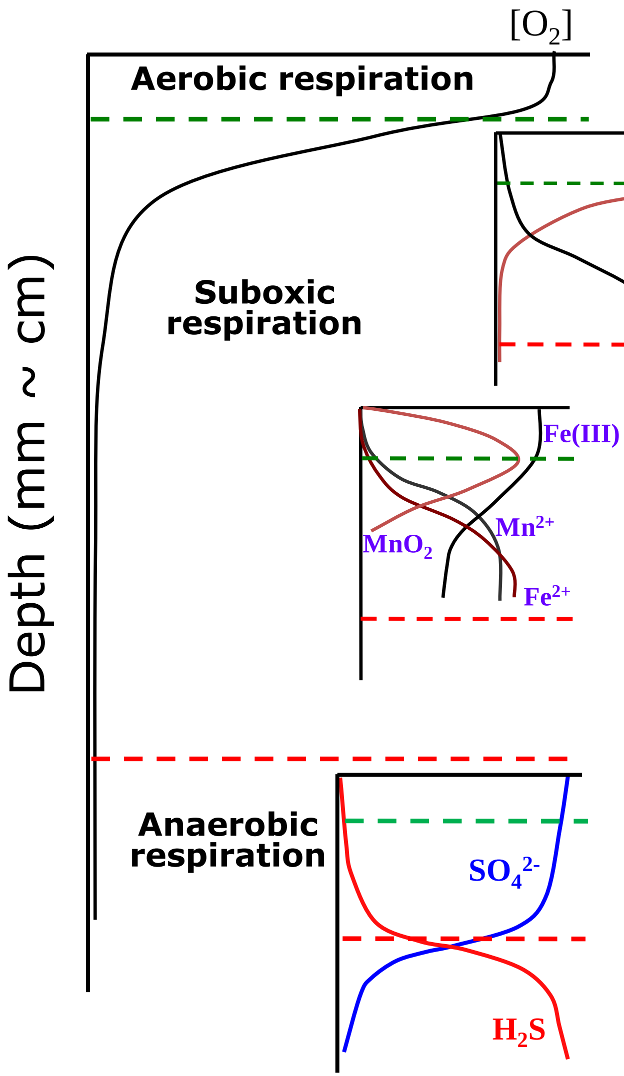
N_2 production through denitrification and anammox in the Ulleung Basin, East/Japan Sea

Taehee Na
(Seoul National University)
Jung-Ho Hyun
(Hanyang University)

Pathways of organic C oxidation in marine sediment



✓O_2 reduction (ΔG^o = - 518 kJ/mol) :

$CH_2O + O_2 = CO_2 + H_2O$

✓Nitrate reduction (ΔG^o = - 354 kJ/mol) :

$5CH_2O + \mathbf{4NO_3^-} + 4H^+ = 5CO_2 + \underline{2N_2} + 7H_2O$

✓Mn(IV) reduction (ΔG^o = - 502 kJ/mol) :

$CH_2O + \mathbf{2MnO_2} + 4H^+ = CO_2 + \underline{2Mn^{2+}} + 3H_2O$

✓Fe(III) reduction (ΔG^o = - 392 kJ/mol) :

$CH_2O + \mathbf{4FeOOH} + 8H^+ = CO_2 + \underline{4Fe^{2+}} + 7H_2O$

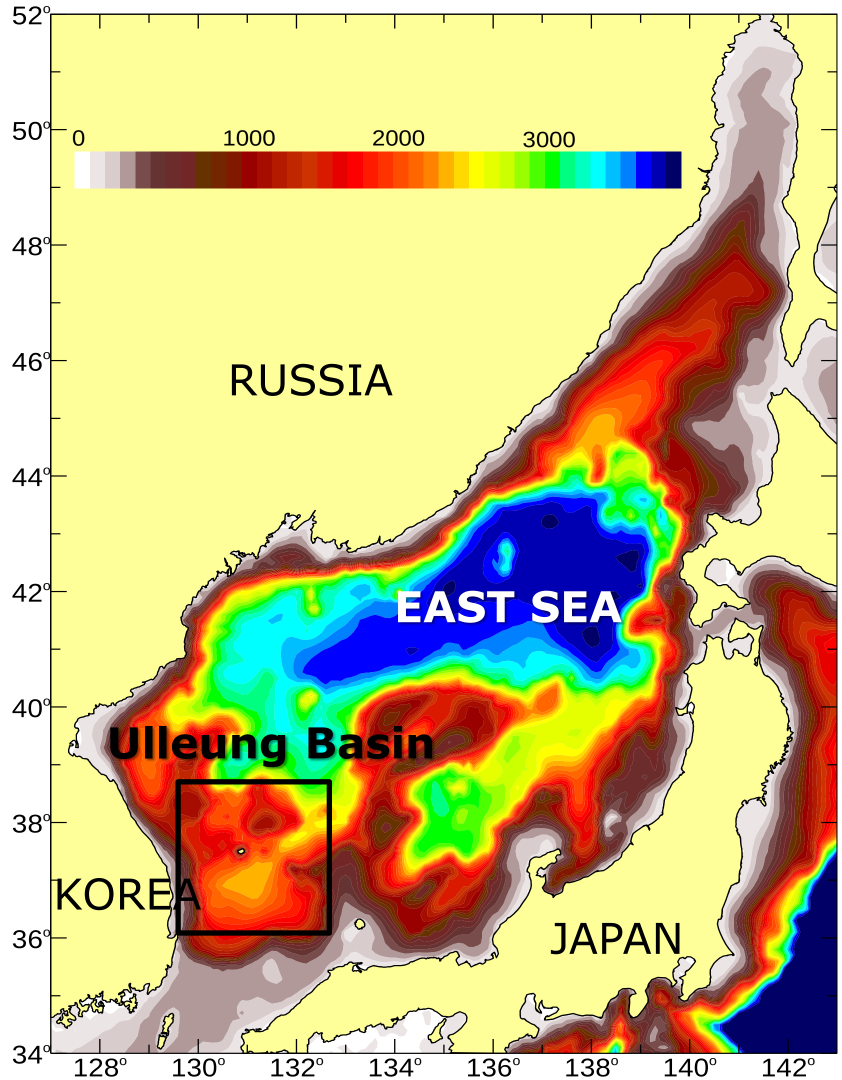
✓Sulfate reduction (ΔG^o = - 247 kJ/mol):

$2CH_2O + \mathbf{SO_4^{2-}} + H^+ = 2CO_2 + \underline{H_2S} + 2H_2O$

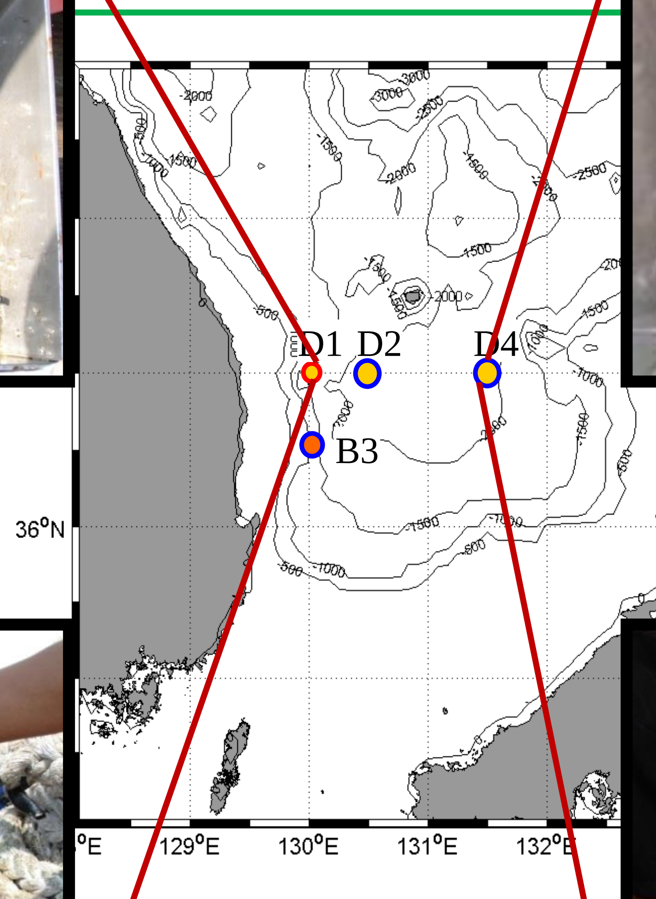
why to understand C oxidation pathways?

