



# Marine Biogeochemistry for CESM

**LANL:** Elliott, Maltrud, Hunke, Jeffery

**LBL:** Reagan, Moridis, Collins

**LLNL:** Cameron-Smith, Bergmann, Bhattacharyya

**ORNL:** Branstetter, Erickson

**ANL:** Jacob

**IARC:** Deal, Jin

**Universities and international...**

*DOE: SciDAC, IMPACTS, Fossil Energy, COSIM core,  
Cloud-Cryosphere, EPSCOR (IARC)*

*Other: New Mexico IAS, IARC/JAMSTEC Cooperative,  
various lab LDRD, international*

# OUTLINE

HISTORY: Sea-air transfer trace GHGs, aerosol precursors

CH<sub>4</sub> & DMS: Emergent, point to organics and ice

STRUCTURE: Montage and teaser for each of...

Methane

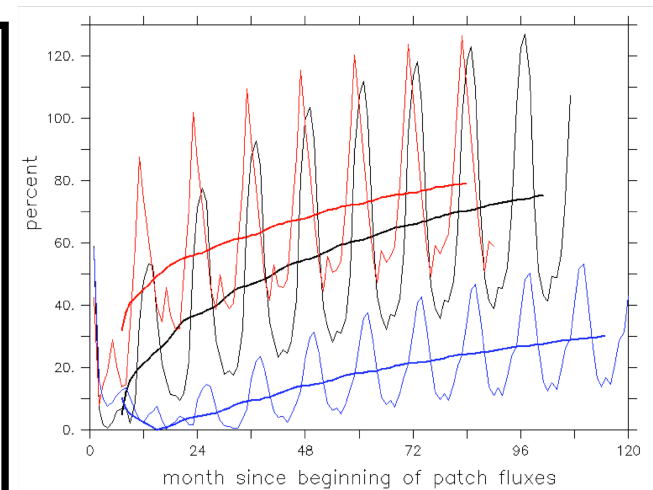
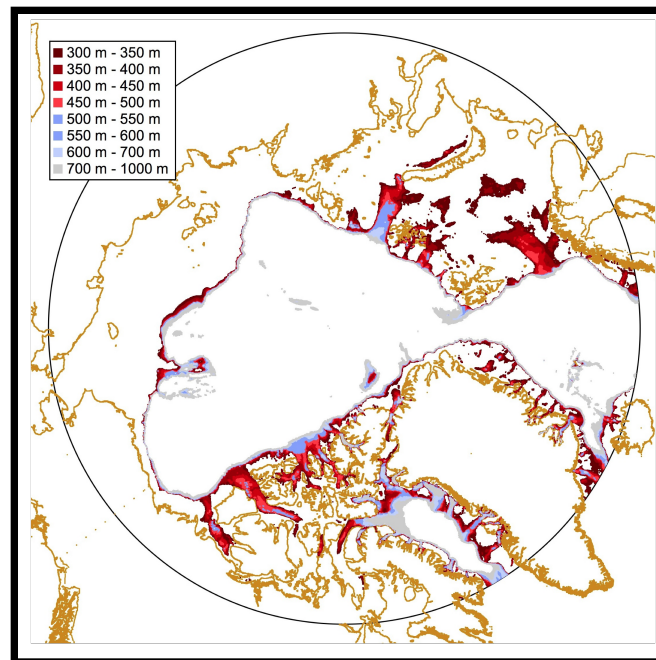
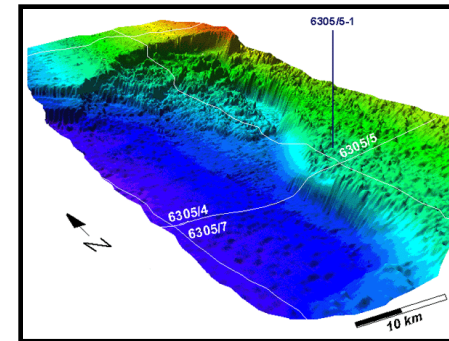
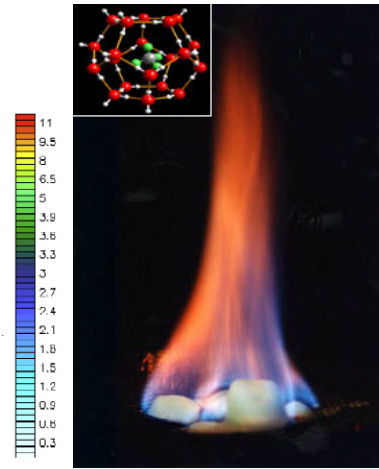
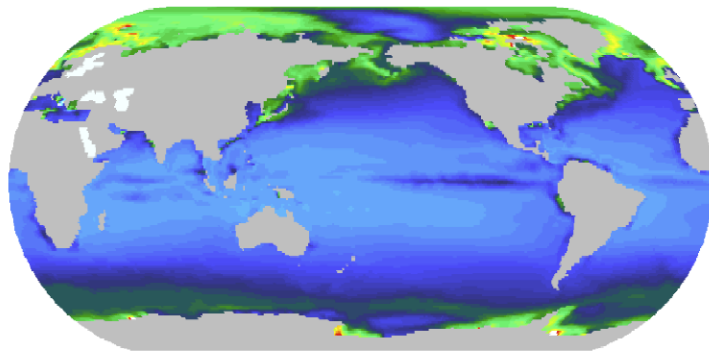
Dimethyl Sulfide

Global O-Chem

Sea Ice Biogeochemistry

# MONTAGE: Methane

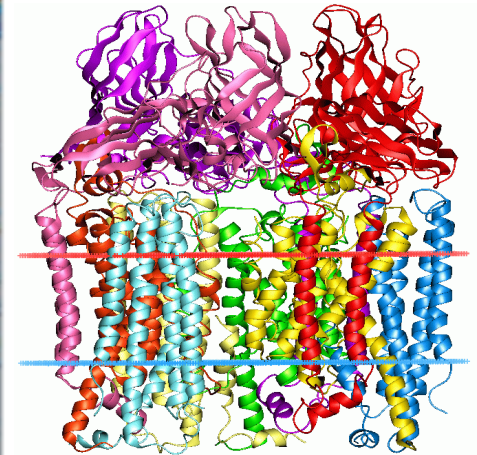
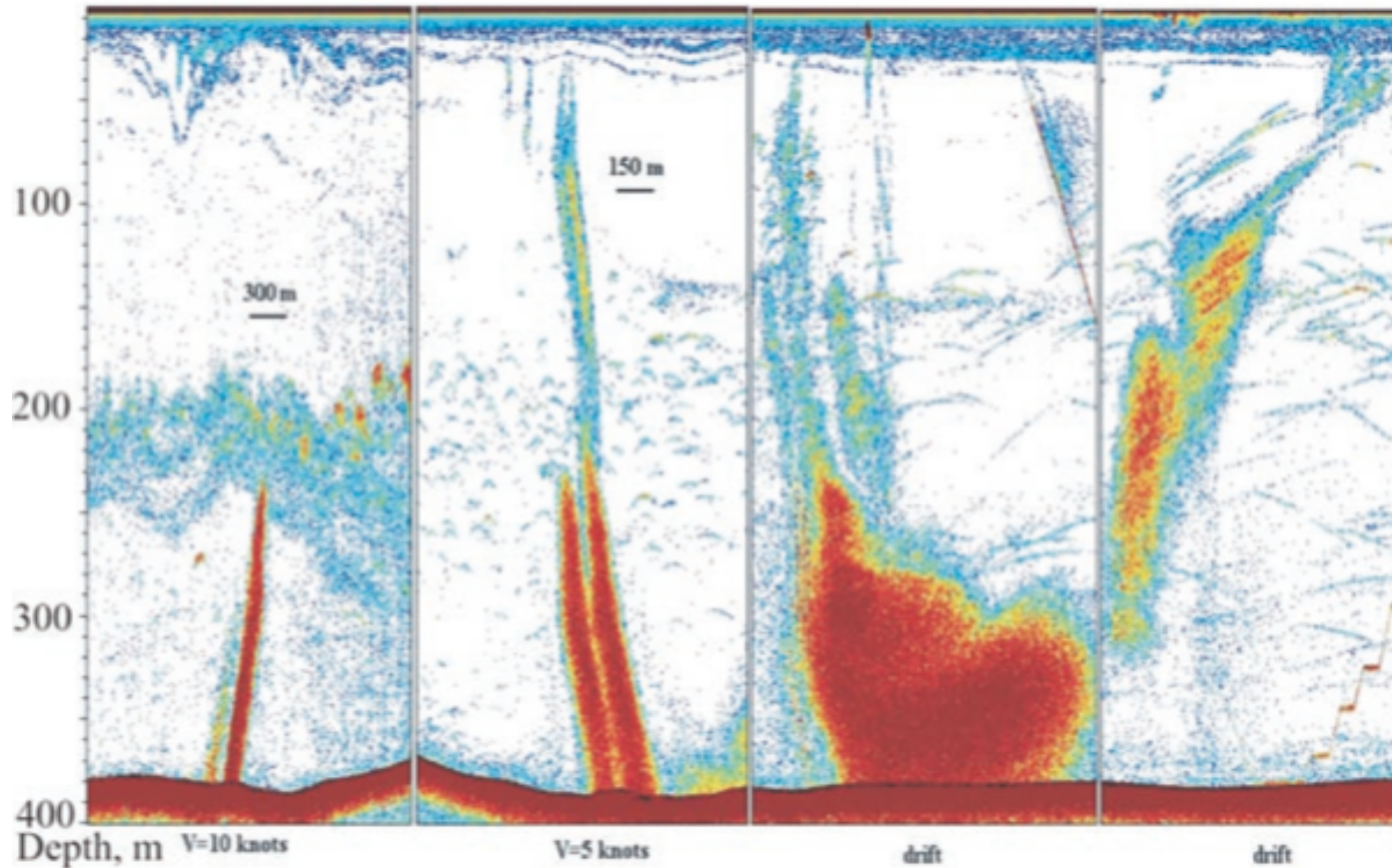
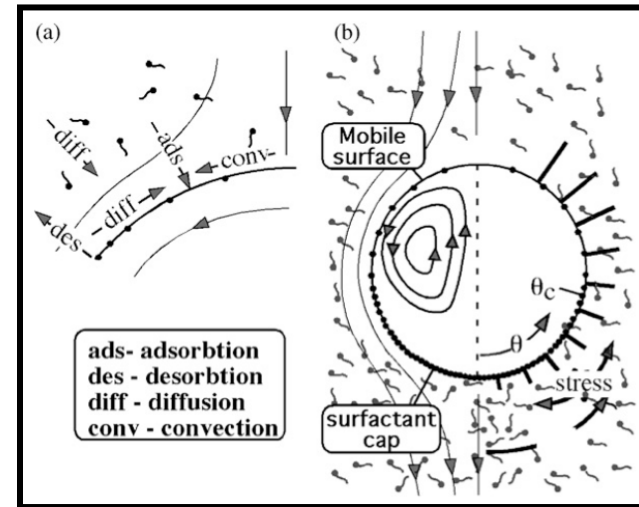
JGR 2011



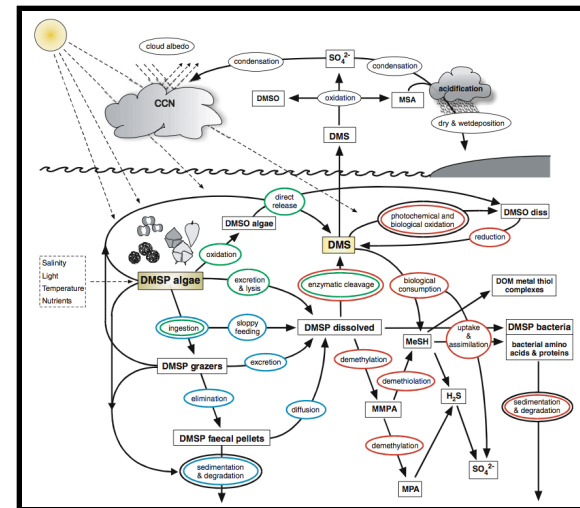
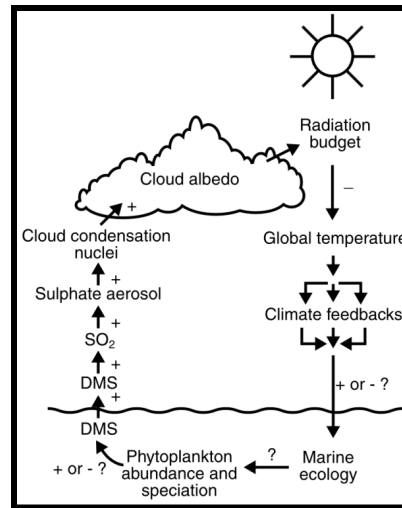
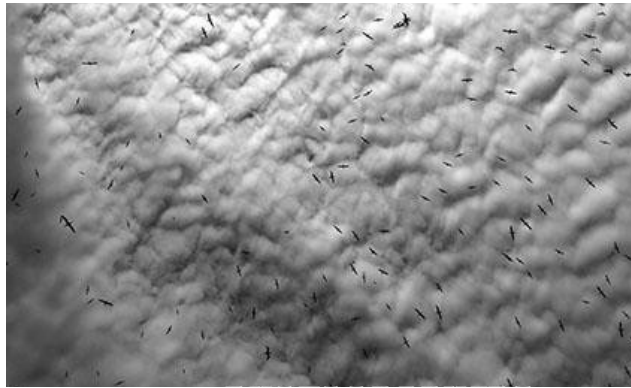
**GRL 2010, JGR 2011**  
**JGR & ICGH in press**

