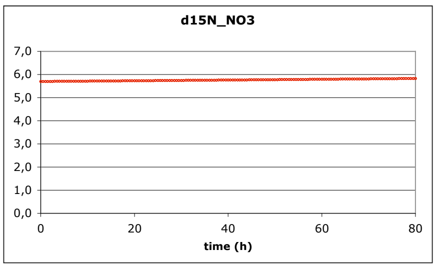


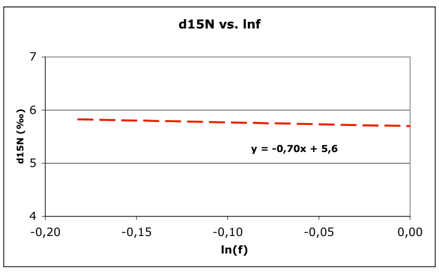


$\varepsilon_{biol} = 28\pm3‰$

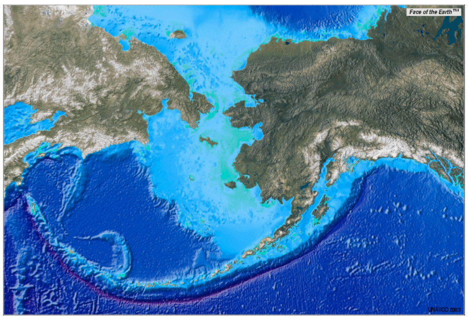
$\varepsilon_{app} = 0.7\pm1‰$

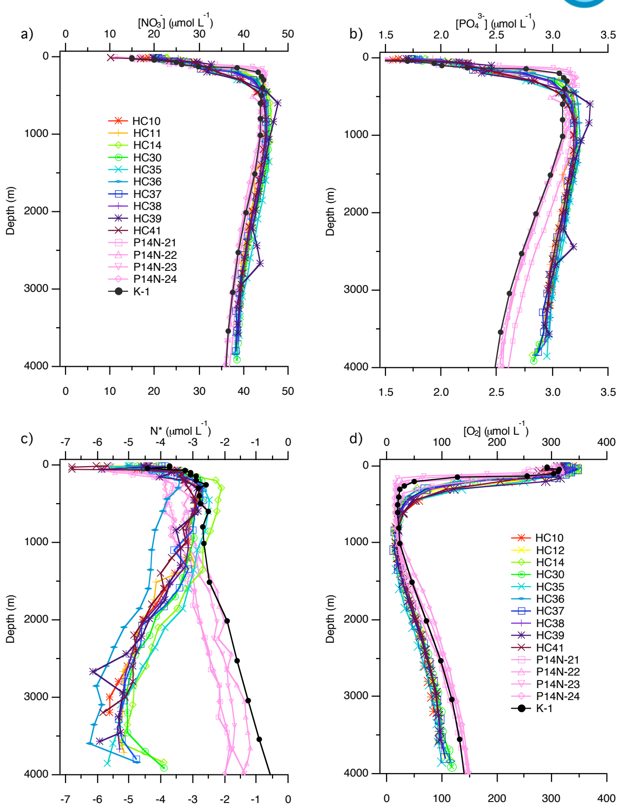






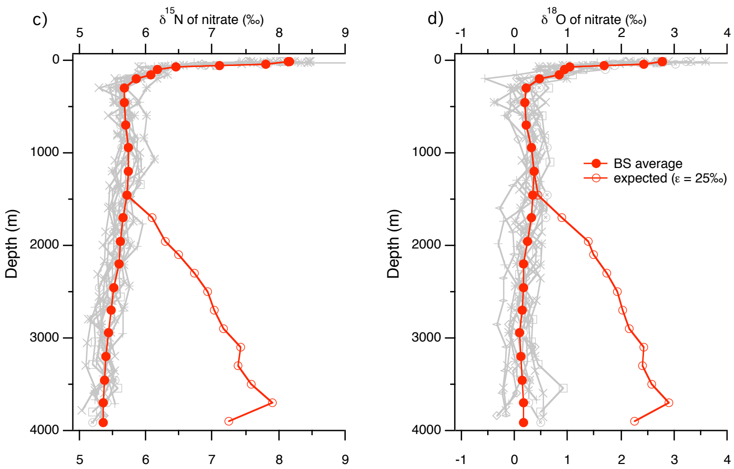
The Bering Sea nitrate deficit





Lehmann et al. 2005

The Bering Sea nitrate deficit



Lehmann et al. 2005

A non-fractionating nitrate consumption process is needed to explain N and O isotope profiles in the BS

Sedimentary denitrification!?

The Bering Sea nitrate deficit

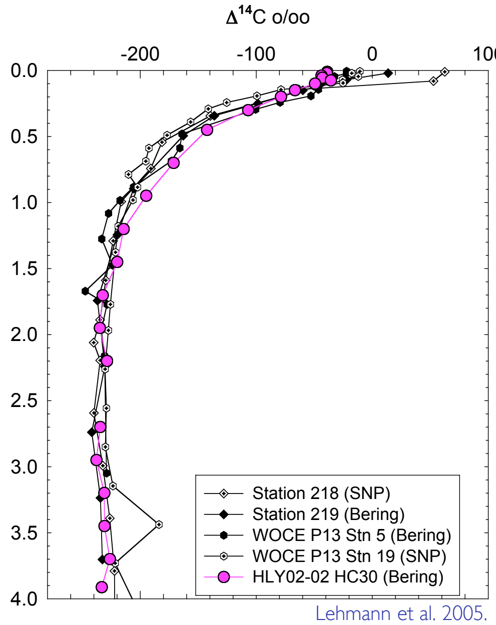
GEOTOP UQAM-McGill Centre de recherche en géochimie et en géodynamique

Why do we see a clear nitrate deficit in the Bering Sea and not elswhere in the (oxygenated) deep ocean?

Are the benthic denitrification rates higher than elsewhere?

Yes!

WOCE and GEOSECS Radiocarbon
Bering Sea and Subarctic North Pacific



Lehmann et al. 2005.

Conclusions

- Nitrate $\delta^{15}O$ and $\delta^{18}O$ are useful biogeochemical tracers
- Combined nitrate N and O isotope analyses allow deconvolution of simultaneously occurring N-cycling reactions
- Linear relationship between N and O isotope enrichment, but different for freshwater and sea water
- Strong expression of nitrate isotope effects for both water column and porewater denitrification
- Organism-level denitrification isotope effects seem to be variable and may not be robust
- Sedimentary denitrification isotope effect barely expressed at scale of sediment-water nitrate exchange (Diffusion limitation)
- Combined with other oceanographic data, nitrate isotopes provide integrative constraints on large-scale N fluxes

Bering Sea:

- Absence of isotope effect associated with nitrate deficit points to the deep sediments as the main sink of fixed N

Open questions/Future Work

- What controls the ratio of ^{18}O vs. ^{15}N isotope enrichment during denitrification?
- What controls variability in N and O isotope effects during denitrification?
- Role of suboxic N_2 production processes other than denitrification (anammox) for N isotope balance?
- Role of NH_4^+ and DON for nitrate isotope signatures in the water column?

"Heavy" NH_4 can increase total apparent N isotope effect significantly (ε = 5‰)