- $106(CH_2O) + 16(NH_3) + H_3PO_4 + 138O_2 = 106(CO_2) + 16(HNO_3^-) + H_3PO_4 + 122(H_2O)$
- $106(CH_2O) + 16(NH_3) + H_3PO_4 + 84.8(HNO_3^-) = 106(CO_2) + 16NH_3 + H_3PO_4 + 42.4(N_2) + 148.4(H_2O)$
- $106(CH_2O) + 16(NH_3) + H_3PO_4 + 212(MnO_2) = 106(CO_2) + 16NH_3 + H_3PO4 + 212(Mn^{2+}) + 308(H_2O)$
- $106(CH_2O) + 16(NH_3) + H_3PO_4 + 424(FeOOH) = 106(CO_2) + 16(NH_3) + H_3PO_4 + 424(Fe^{2+}) + 848(H_2O)$
- $106(CH_2O) + 16(NH_3) + H_3PO_4 + 53 H^+ + 53(SO_4^{2-}) = 106(CO_2) + 16NH_3 + H_3PO_4 + 53(HS^-) + 106(H_2O)$
- $106(CH_2O) + 16(NH_3) + H_3PO_4 = 53(CO_2) + 16(NH_3) + H_3PO_4 + 53(CH_4)$

Ulleung Basin, East Sea



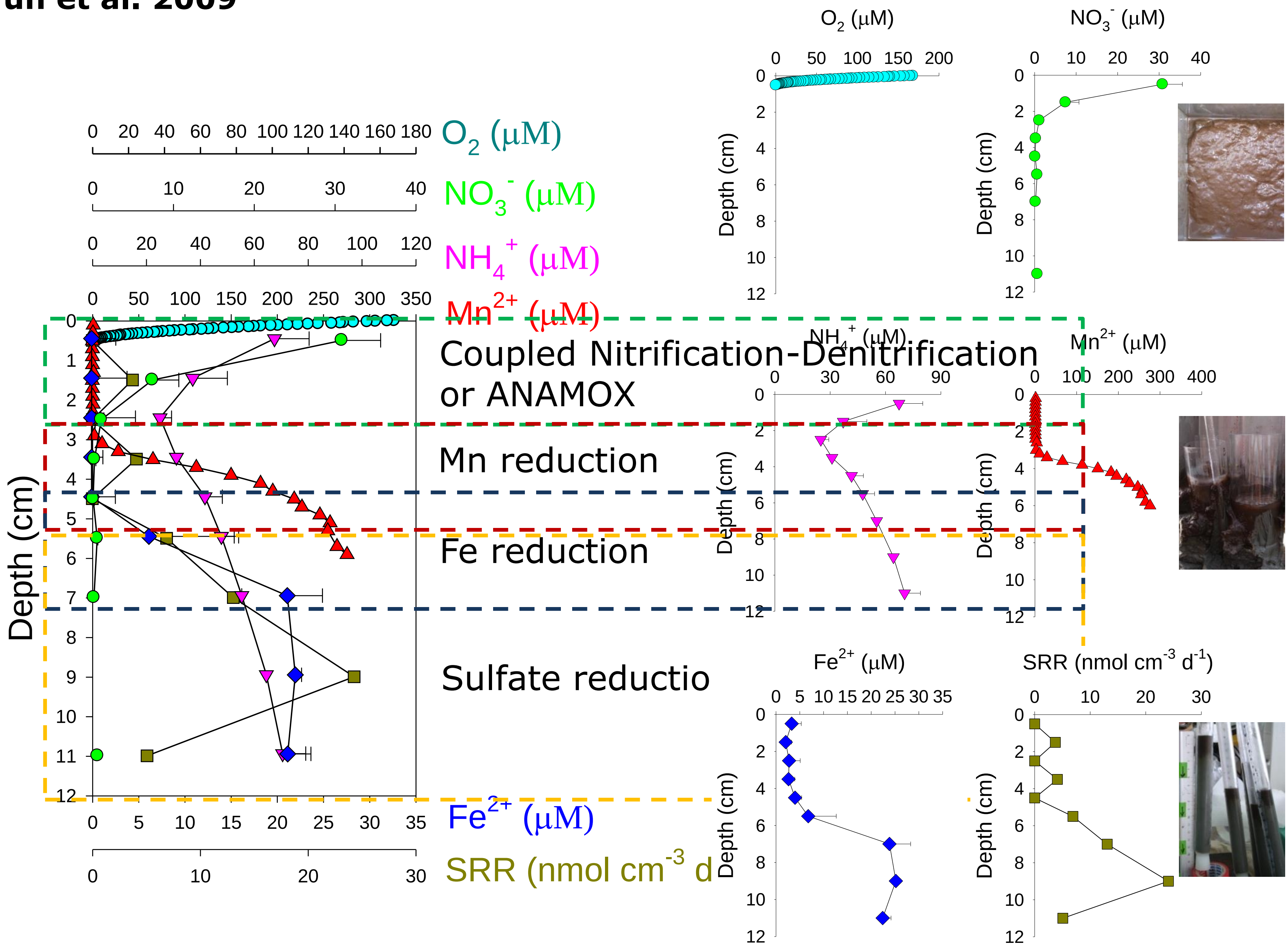
Geochemical properties of sediment : Intriguing !



Slope (D1):
Typical mud

Basin (D4) :
Reddish color

Hyun et al. 2009

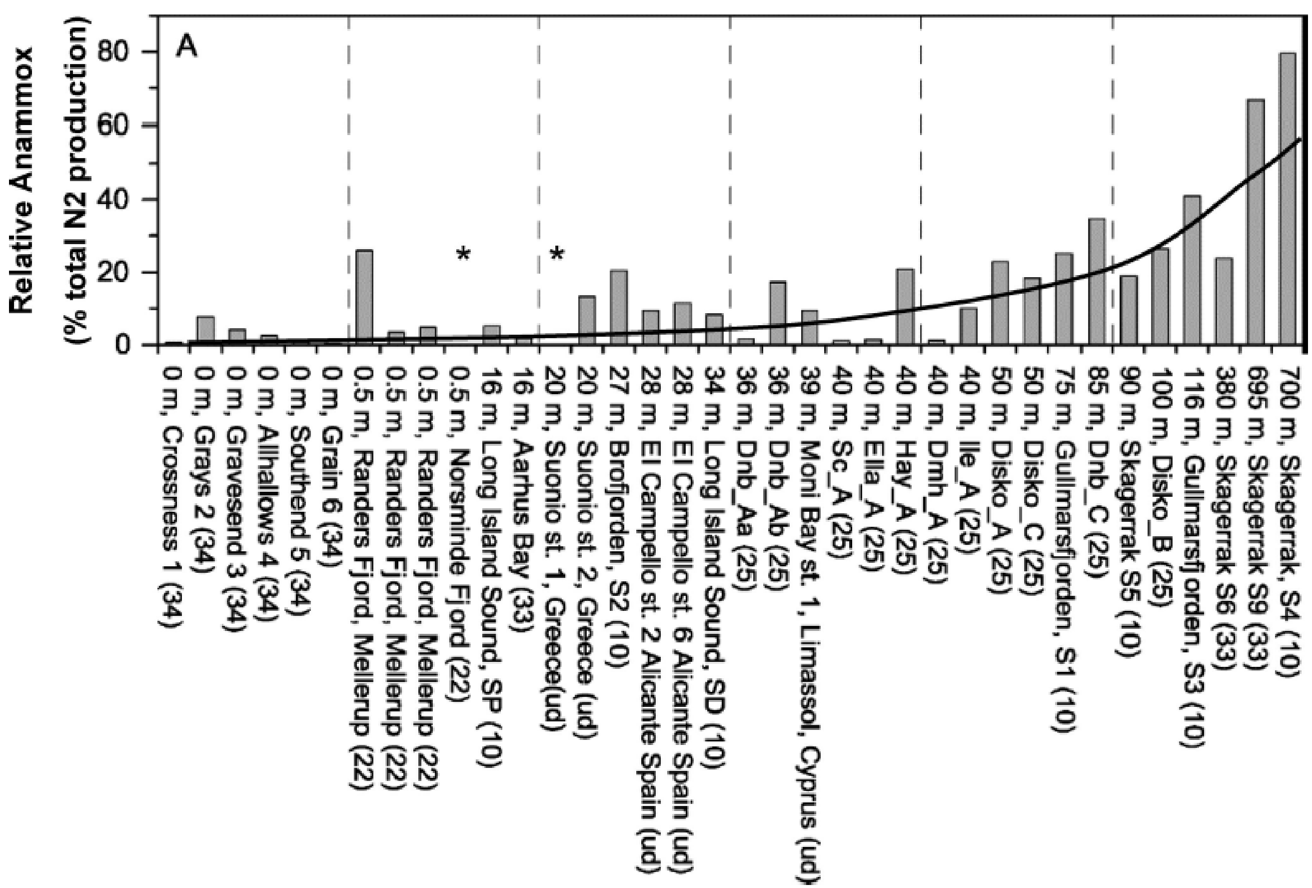


Ulleung Basin (UB)