## A Scientific Win-Win\*

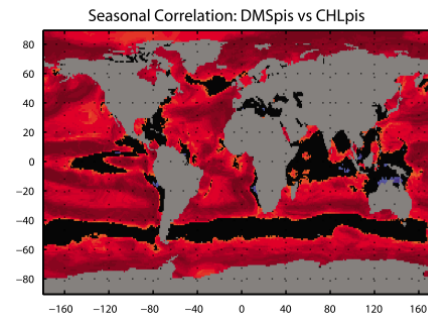
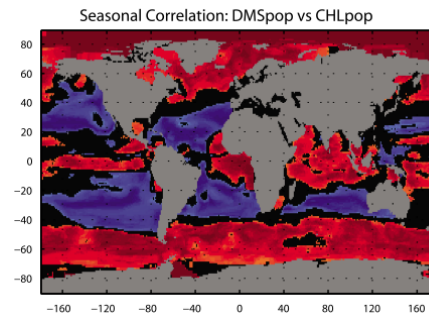
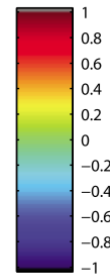
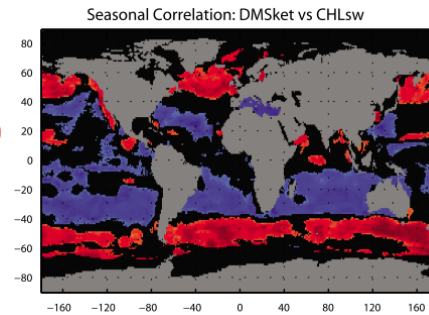
CH<sub>4</sub> in atmosphere: GWP 30  
 CH<sub>4</sub> in seawater: Reductant



# MONTAGE: Dimethyl Sulfide

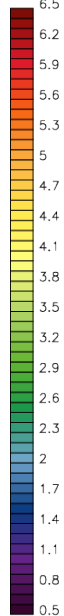
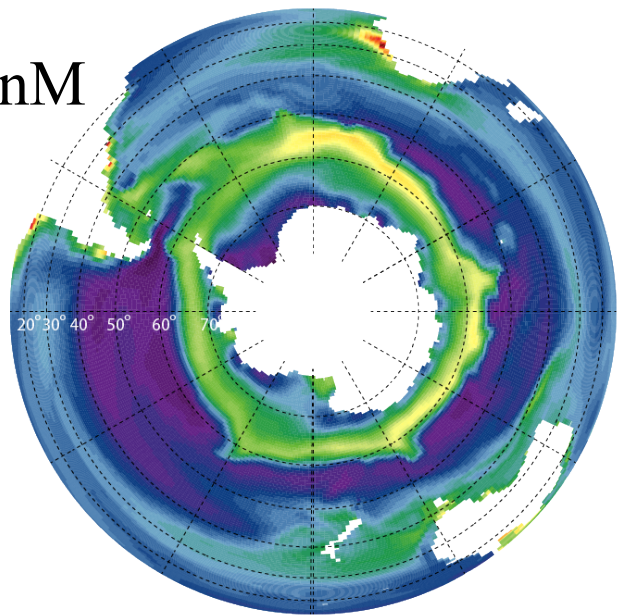


JGR 2009  
GBC 2010

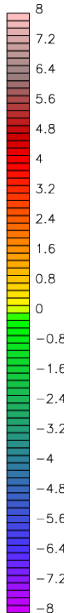
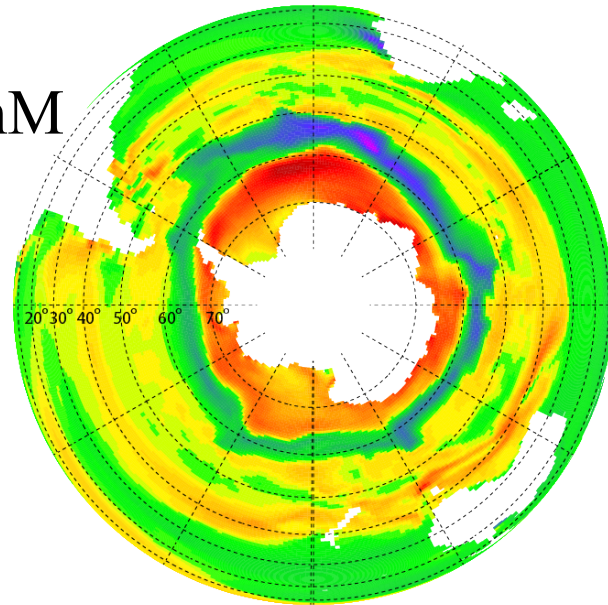


# Once and future DMS in CCSM: **GRL 2011**

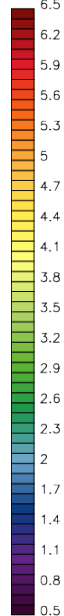
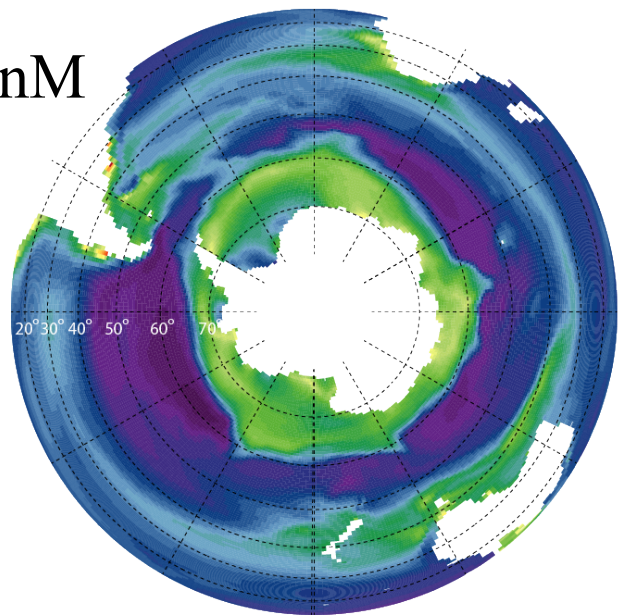
y2000, nM



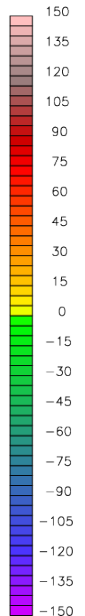
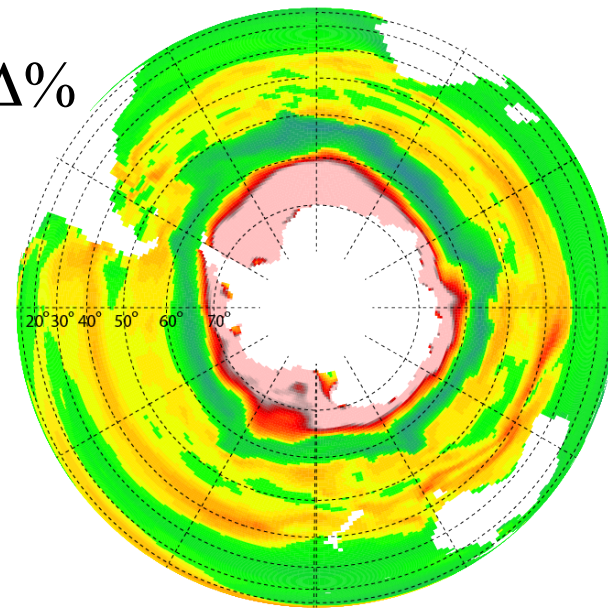
$\Delta nM$



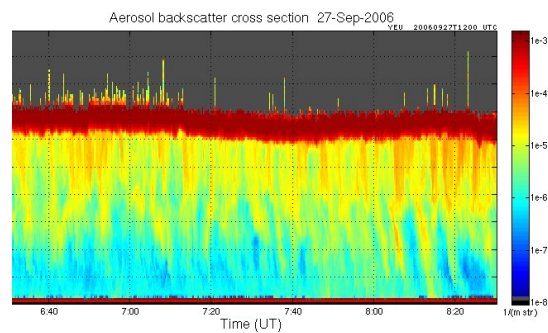
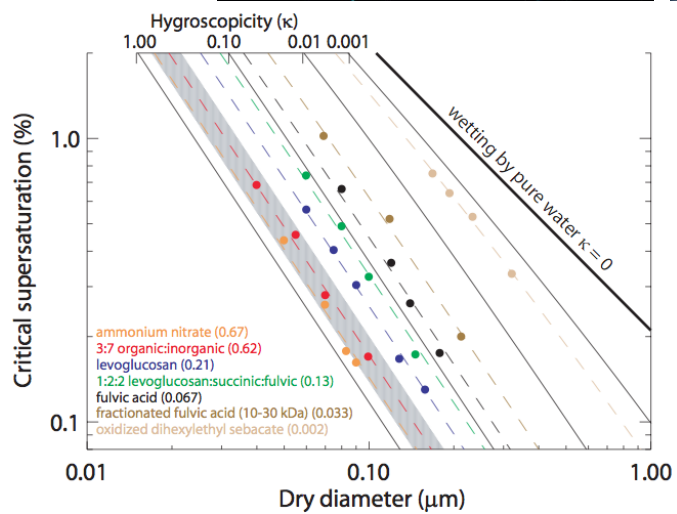
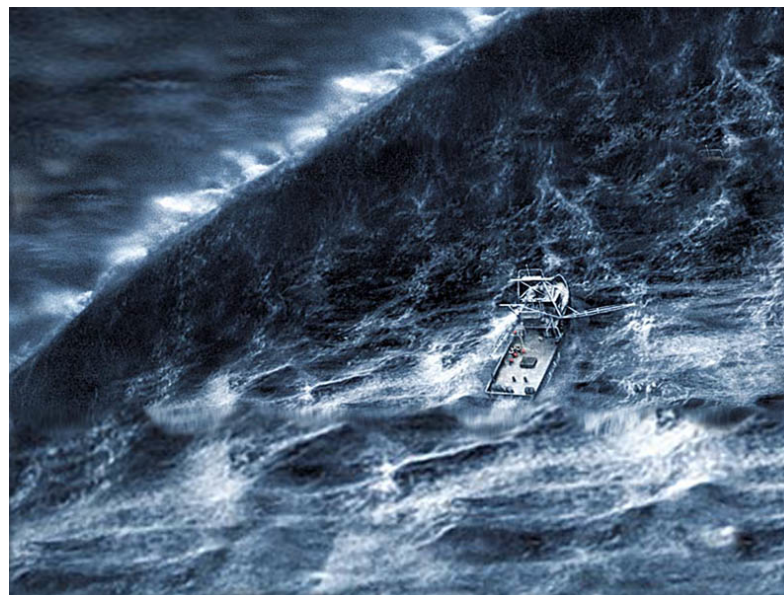
y2100, nM