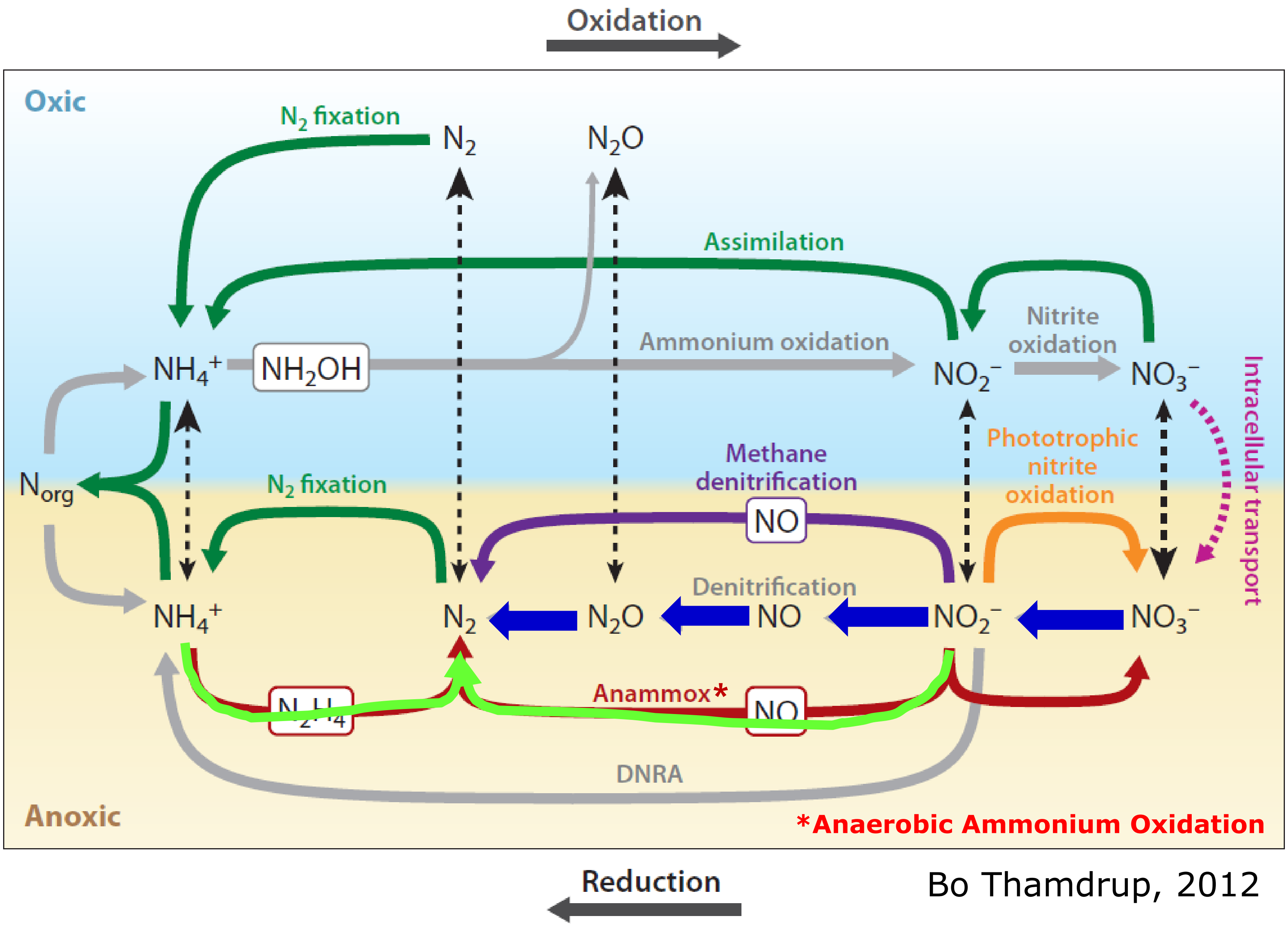
Rare and Unique sediments of the Ulleung Basin

- High organic carbon contents at depths greater than 2,000m (>2.5% dry wt.) (Lee *et al*. 2008)
- Higher sulfate reduction rate (<u>0.72~1.89mmol m^{-2} d^{-1}</u>) than those of other parts of the world (Hyun *et al*. 2010)
- Mn oxide enriched ([MnIV]> 200μmol cm^{-3}) sediments (Hyun *et al*. 2010)
- **Nitrogen study of the East Sea (deep sediment) is still very scarce.**

Nitrogen cycle in a marine sediment



Nitrogen cycle



Bo Thamdrup, 2012

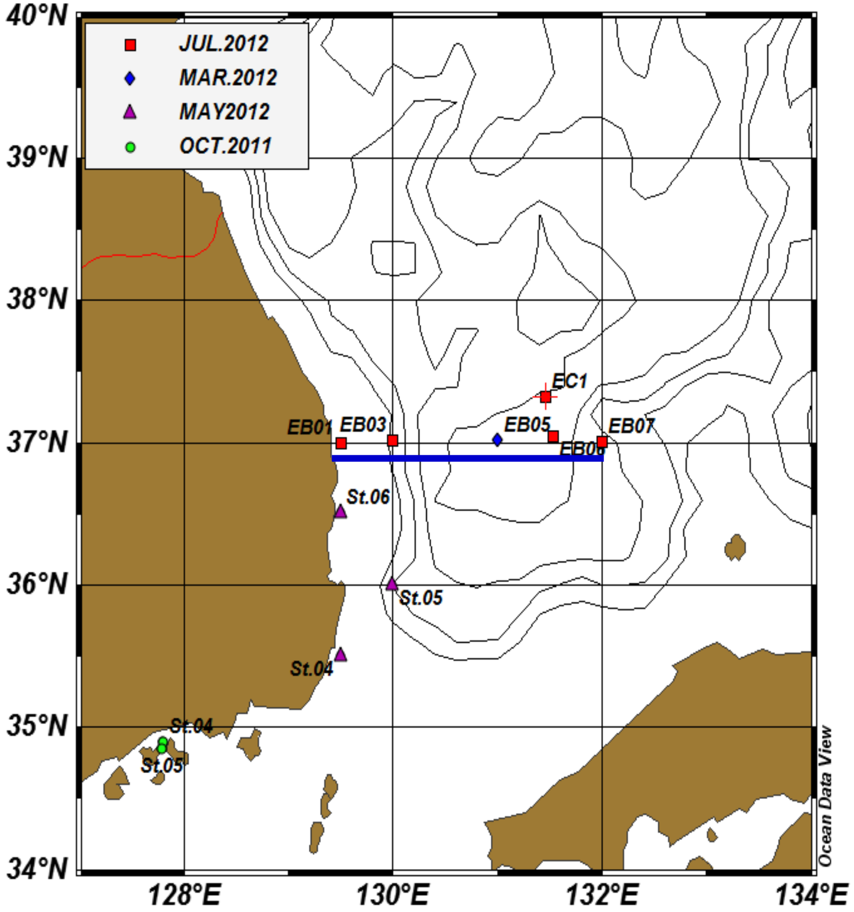
Denitrification and anammox

From continental shelf to center of the Ulleung Basin

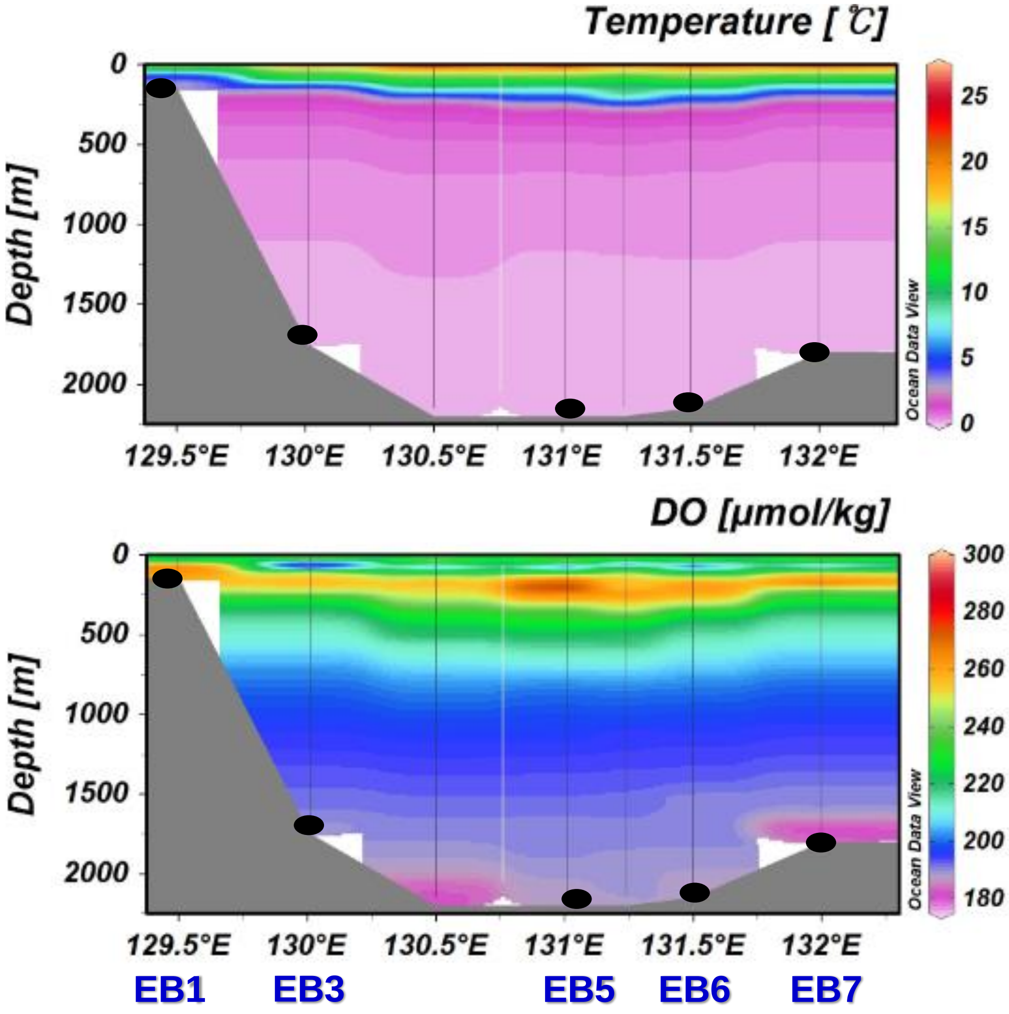
- ^{15}N isotope slurries and intact core incubations
- Relative importance of denitrification and anammox for sediment N removal
- Total N_2 production rates

: a continental shelf (>100m) to Basin (>2,000m)

Study Area

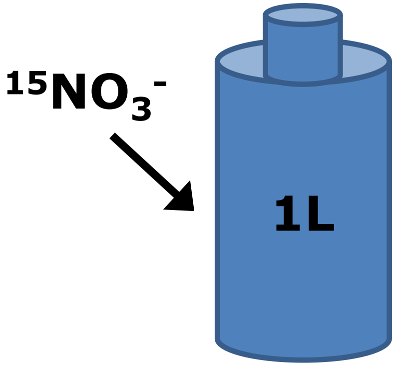


JUL.2012
MAR.2012
MAY2012
OCT.2011
40°N
39°N
38°N
37°N
36°N
35°N
34°N
128°E
130°E
132°E
134°E
EC1
EB01
EB03
EB05
EB06
EB07
St.06
St.05
St.04
Ocean Data View

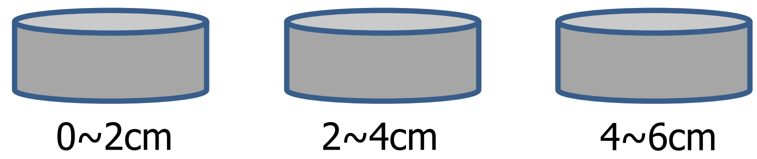


Temperature [℃]
Depth [m]
0
500
1000
1500
2000
129.5°E
130°E
130.5°E
131°E
131.5°E
132°E
25
20
15
10
5
0
Ocean Data View
DO [μmol/kg]
300
280
260
240
220
200
180
EB1
EB3
EB5
EB6
EB7

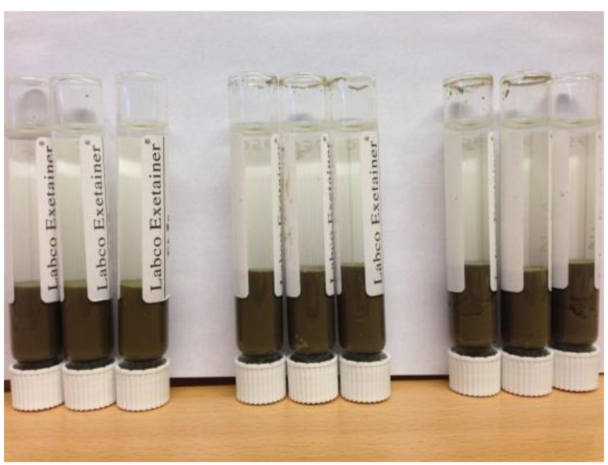
Slurry incubation



Bottom water
: **50μM** ^{15}N-nitrate (99 atom %)

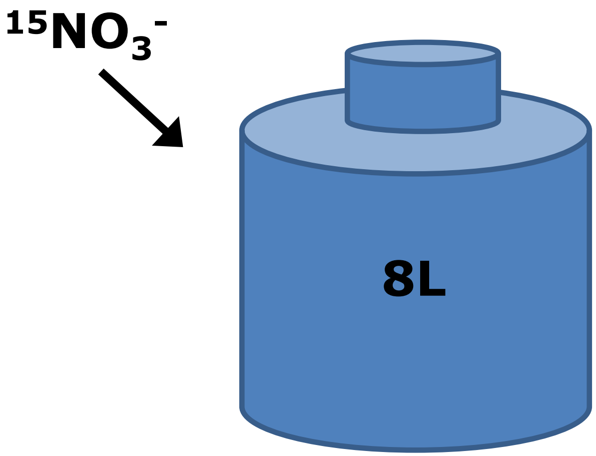


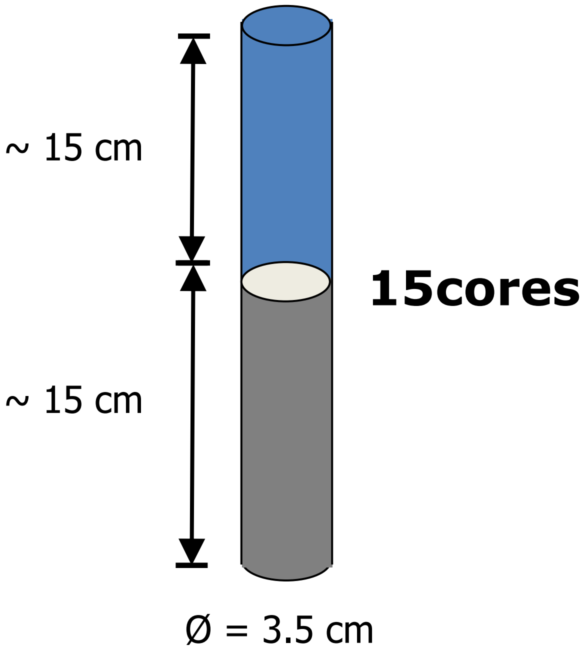
Slurries sediments



- N_2 production from anammox (ra %)
- ^{15}N tracers (Thamdrup and Dalsgaard 2002)
- 2.5ml of homogenized sediments (0-2cm, 2-4cm, 4-6cm)
- 1L bottom water was sparged with N_2
- 12hrs(coastal)-72hrs(open sea) incubations
- Injection of 250 μL $ZnCl_2$ (50% w/v)