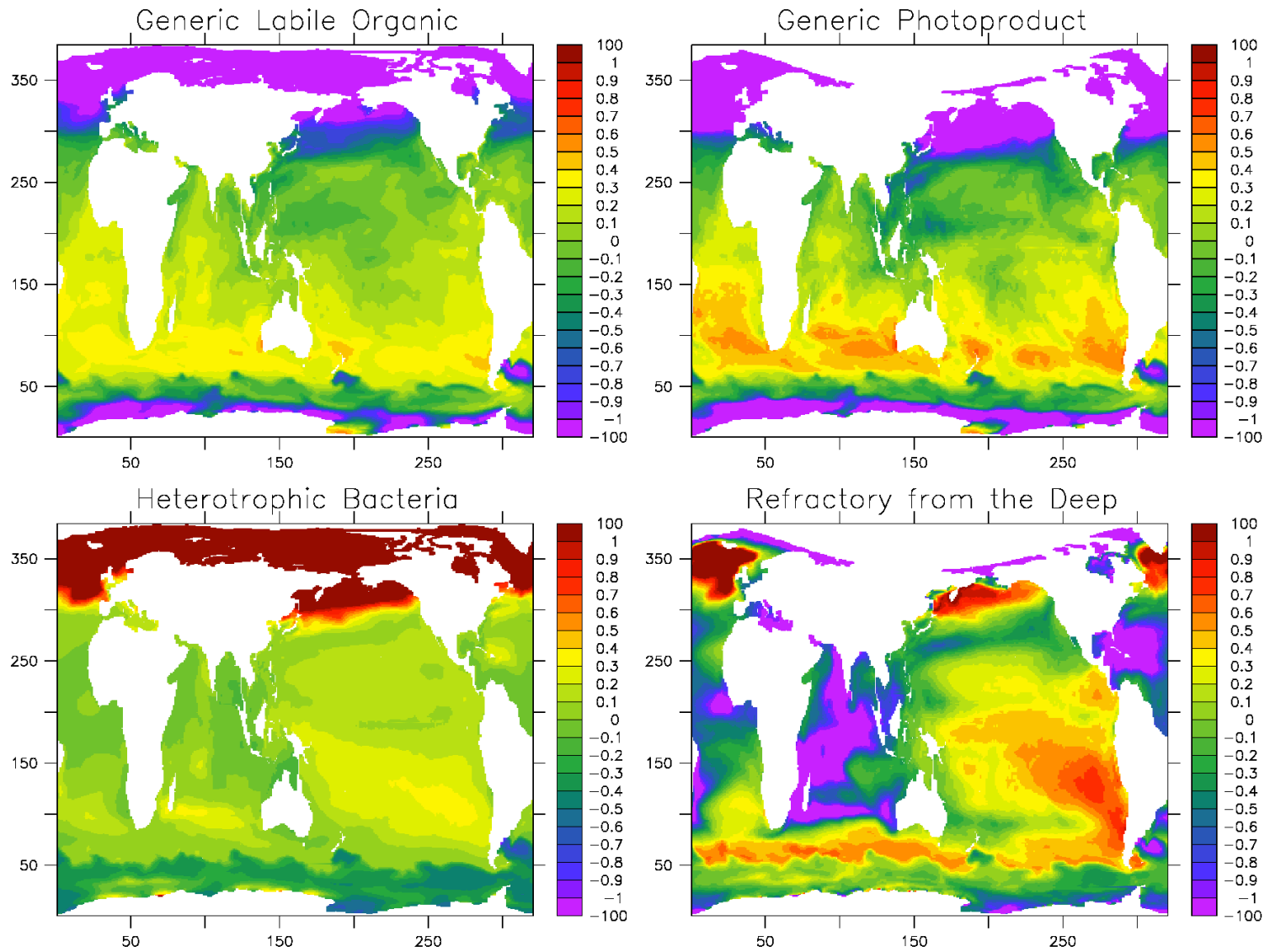
$\Delta\%$



# MONTAGE: O-Chem

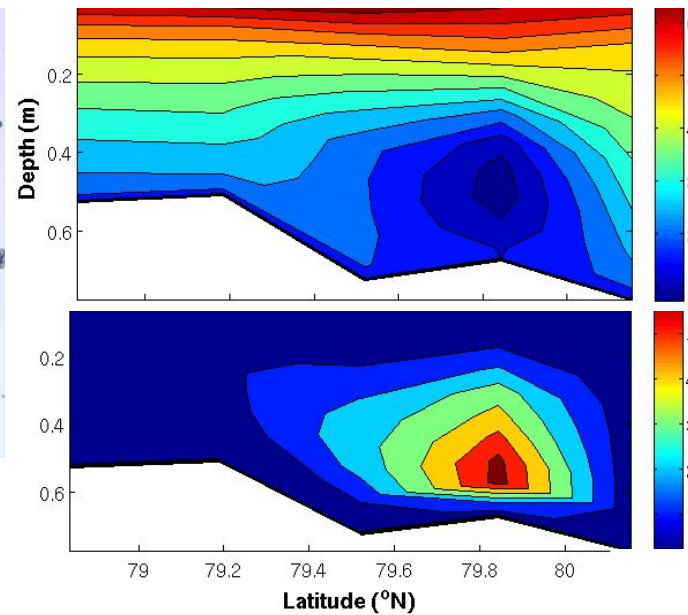
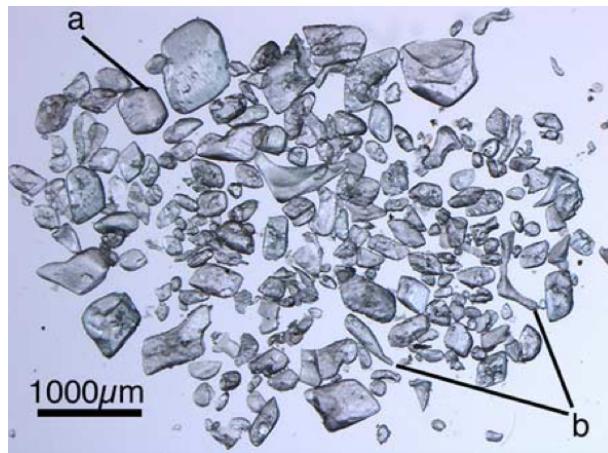


Log10(Relative Normalized Deviation), Organics to Chlorophyll



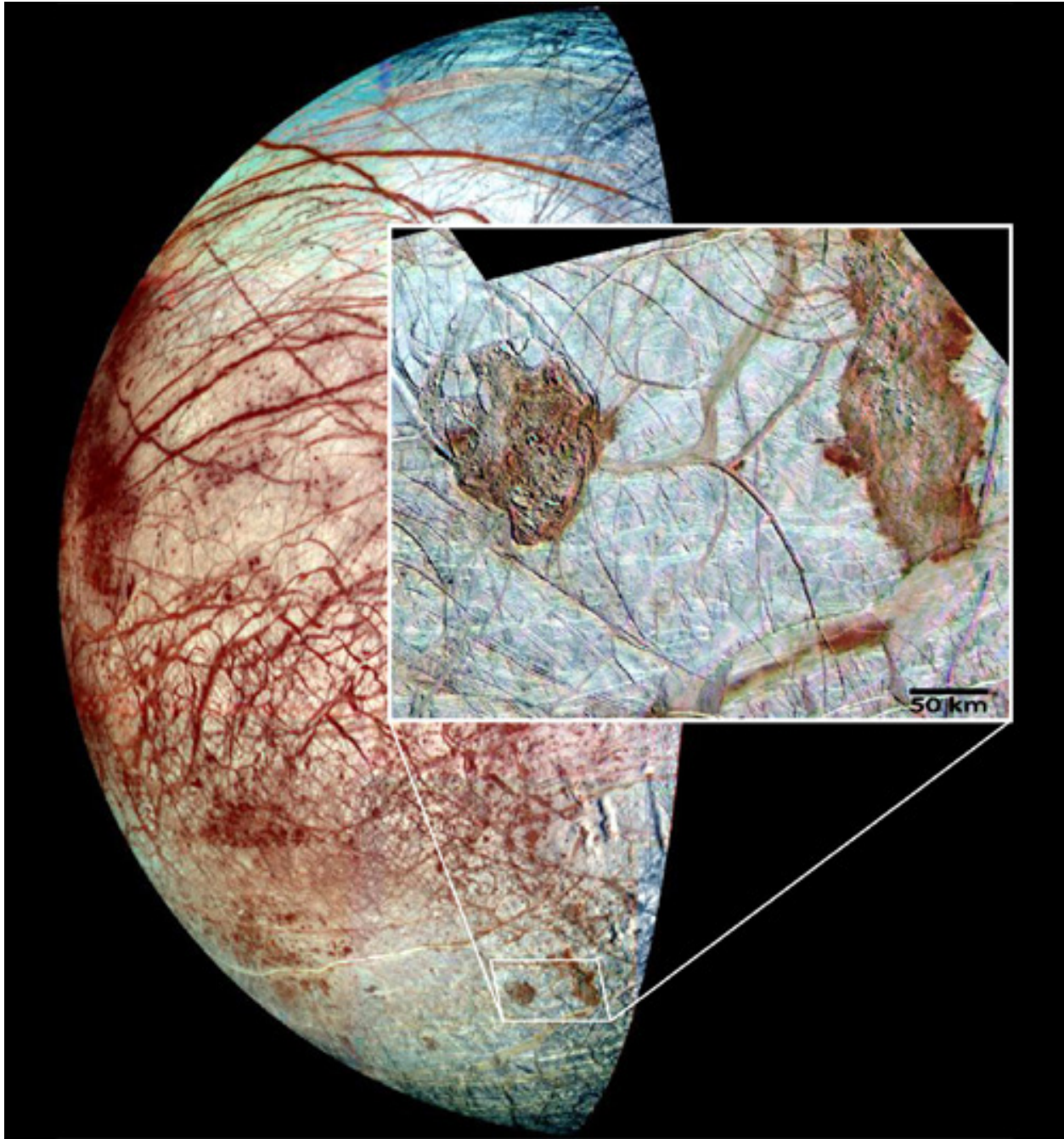


# MONTAGE: Ice BGC



JGR 2011  
(algorithm)

$\mu\text{M}$  nitrate  
 $\text{mg}/\text{m}^3$  chl



Europa

# SUMMARY

HISTORY: Sea-air transfer trace GHGs, aerosol precursors

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STRUCTURE: Montage and teaser for each of...

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Dimethyl Sulfide

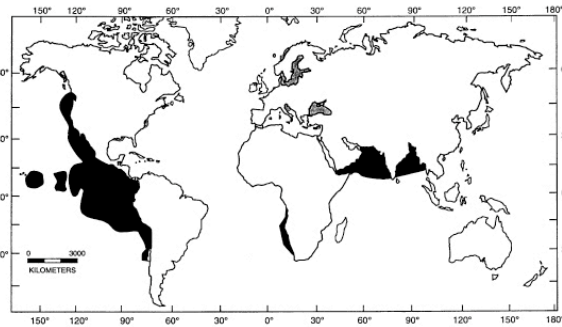
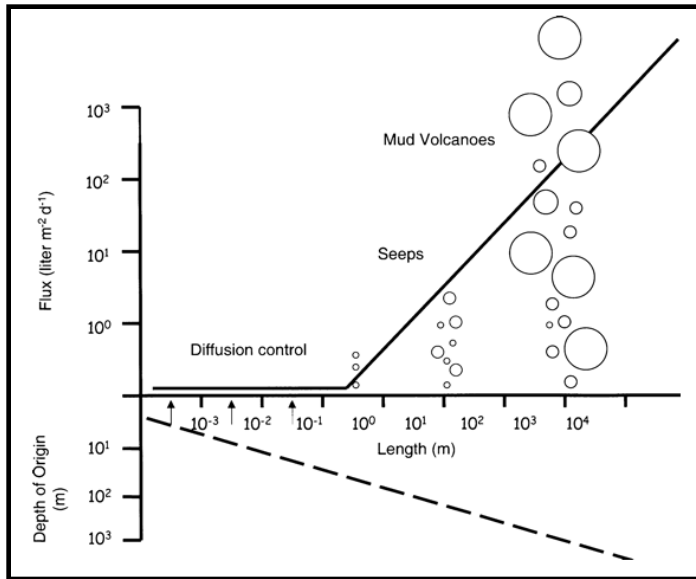
Global O-Chem

Sea Ice Biogeochemistry

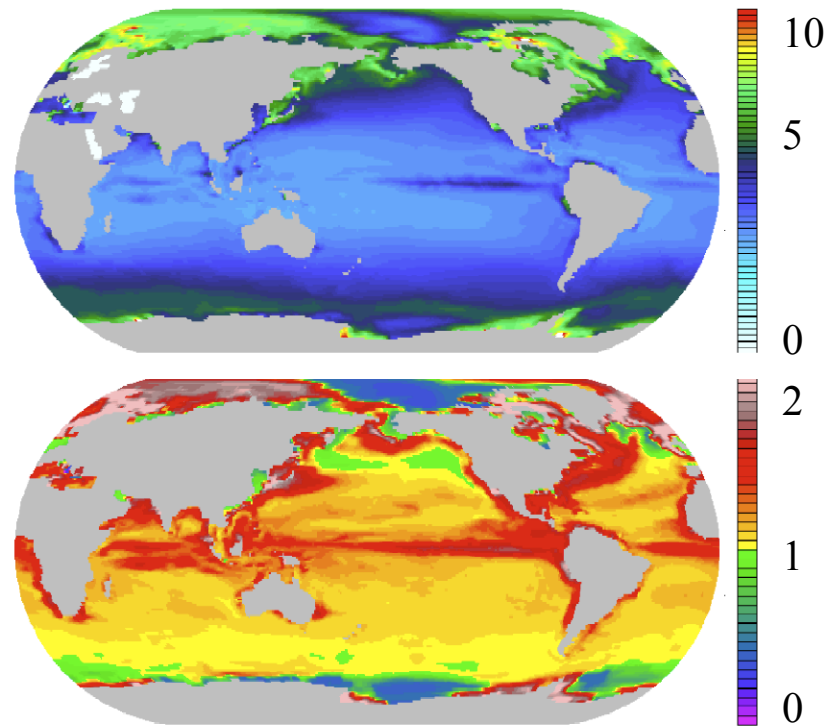
NEXT: Expand effort in CESM

EXTRAS

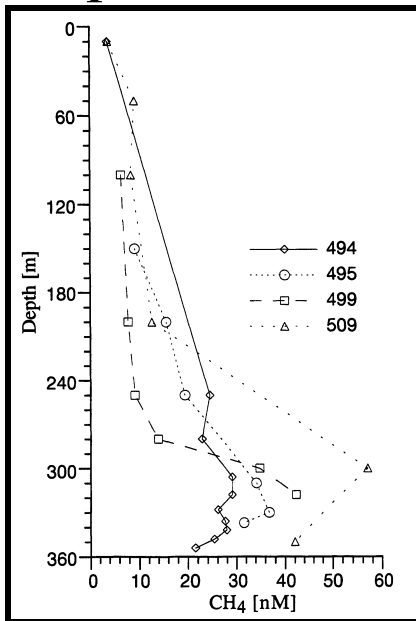
# Average seabed fluid flow and particulate sources



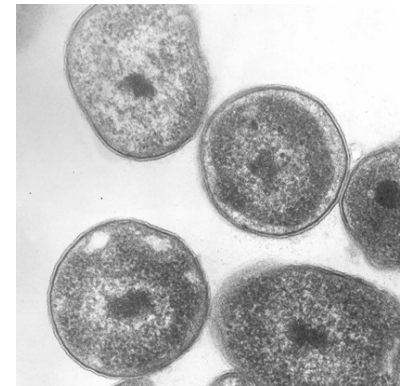
Surface concentration (nM),  
Saturation ratio



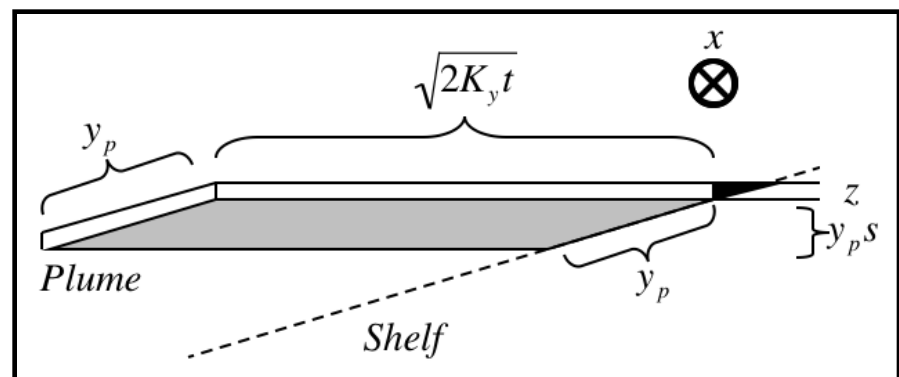
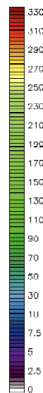
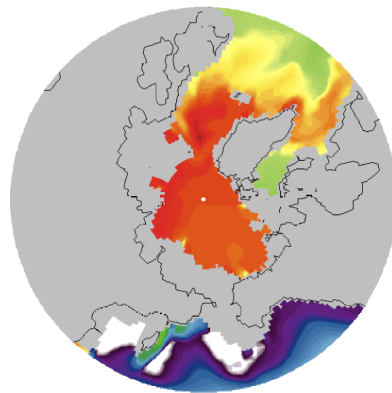
Empirical  $\tau$  - Less is more