Intact core incubation

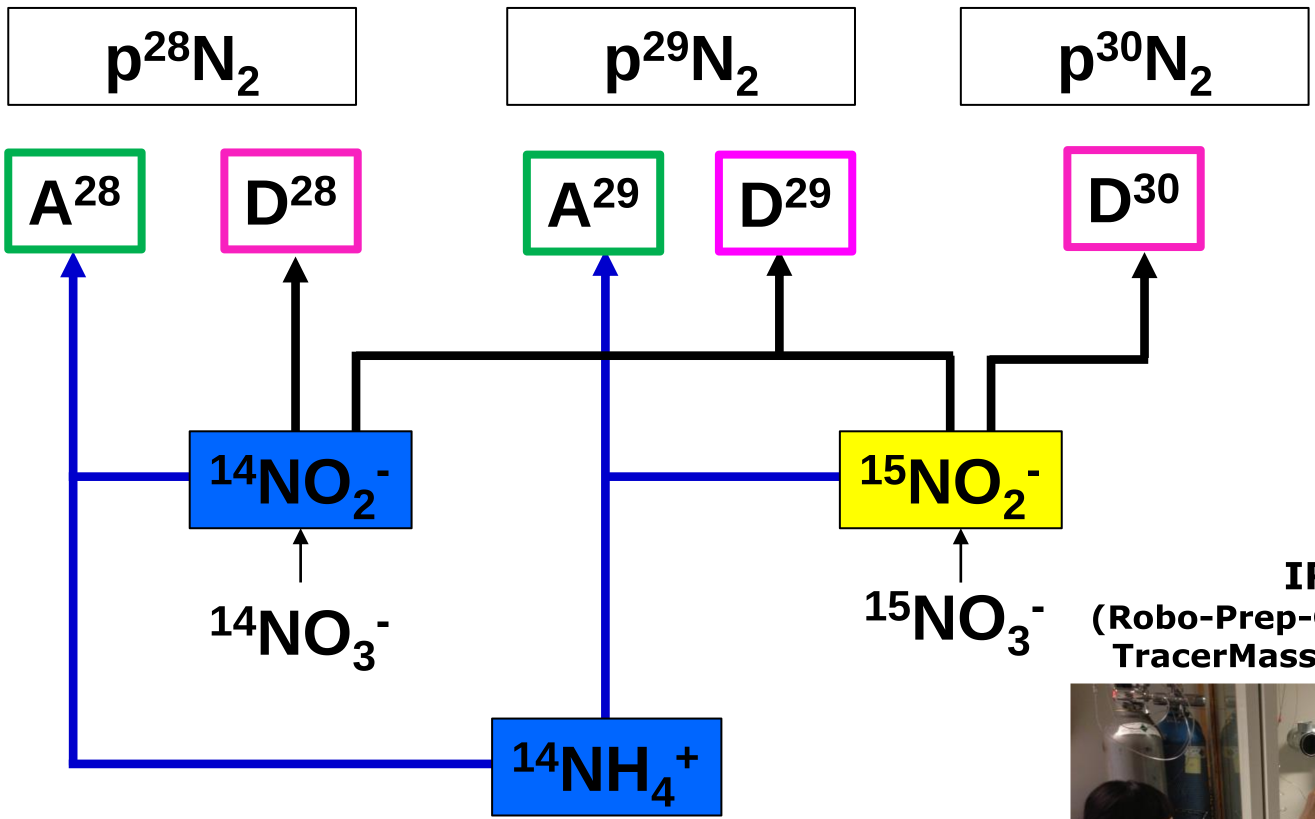




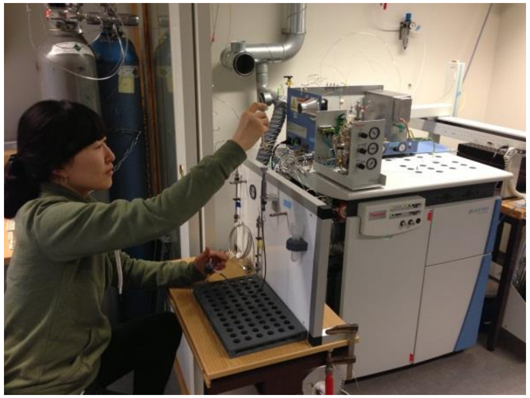
Bottom water
: **50μM** ^{15}N-nitrate (99 atom %)

- Total N_2 production rate
- 15 cores from each sites = =triplicates*5 time points
- 8L bottom water with O_2
- 12hrs(coastal)-72hrs(open sea) incubations
- Injection of 250-mL $ZnCl_2$ (50% w/v) to surface sediment
- Mix the sediment to 6cm

Isotope Paring Technique



IRMS
(Robo-Prep-G+ in line with TracerMass)



Thamdrup and Dalsgaard 2002

Risgaard-Peterson *et al*. 2003

Calculations

Slurry incubation

- The fraction of $^{15}NO_3^-$ ($\mathbf{F_N}$) = $^{15}NO_3^-$ /[$^{14}NO_3^-$] + [$^{15}NO_3^-$]
- The production of $^{14}N^{15}N$ ($\boldsymbol{p^{29}N_2}$)
- The production of $^{15}N^{15}N$ ($\boldsymbol{p^{30}N_2}$)
- Denitrification potential rate (nmol N cm^{-3} h^{-1}) = $\boldsymbol{p^{30}N_2} \cdot \mathbf{F_N}^{-2}$
- Anammox potential rate (nmol N cm^{-3} h^{-1}) = $\mathbf{F_N}^{-1} \cdot [\boldsymbol{p^{29}N_2} + 2 \cdot (1 - \mathbf{F_N}^{-1}) \cdot \boldsymbol{p^{30}N_2}]$
- **ra** = Anammox / (Anammox + Denitrification)

Intact core incubation

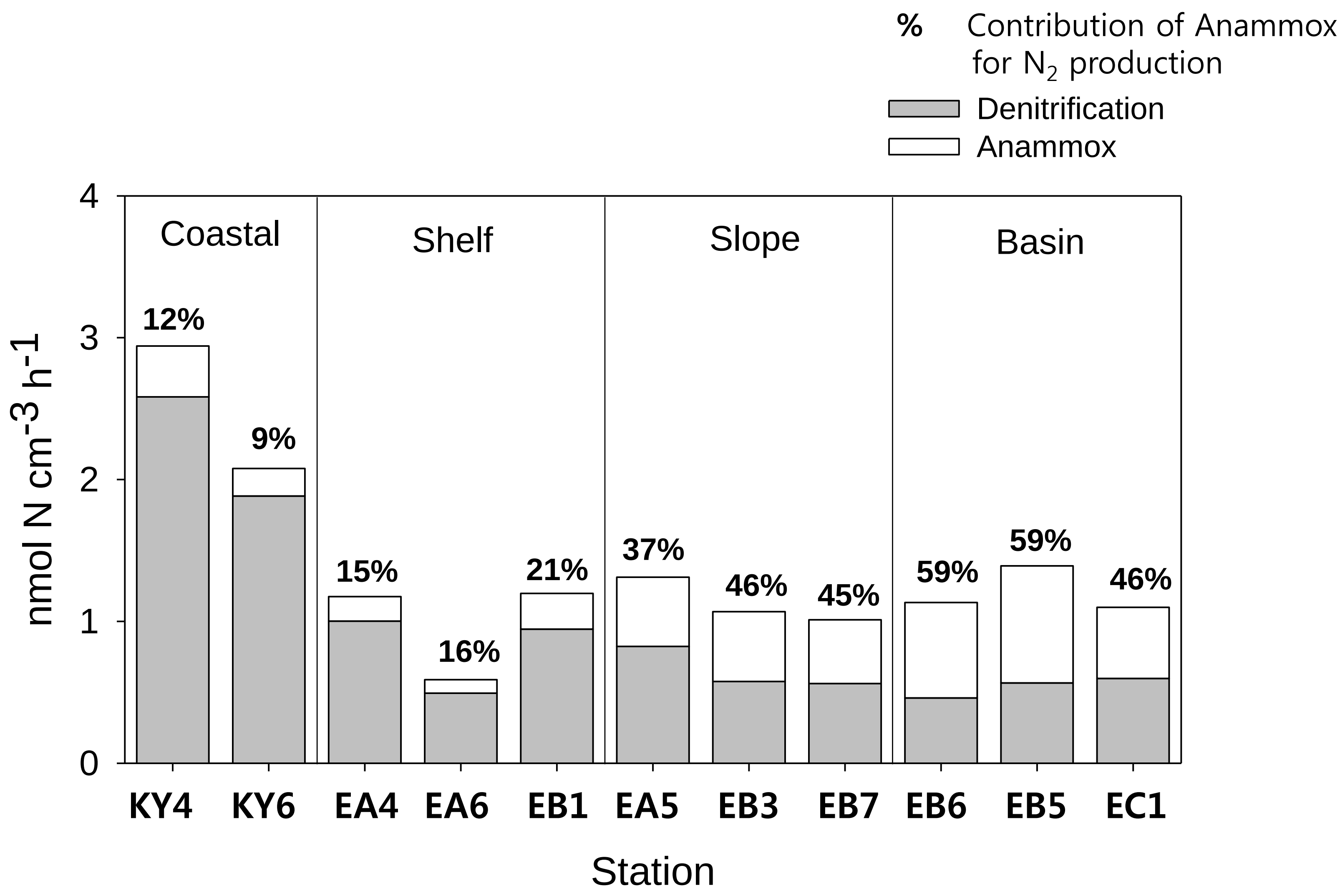
- Total N_2 production rate ($\boldsymbol{p_{14}}$) = $(\boldsymbol{p^{29}N_2} + 2 \cdot \boldsymbol{p^{30}N_2}) \cdot (\boldsymbol{p^{29}N_2} / \mathbf{2} \cdot \boldsymbol{p^{30}N_2})$
- Denitrification rate ($\mathbf{D_{14}}$) (μmol N m^{-2} h^{-1}) = $\boldsymbol{p_{14}} \cdot$ **ra**
- Anammox rate ($\mathbf{A_{14}}$) (μmol N m^{-2} h^{-1}) = $\boldsymbol{p_{14}} \cdot (1 - \mathbf{ra})$

Results

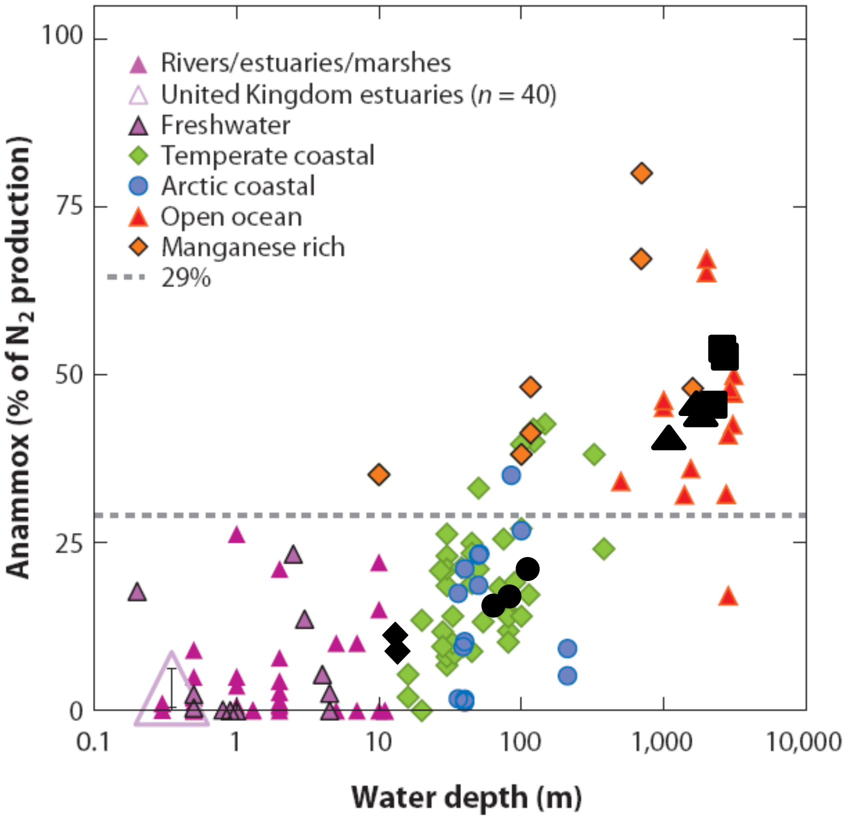
1. Potential N_2 production rate (denitrification & anammox)
2. Contribution of anammox for N_2 production (ra %)
3. Total N_2 production rate (0-6cm)

Slurry incubation

Potential N_2 production rate



Denitrification vs. Anammox



Bo Thamdrup 2012

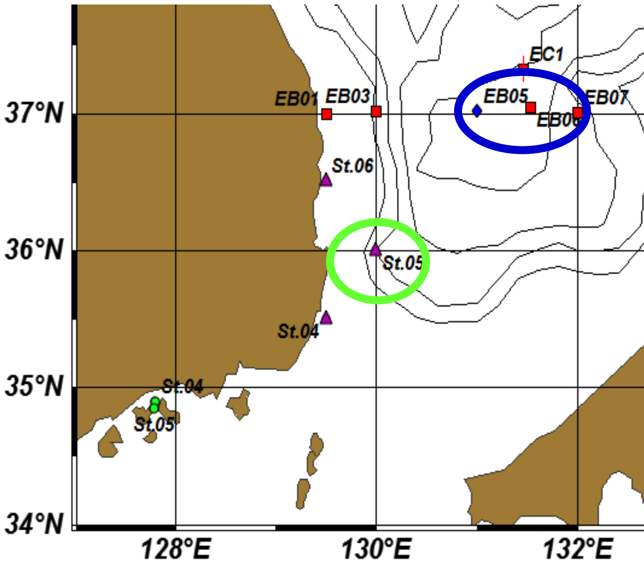
- Denitrification decreases relative to anammox with increasing water depth offshore.
- The associated decrease in availability of organic carbon needed to drive sediment mineralization (Thamdrup and Dalsgaard 2002; Dalsgaard *et al*. 2005; Engström *et al*. 2005).

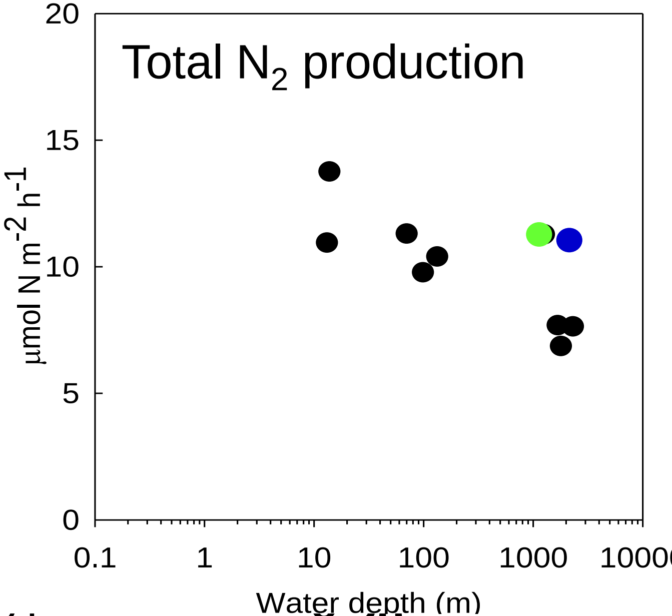
Black symbol from this study

Total N_2 production

Sites		Depth (m)	Total N_2 $\mu mol\ N\ m^{-2}\ h^{-1}$
Coastal	KY 4	20	**14.05**
	KY 6	20	**10.91**
Shelf	EA 4	72	**11.28**
	EA 6	88	**9.76**
	EB 1	135	**10.38**
Slope	EA 5	1274	**11.26**
	EB 3	1697	**7.67**
	EB 7	1817	**6.84**
Basin	EB 6	2159	**11.02**
	EB 5	2202	**11.06**
	EC 1	2342	**7.62**