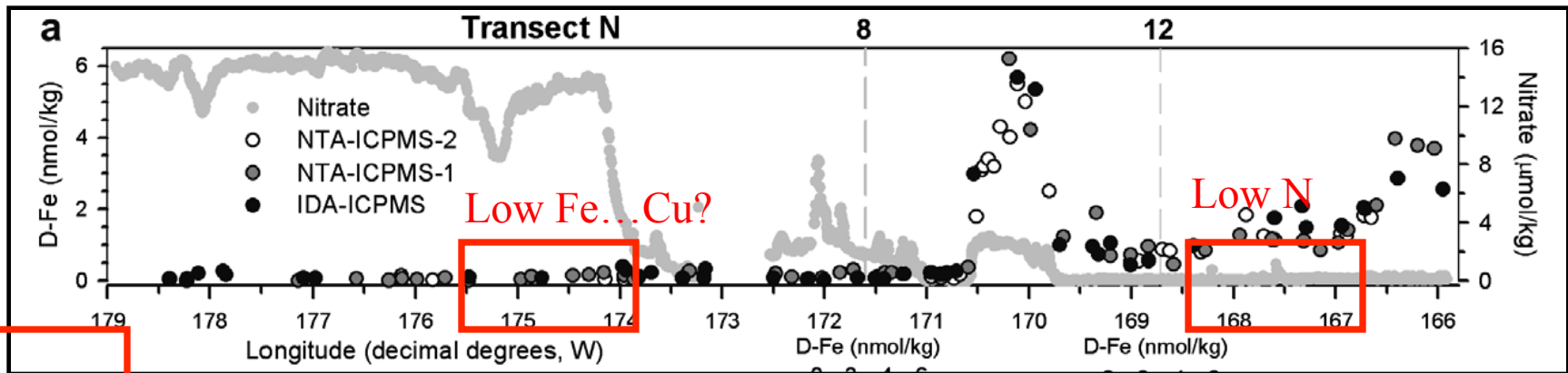
CH<sub>4</sub>, nM  
Bear Island



# Methanotrophs, Resource Limits

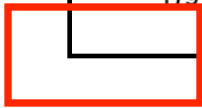


GRL 2010  
JGR 2011

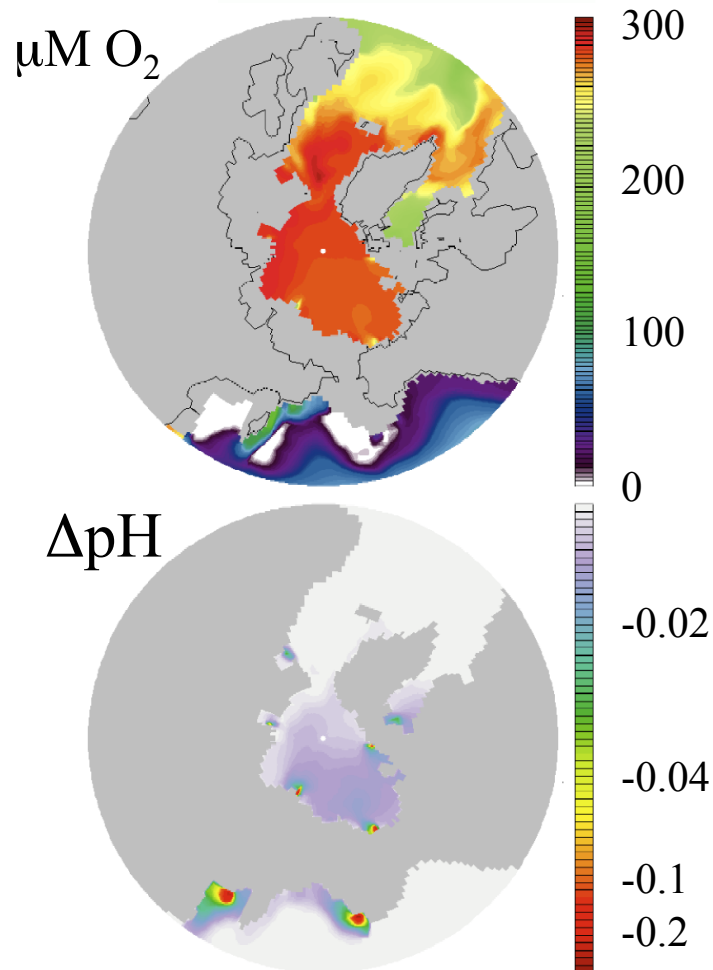
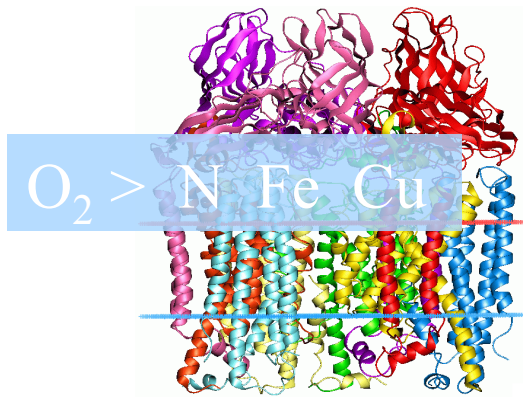


Low Fe...Cu?

Low N



Low O<sub>2</sub>, acidification



# 1<sup>st</sup> CUT: RESOURCES

METHANOTROPHS, LBL patches

POP: 8 sites, 300 meters, 30 years

RESULTS: Hypoxia, acidification

OFFLINE: Gaussians, observations

FURTHER: N, Fe, Cu loss

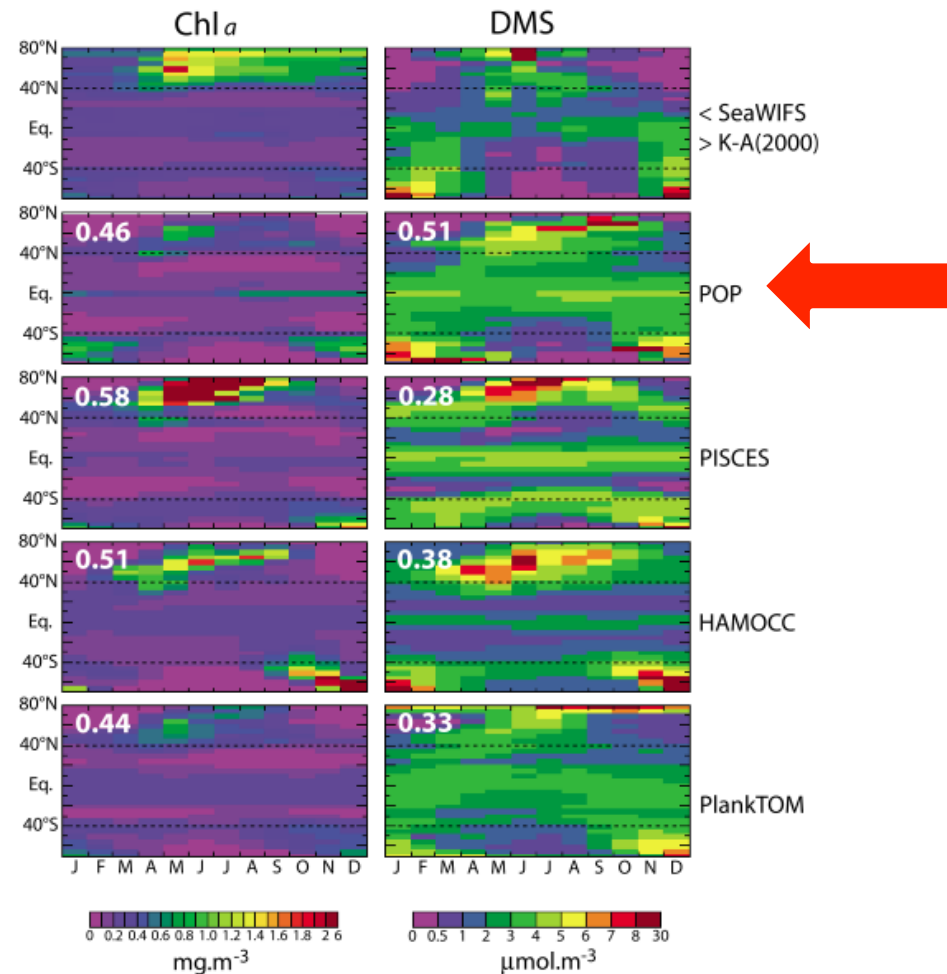
GENERAL:

Regional depletions

CH<sub>4</sub> plume expansion

GRL 2010, JGR 2011

# CODiM Results



**Figure 2.** Latitude-time (Hovmöller) plots of (top row) climatologies and (following rows) results from 4 global models for (left column) chlorophyll *a* (Chl *a*) ( $\text{mg} \cdot \text{m}^{-3}$ ) and (right column) DMS ( $\mu\text{mol} \cdot \text{m}^{-3}$ ). Data were binned and averaged in  $5^\circ$  latitude  $\times$  1 month boxes and are displayed here from  $70^\circ\text{S}$  to  $80^\circ\text{N}$  on a linear color scale. Models are identified in Table 1. Numbers in the upper left-hand corner of each model plot are the Spearman rank correlations between the variables (Chl *a* or DMS) simulated by the corresponding model and the SeaWiFS or *Kettle and Andreae* [2000] climatologies represented in the top panels.



337 **Table 2.** Annual average increase in DMS flux going from a present-day climate to a  
 338 future climate, in 10° latitude bands, for the models in Table 1<sup>a</sup>.

| Reference                     | Degrees South Latitude |       |       |       |       |       |       |       | Interpretation                                       |
|-------------------------------|------------------------|-------|-------|-------|-------|-------|-------|-------|--|
|                               | 80-70                  | 70-60 | 60-50 | 50-40 | 40-30 | 30-20 | 20-10 | 10-Eq |  |
| <i>Gabric et al., 2001,03</i> |                        | +30   |       | +5    |       |       |       |       | Ice cover dominates                                  |
| <i>Gabric et al., 2004</i>    |                        | +50   | +105  | +30   | +10   | +5    | +5    | +5    | ML <sup>b</sup> changes dominate                     |
| <i>Vallina et al., 2007</i>   | -5                     | 0     | +5    | +5    | 0     | 0     | +5    | +5    | ML <sup>b</sup> changes dominate, notes <sup>c</sup> |
| <i>Bopp et al., 2003</i>      |                        | 0     | (+10) | +30   | +10   | (0)   | (-10) | -15   | See text, notes <sup>e,g,i</sup>                     |
| <i>Kloster et al., 2007</i>   | >+30                   | +10   | -20   | 0     | 0     | -10   | -10   | -10   | See text, notes <sup>d,f</sup>                       |
| This work                     | +170                   | +70   | -15   | +5    | 0     | -10   | -10   | -10   | See text.  |

PNAS 2007

GRL 2011

339 <sup>a</sup>The percentage changes are taken directly from text interpretations in the original work

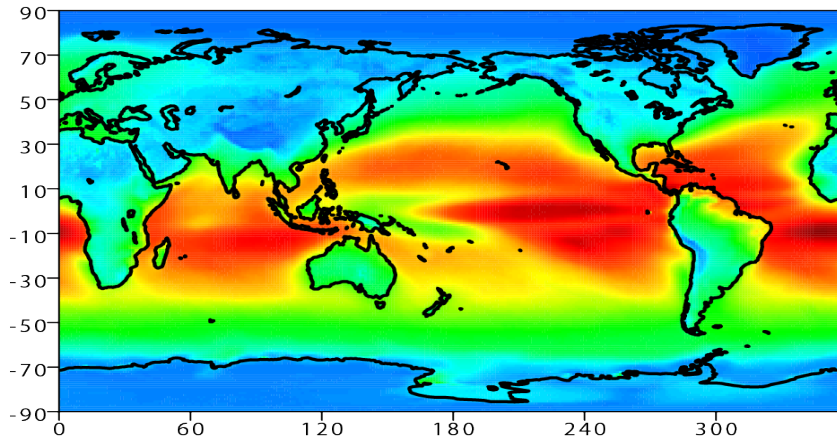
340 wherever possible, and rounded to the nearest 5%.

341 <sup>b</sup>ML stands for 'mixed layer'.

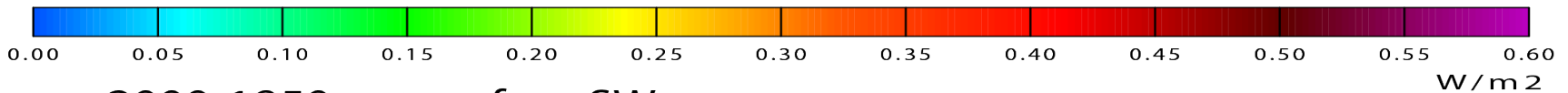
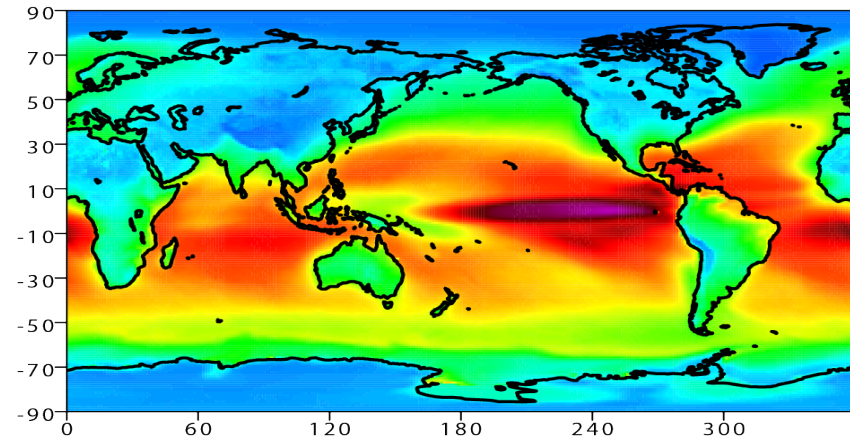
# 20<sup>th</sup> Century change in net SW radiation from *direct* DMS sulfate –up to tenths W/m<sup>2</sup>



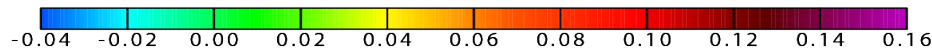
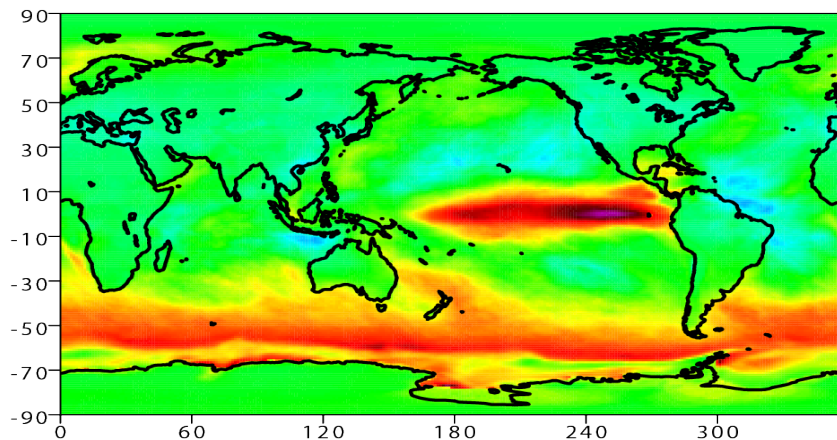
1850 net surface SW



2000 net surface SW



2000-1850 net surface SW



The effect of sulfate from DMS is enhanced in tropics because of  
a) higher solar radiation,  
b) faster oxidation of SO<sub>2</sub> to SO<sub>4</sub>.

C, chlorophyll major phyto-classes

Inorganic Ballast ( $\text{SiO}_2$  &  $\text{CaCO}_3$  with hanging chad)

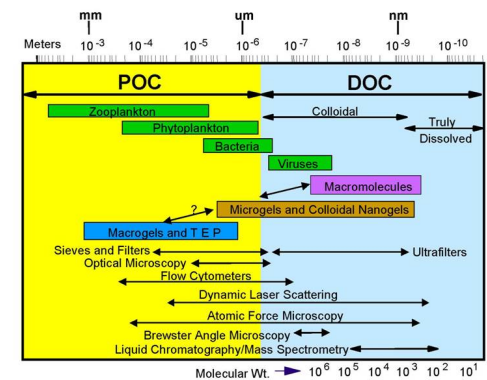
POM, DOM



ESM have above  
ESM need below

..Cysteine, methionine, *DMSP, DMS, DMSO*  
Polysaccharides carboxylated and otherwise  
Amino acids, peptides, proteins, derivatives  
Lipids, peptidoglycan, chitin, lignin  
Isoprene and monoterpenes  
Volatile organics and halogenates  
Bacteria, viruses, bioparticles

*JGR, GBC, GRL*



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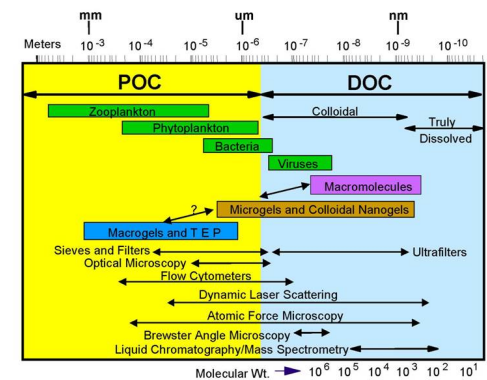
*Lipids*, peptidoglycan, chitin, lignin

Isoprene and monoterpenes

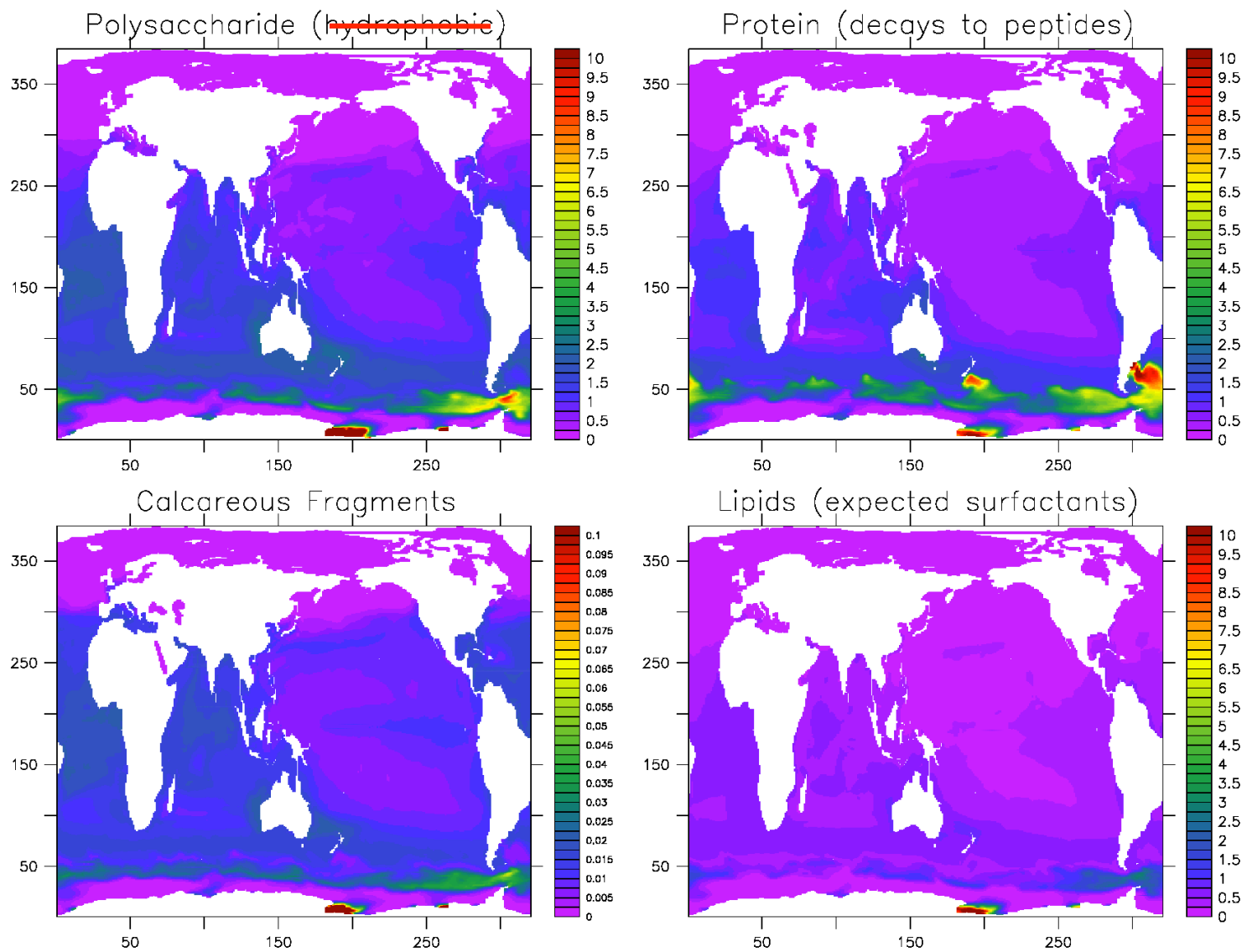
Volatile organics and halogenates

Bacteria, viruses, *bioparticles*

*JGR, GBC, GRL*

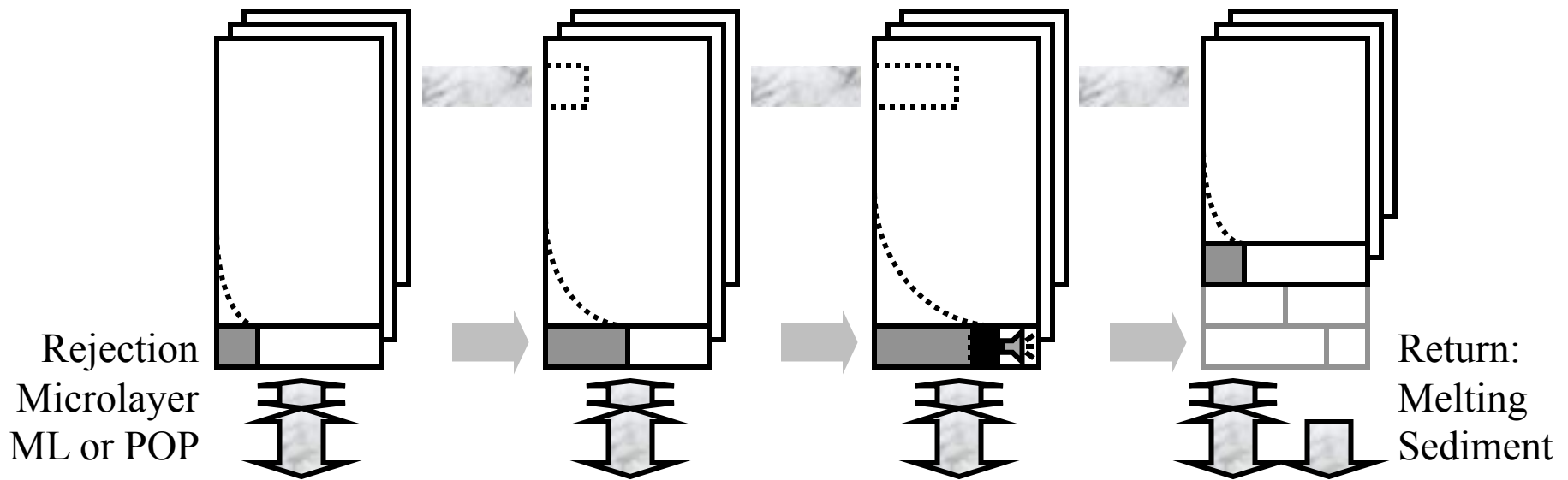


# Hawkins/Russell Primary Organics, Micromolar



# CICE Bottom Layer BGC

Ice categories with evolving box SKL, expand outward



**General:** Nutrient data

Monod  $L_i$   
Redfield ratios

Graze 10%  
N/S routing

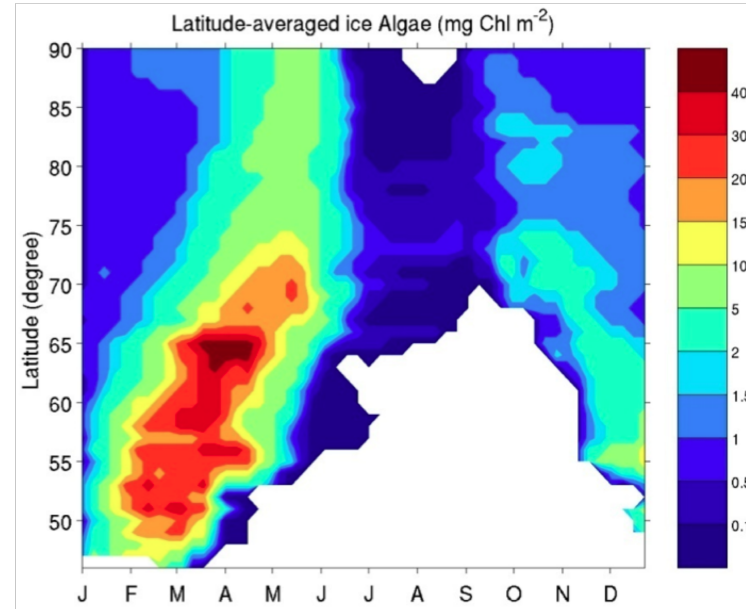
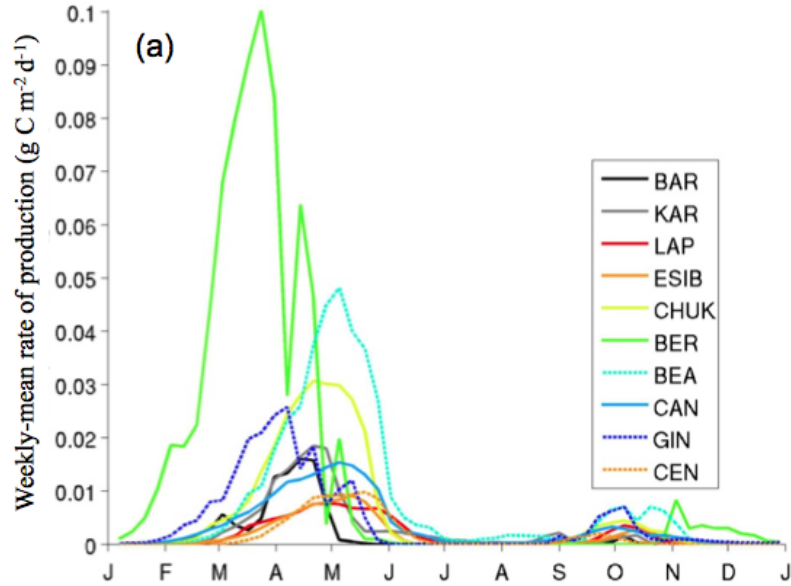
Fractional return  
of N, Si, C, S