Denitrification vs. Anammox





			al N_2 N m^{-2} h^{-1}	ra (%)		ox
			14.05			1.33
			10.91			1.28
			11.28			1.66
			9.76			1.57
			10.38	21	8.20	2.18
Slope	EA 5	1274	11.26	37	**7.07**	**4.19**
	EB 3	1697	7.67	46	**4.13**	**3.54**
	EB 7	1817	6.84	45	**3.80**	**3.05**
Basin	EB 6	2159	11.02	59	**4.47**	**6.55**
	EB 5	2202	11.06	59	**4.50**	**6.55**
	EC 1	2342	7.62	46	**4.15**	**3.47**

Higher Total N_2 production in the UB

Sites	Depth (m)	Total N_2	Anammox	Denitrification
			$\mu mol\ N\ m^{-2}\ h^{-1}$	
Thames Estuary	2-4	241.84	48.94	192.9
North Atlantic	30-81	0.8 - 26.9	0.2 - 5.6	0.6 - 21.2
Baltic Sea	33-85	1.4-9.5	0.1 - 0.9	1.3 - 8.6
Arctic sediments	3-100	1.4 - 14.3	0.0 - 3.8	1.4 - 10.7
Colne Estuary	653	544.5	157.3	387.2
Skagerrak, Kattegat	36-700	6.3 - 9.5	1.2 - 4.4	1.9 - 8.3
Sagami Bay*	1450	36.5 - 51.4	12.8 -18.5	23.8 - 32.9
Ulleung Basin	1700-2300	**6.8 - 11.1**	**3.0 - 6.6**	**3.8 - 4.5**
Washington Margins	2740-3110	1.9 -8.1	0.7 - 3.4	1.3 - 4.7

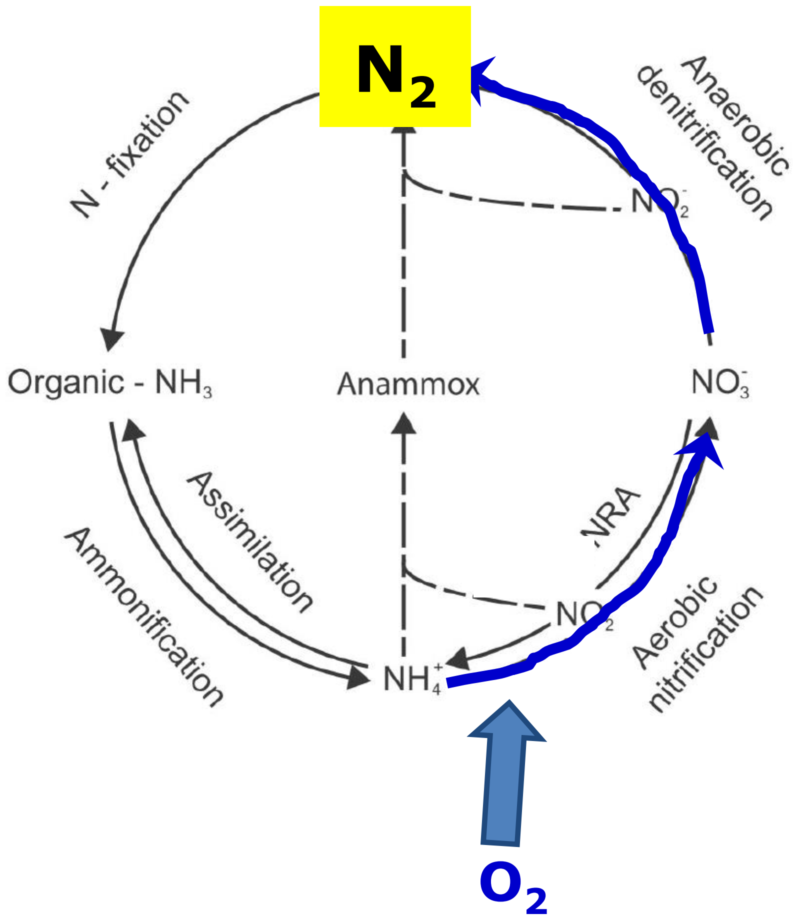
*Low oxygen saturation(15% air saturation) and up to 40μM NO_3^-

Higher **denitrification** at EA5?

Higher **N_2 production** in the UB?

Importance of **Anammox** in the UB?

Higher **denitrification** at EA5?

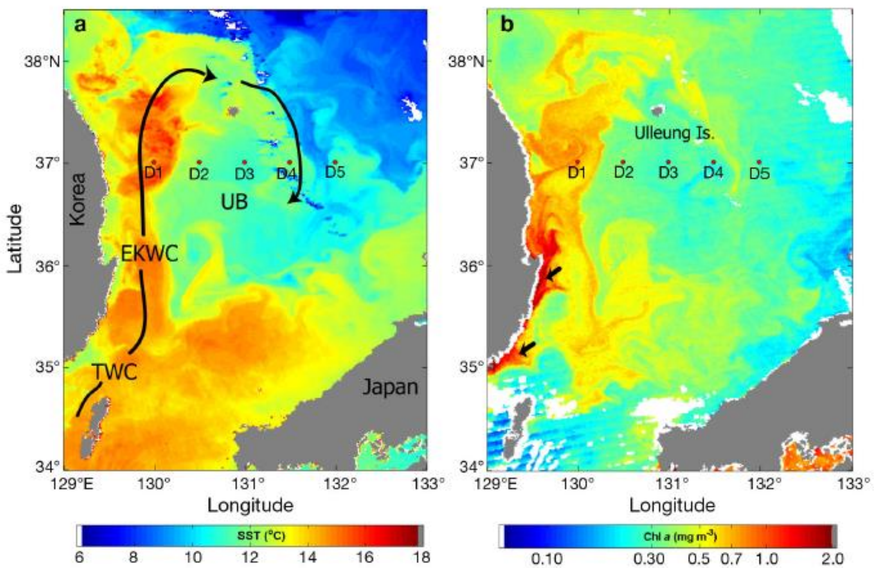


Biological activity
: shellfish, polychaete

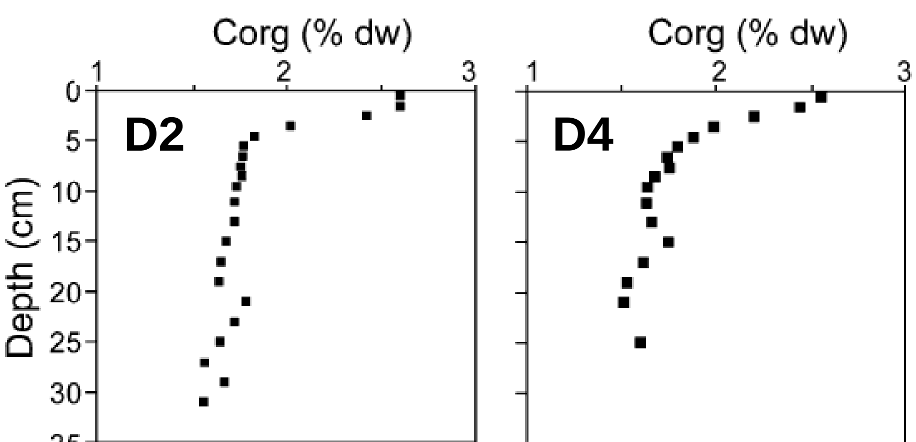
Transfer of O_2
to anoxic zone

Enhanced the coupled nitrification-denitrification

Higher N_2 **production** in the UB?