**Jin et al.:** Brine flushing

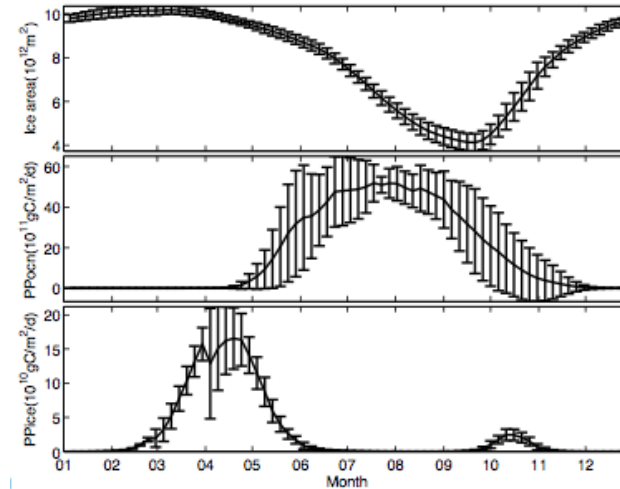
Continuous L  
Adjust absorption

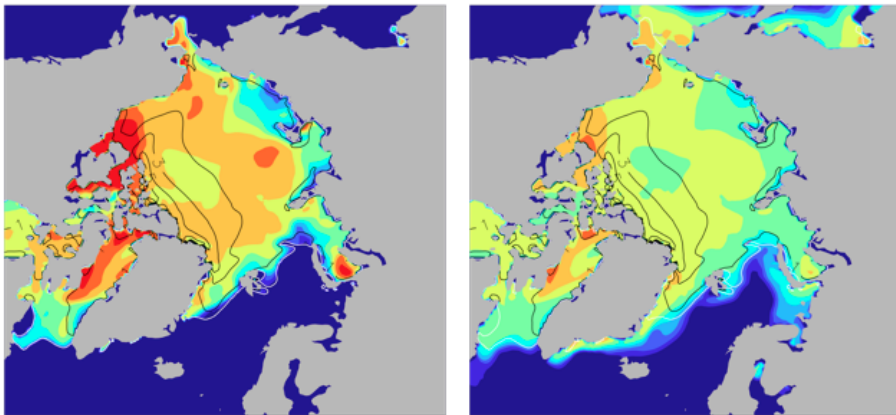
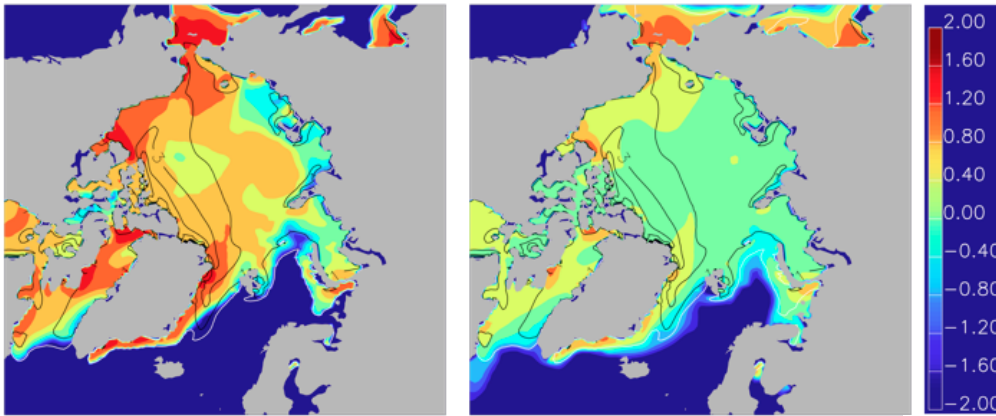
Algal flushing

# All roads lead first to ecodynamics...



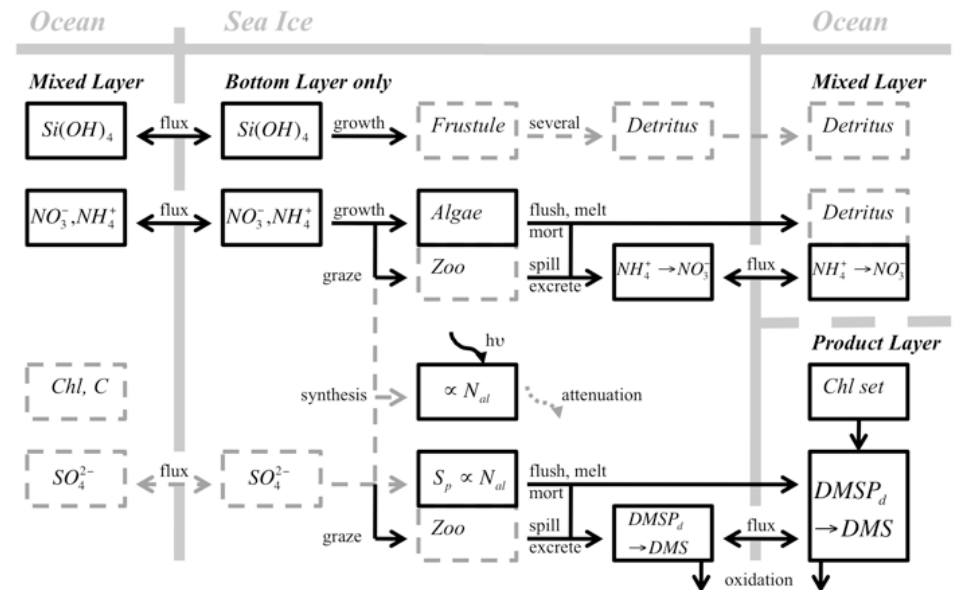
JGR and DSR





$\log_{10}$ Chl (l),  $\text{mg}/\text{m}^2$   
May 1992 (upper)  
June 1992 (lower)

$\log_{10}$ DMS (r), nM

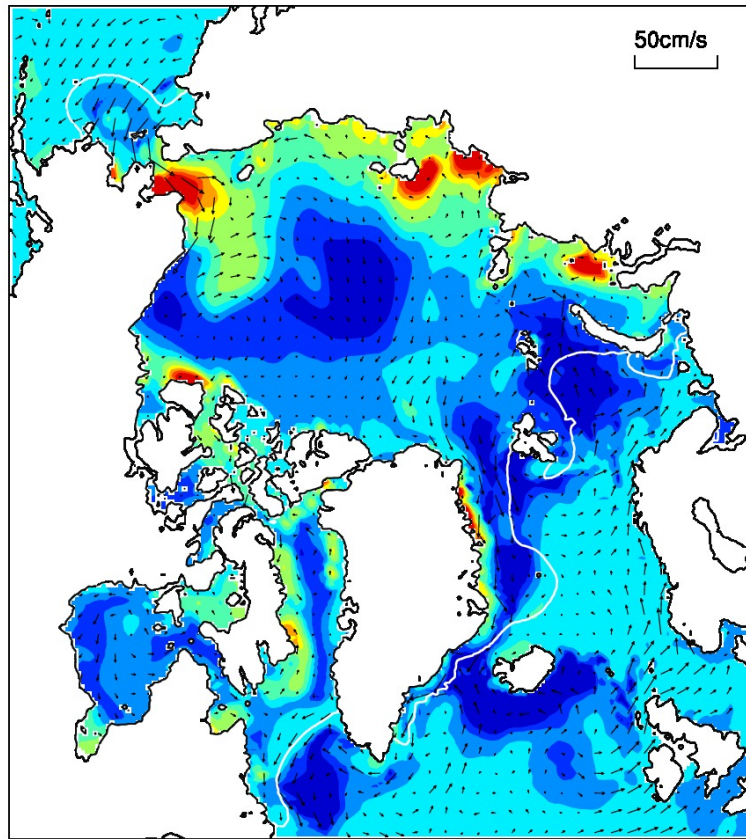


Chl in, DMS from bottom:  
JGR, in revision

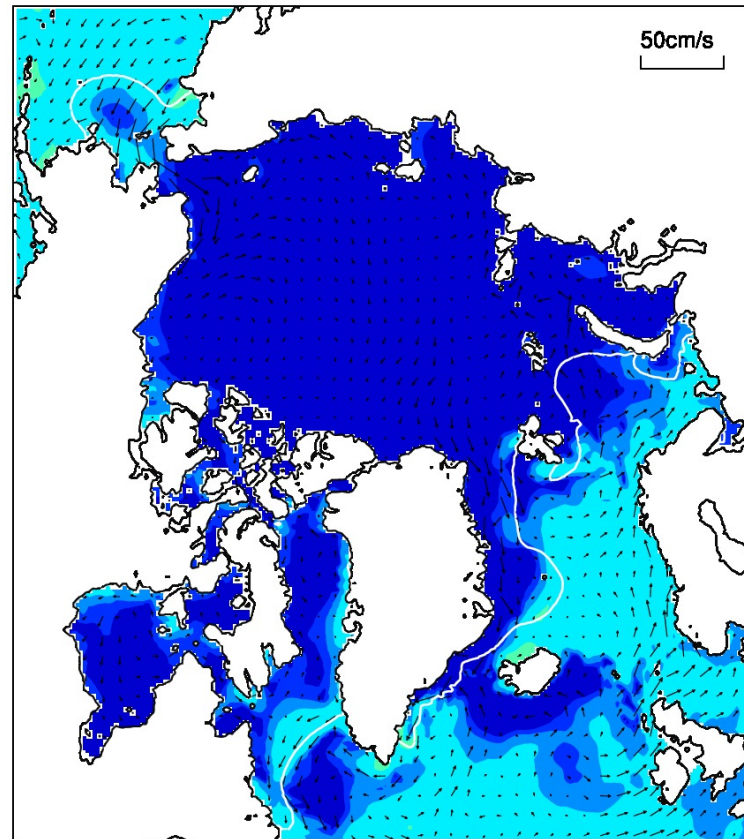


# DMS: CICE bgc on-off

DMS (mmol S/m<sup>3</sup>) 1992 05 11



DMS (mmol S/m<sup>3</sup>) 1992 05 11



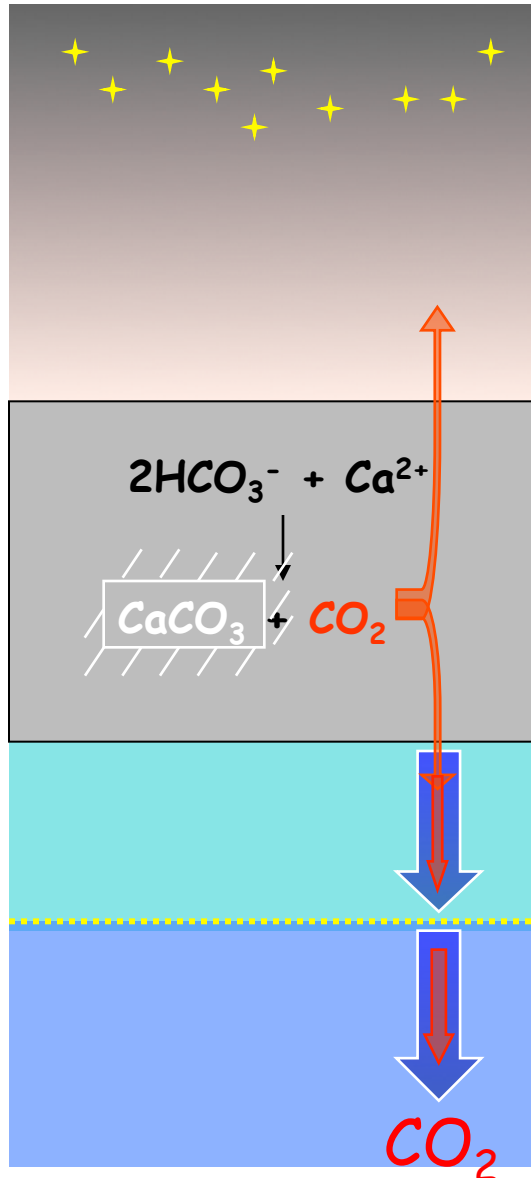
DSR, sulfur in revision JGR



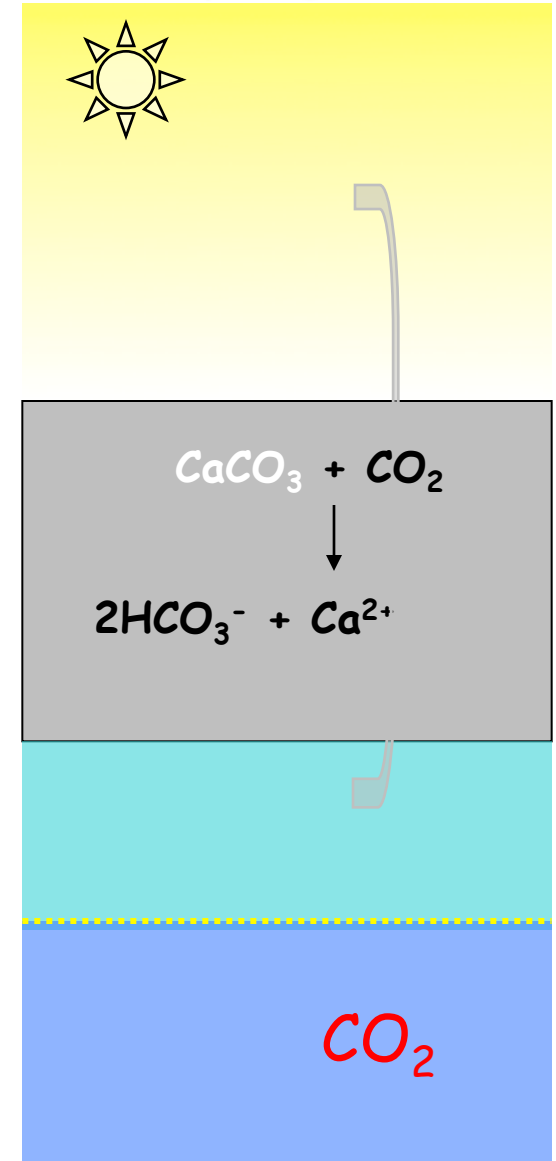
# GAS COMPOSITION IN SEA ICE

A potential abiotic  $\text{CaCO}_3$  Carbon pump

fall/winter



spring

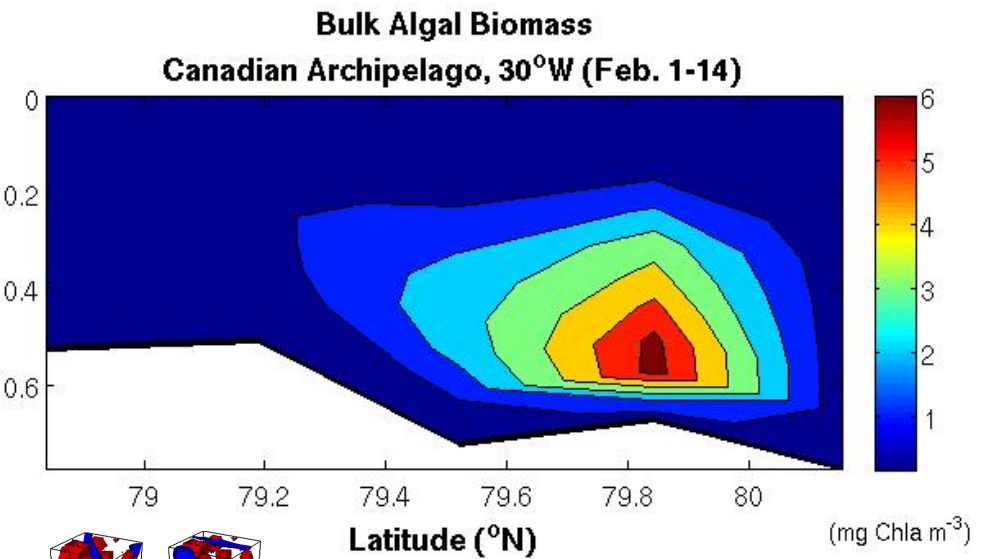
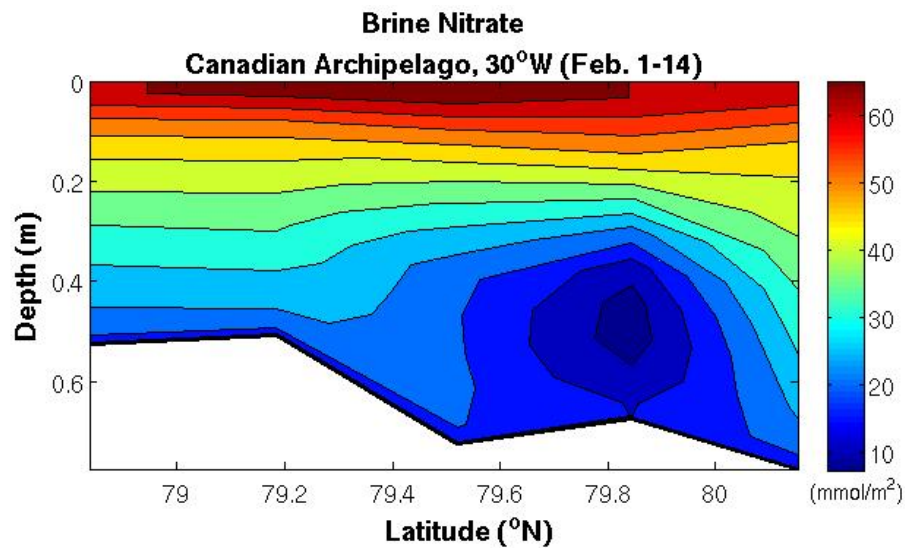
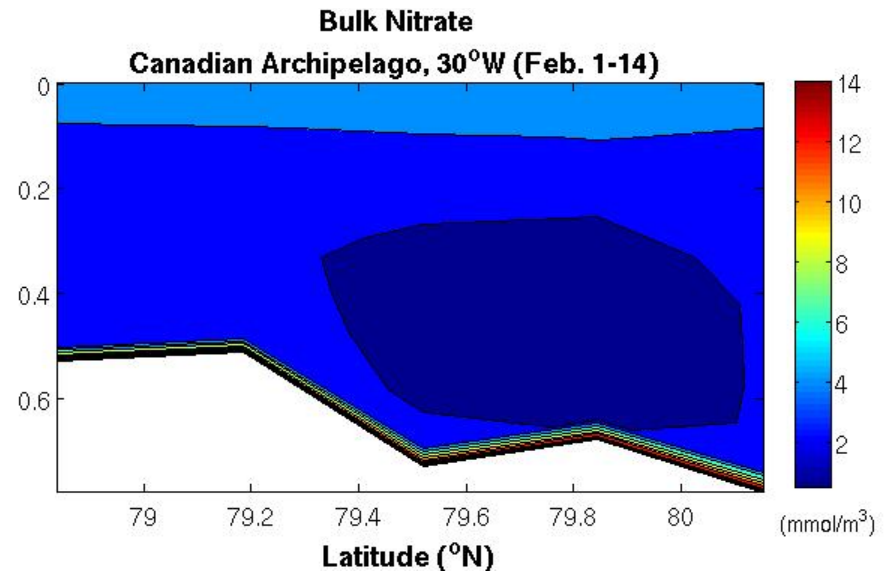
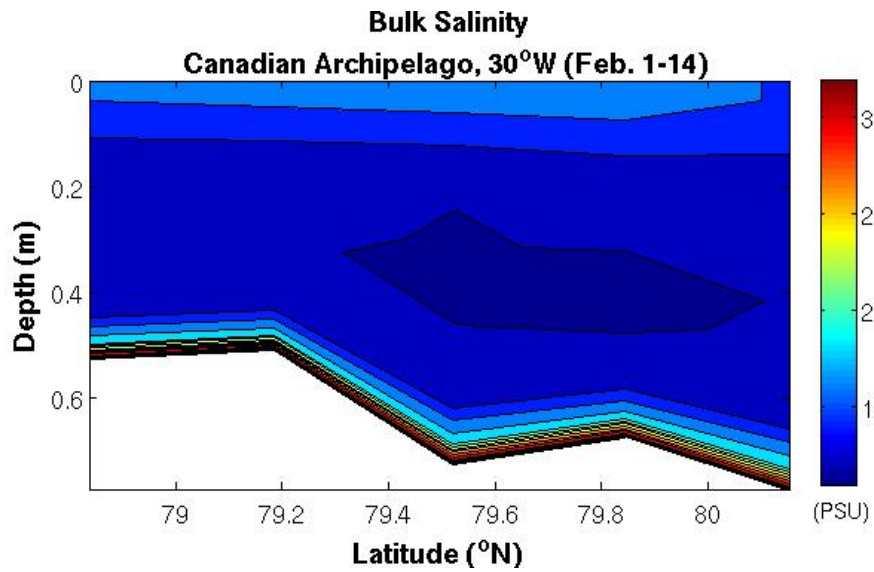


- In spring,  $\text{CaCO}_3$  trapped within sea ice dissolves. This process consumes  $\text{CO}_2$ .

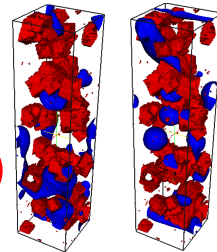
- Budget of winter and spring processes is a net sink of  $\text{CO}_2$ . It depends on:

- ratio of  $\text{CaCO}_3$  trapped vs  $\text{CO}_2$  expelled (?)
- quantity of  $\text{CO}_2$  which pass below the pycnocline during the autumn-winter (?)

*Rysgaard et al., 2007, Delille et al., in prep.*



algorithm in press, JGR  
(Nicole, don't forget the bubbles)



EXTRA EXTRAS

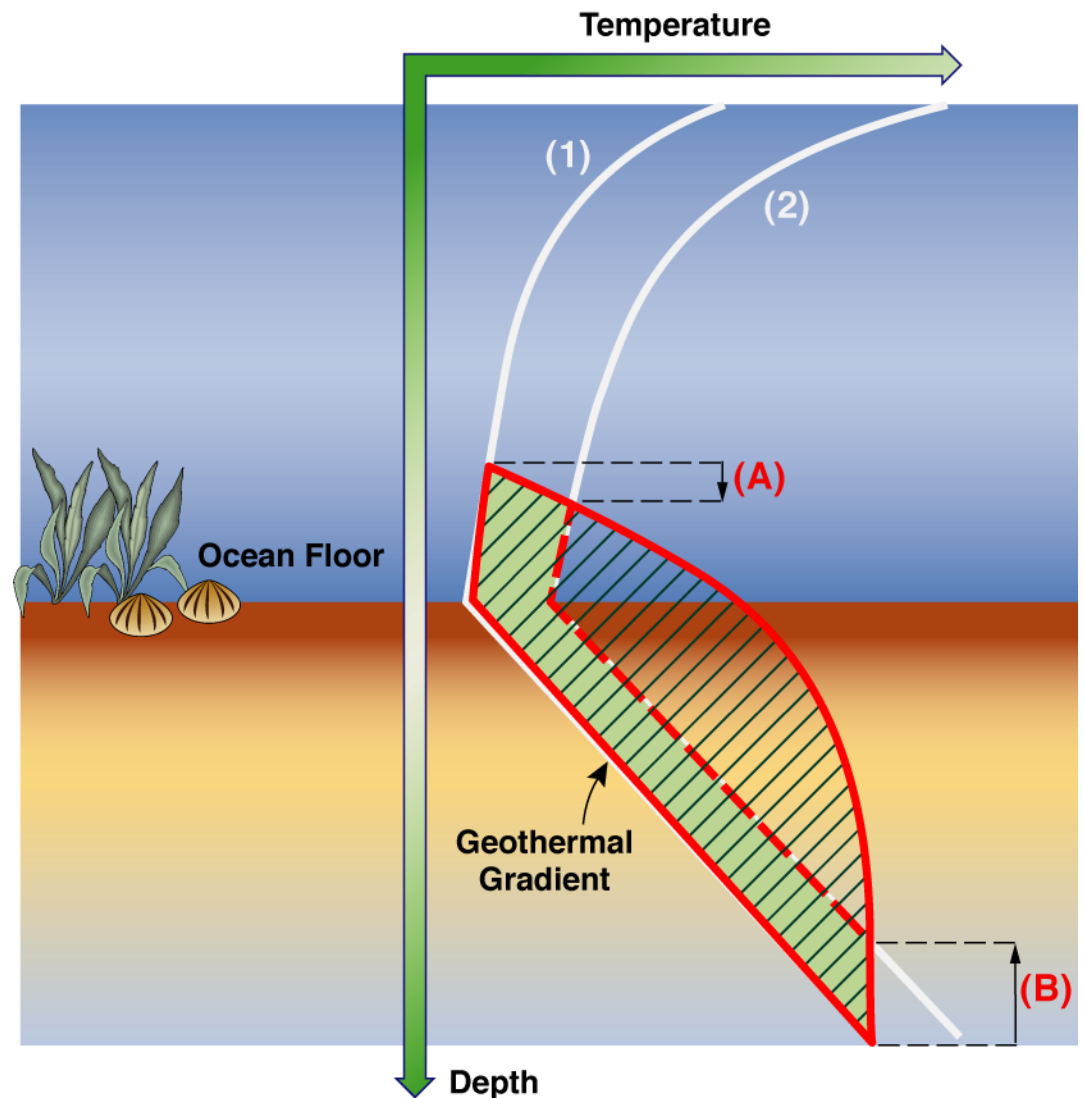
# Oceanic Gas Hydrates: Dissociation

Climate change alters ocean temperature (and geothermal gradient)

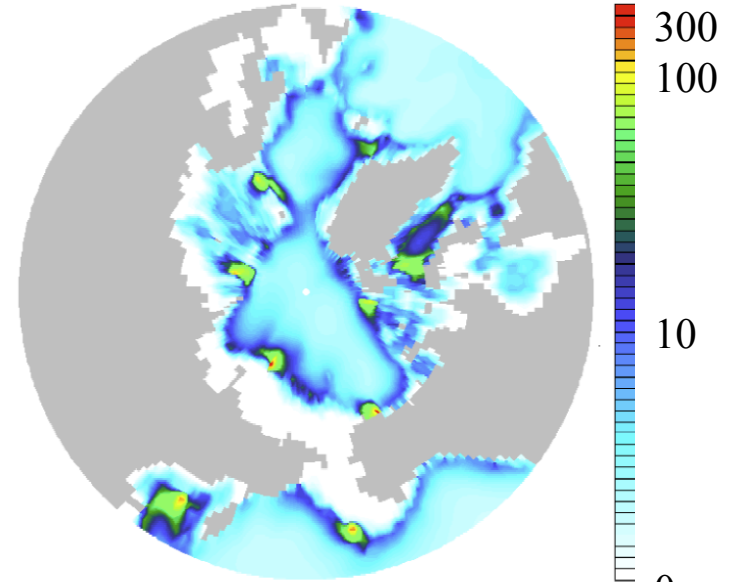
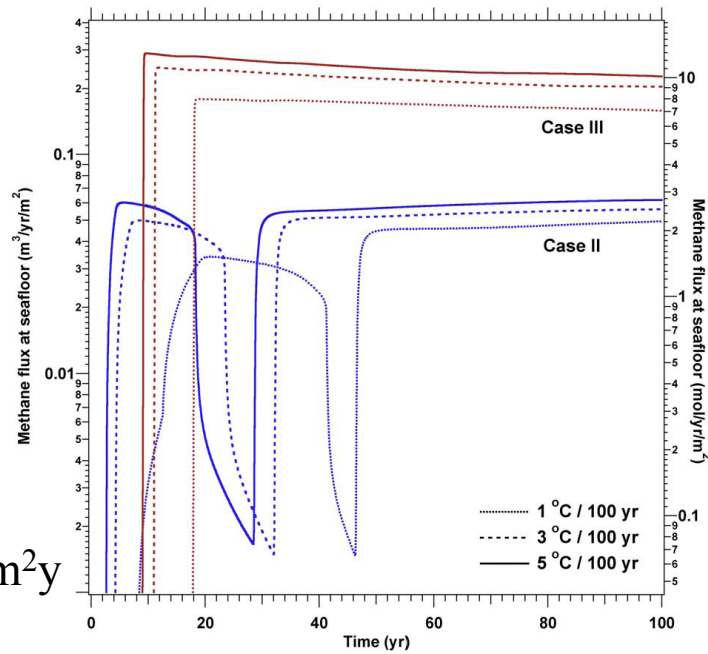
Decreases hydrate stability region

Methane release to ocean by hydrate dissociation

What happens between (1) and (2)?