Hyun *et al*. 2009

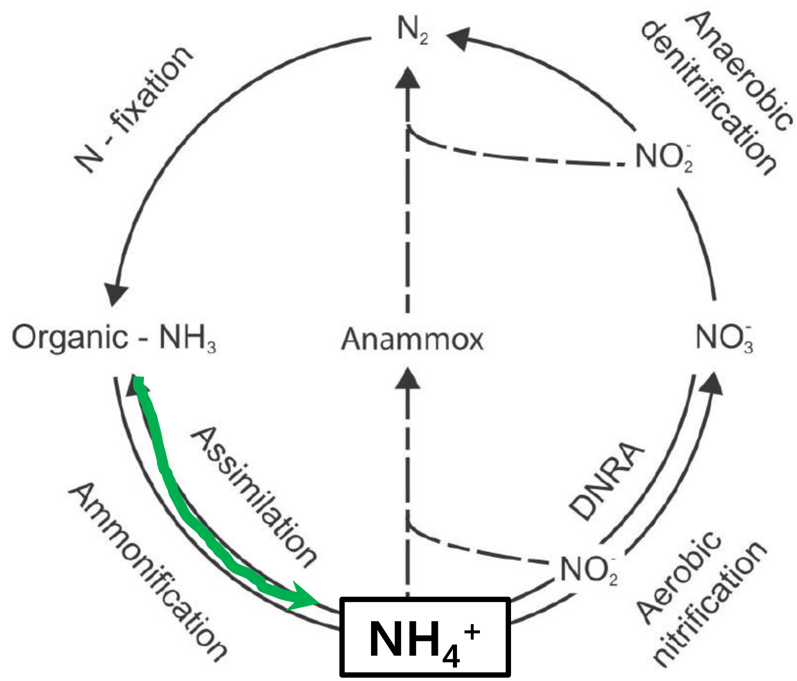


Lee *et al*. 2008

- **Enhanced primary production** associated with coastal upwelling and its subsequent delivery in the basin via Ulleung Warm Eddy (Hyun *et al*. 2009)
- **High export flux** below 200m depth of the water column (Kim *et al.* 2009)

Higher organic carbon content in the UB (>2.5% dry wt.) (Lee *et al*. 2008)

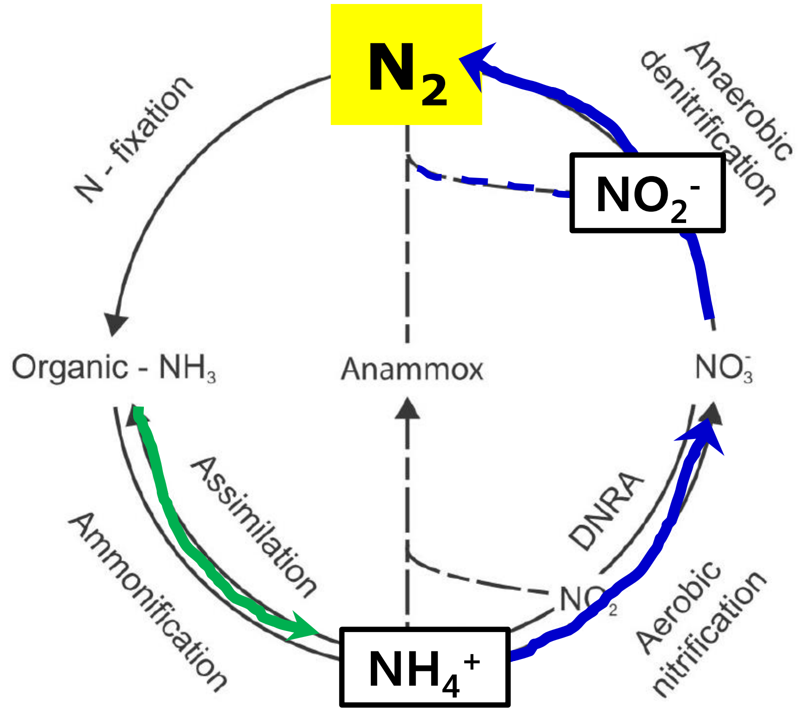
Importance of **Anammox** in the UB?



$$NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O$$

1. No limitation of NH_4^+

Higher **Anammox** in the UB



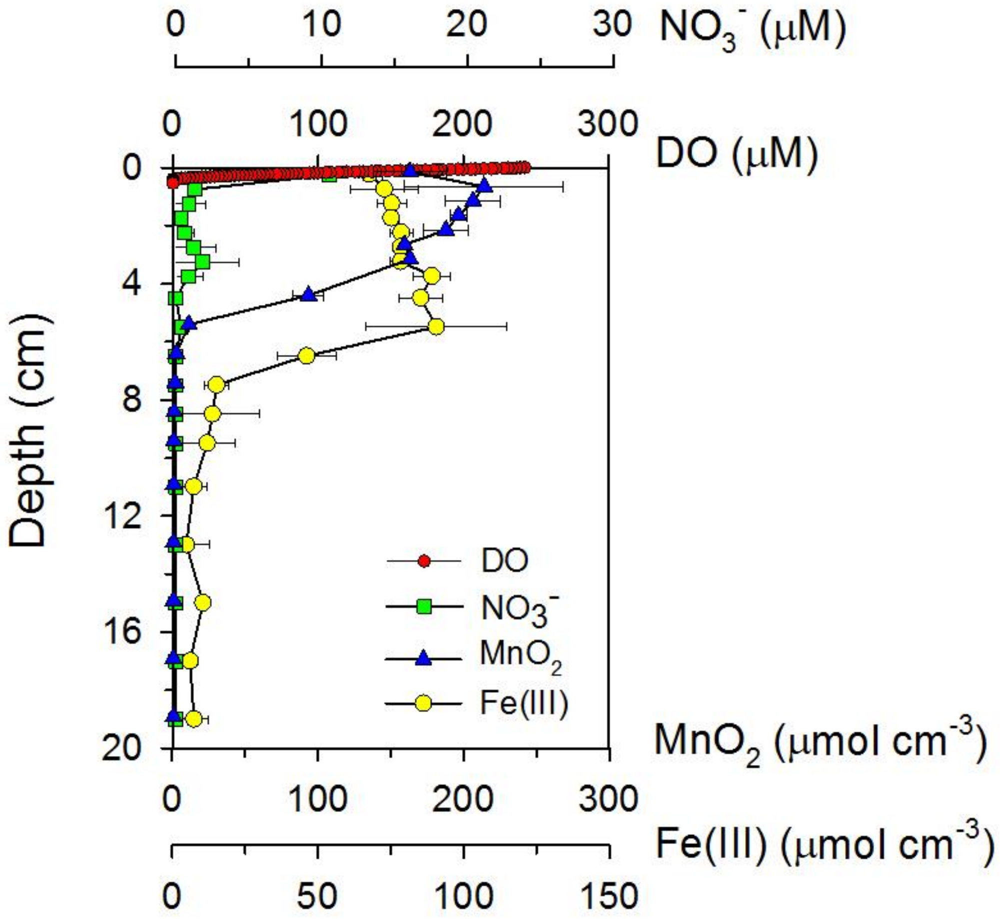
$$NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O$$

1. No limitation of NH_4^+
2. Higher denitrification → NO_2^-

Possible explanations…

Potential for a[…] fate reduction

(Thamdrup & Dals[…]



Hypothetic pa[…]

Mn(IV)-depend[…] $[…]n^{2+} + 2H_2O$

Mn(IV)-depend[…] $[…]n^{2+} + 4H_2O$

Fe(III)-depend[…] $[…]Fe^{2+} + 6H_2O$

Fe(III)-depend[…] $[…]6Fe^{2+} + 10H_2O$

Sulfate-depend[…] $[…]H_2O + \frac{5}{8}H^{+}$

Summary

- We conducted ^{15}N isotope incubations to determine the rates of denitrification and anammox from continental shelf (>100m) to center of UB (>2,000m).
- Total N_2 production rates using the intact core incubation ranged from 6.8 to 11.1 μmol N m^{-2} h^{-1}.
- The anammox comprised 15~59% of total N_2 production, and its relative significance increased with increasing water depth from shelf (ave. 17%) to the basin (ave. 55%).
- Anammox (3.0~6.6 μmol N m^{-2} h^{-1}) and denitrification rates (3.7~4.8 μmol N m^{-2} h^{-1}) in the UB were shown to be higher than those observed at other deep marginal sediments.
- Higher organic carbon contents are responsible for the higher total N_2 production rates in the UB.
- Althtough our results demonstrate that anammox is an important N removal pathway in the UB sediments, there still are no its direct evidence.
- Future work is necessary to identify the key factor controlling anammox in the UB.

Благодаря!