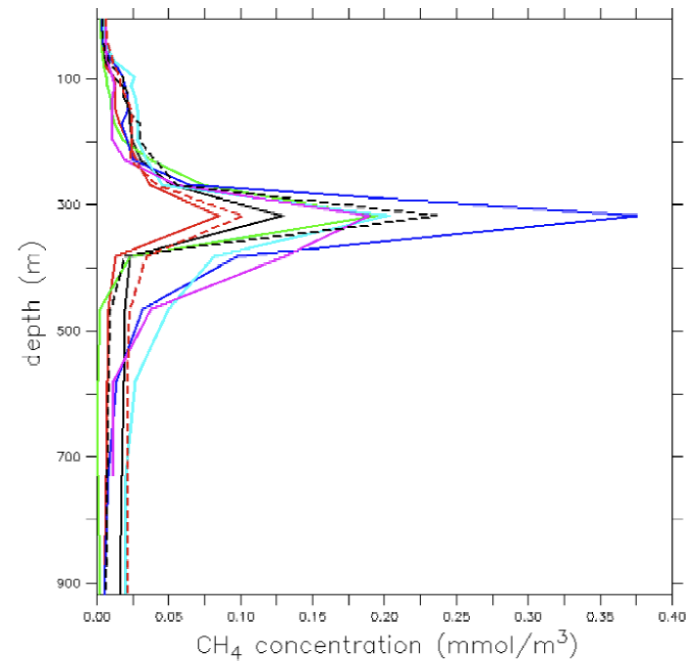


LBL,  
mole/m<sup>2</sup>y



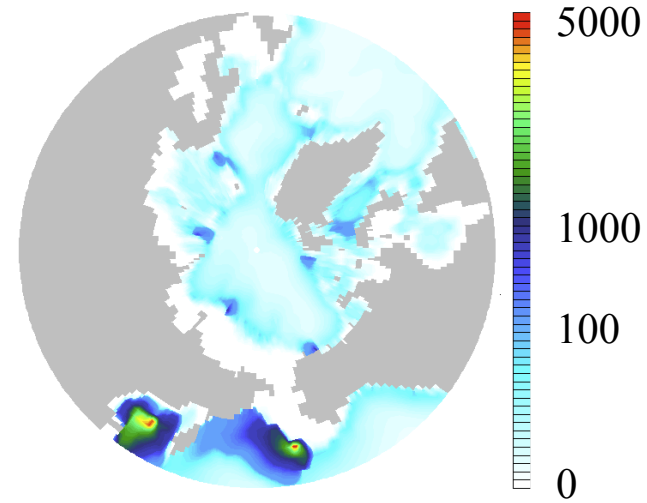
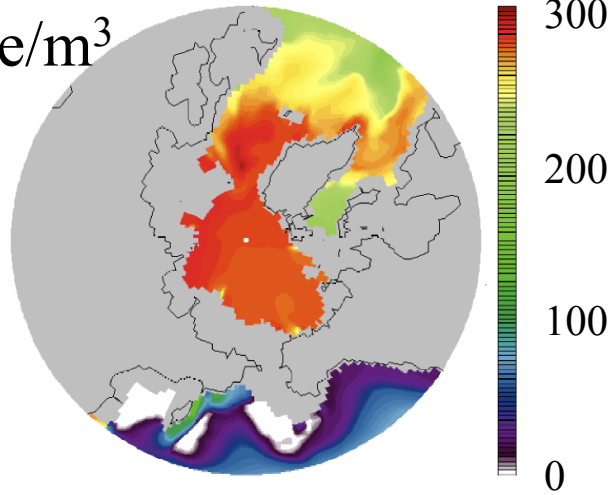
CH<sub>4</sub> (millimole/m<sup>2</sup> and /m<sup>3</sup>)

320 meter fluxes  
8 one-cell sites  
Empirical  $\tau$   
30 years, coarse POP

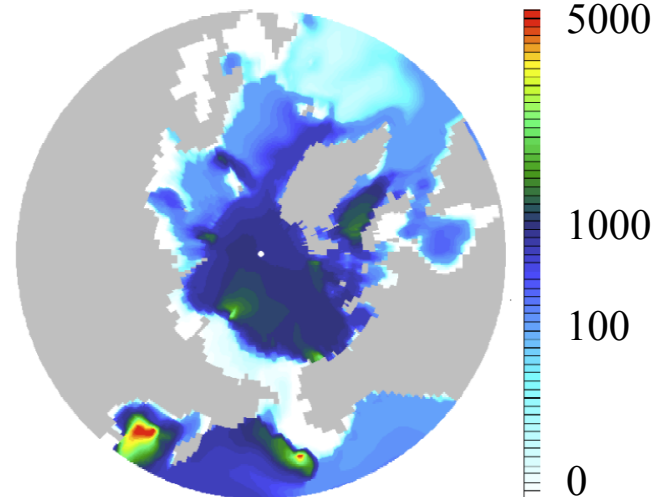
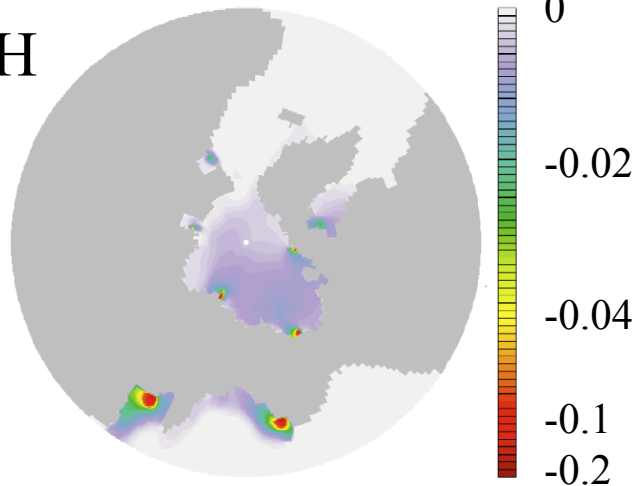


# O<sub>2</sub>, CO<sub>2</sub> and Plume Expansion

millimole/m<sup>3</sup>  
O<sub>2</sub>



ΔpH



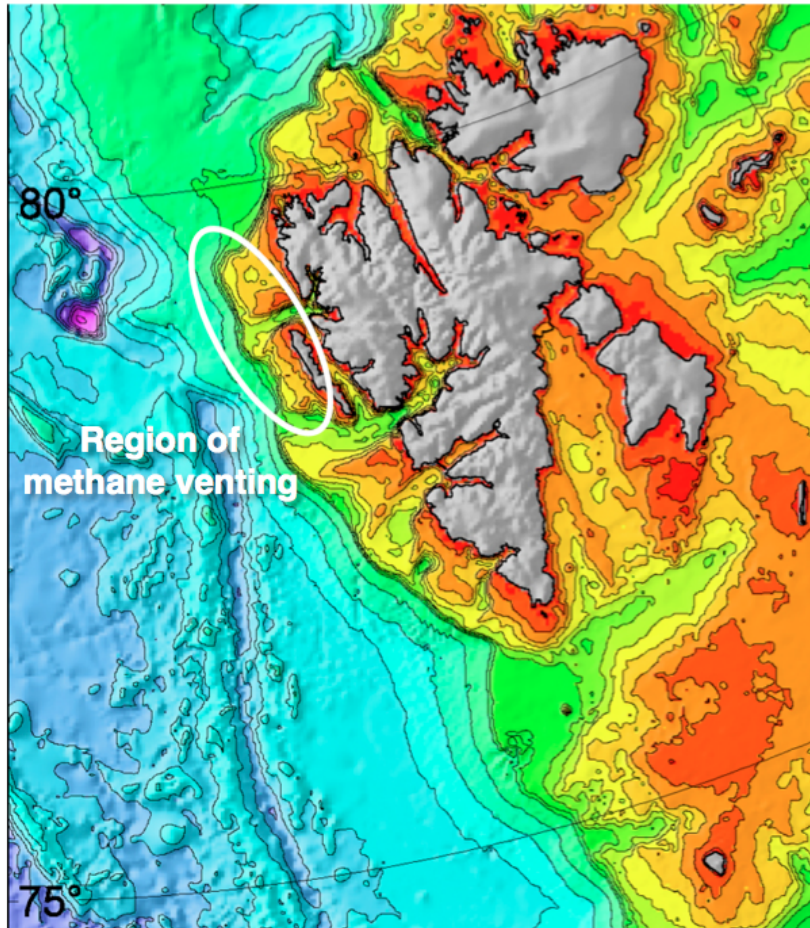
CH<sub>4</sub>, millimole/m<sup>2</sup>

300 meters, 30 years

## 2-D Hydrate Dissociation Model



from NOAA/IBCAO (<http://www.ngdc.noaa.gov/>)



- Methane plumes reported west of Svalbard at the upper limit of a receding GHSZ<sup>4</sup>
- Region affected by recent measured warming
- Could shallow hydrates alone produce such plumes?
- Could similar systems exist elsewhere?
- How much methane could be released on short timescales?
- Do we need to supplement the 1-D column model?

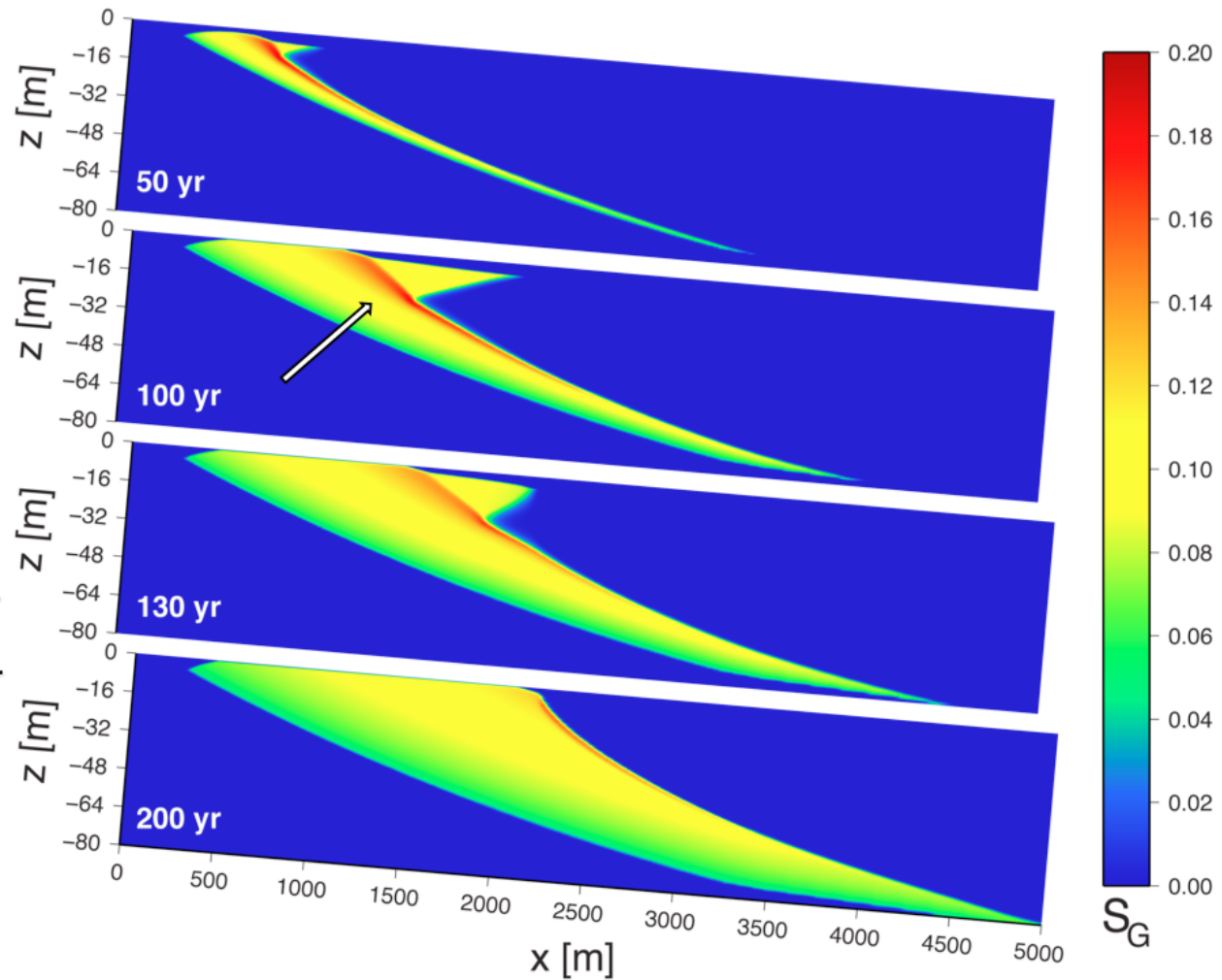
<sup>4</sup>Westbrook, G.K., *et al.*, Escape of methane gas from the seabed along the West Spitsbergen continental margin *Geophys. Res. Lett.*, **36**, L15608, doi: 10.1029/2009GL039191, 2009.



## 2-D Hydrate Model: Rapid Change

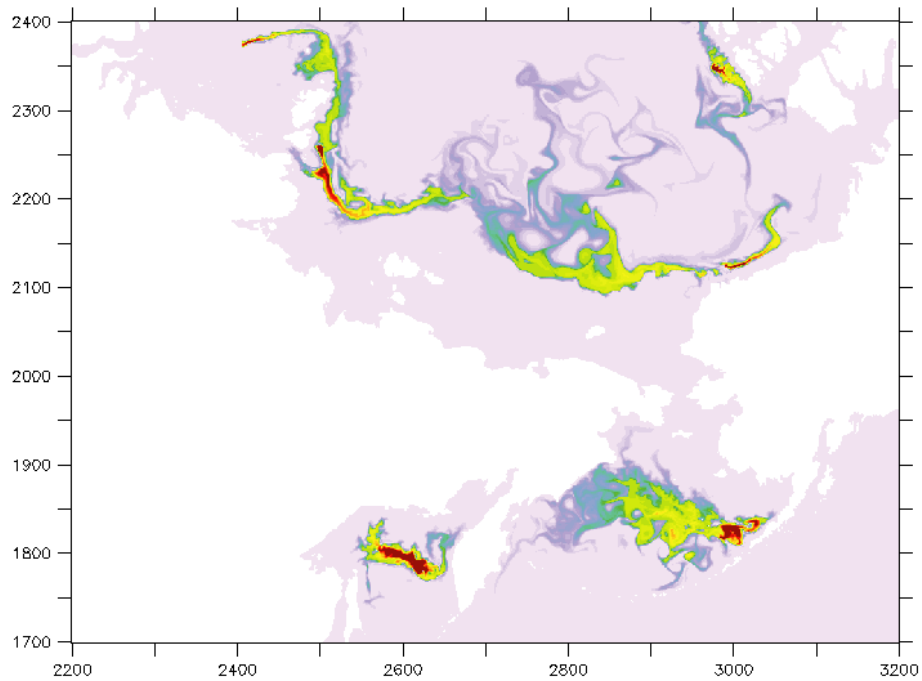


- A linear change of  $3^{\circ}\text{C}/100\text{ yr}$  imposed for 100 yr, then temperature held constant
- A “plume” of high gas saturation forms at upper limit of dissociating hydrates
- Plume focused by the remaining hydrate layer
- Plume reaches seafloor and moves downslope within the sediments

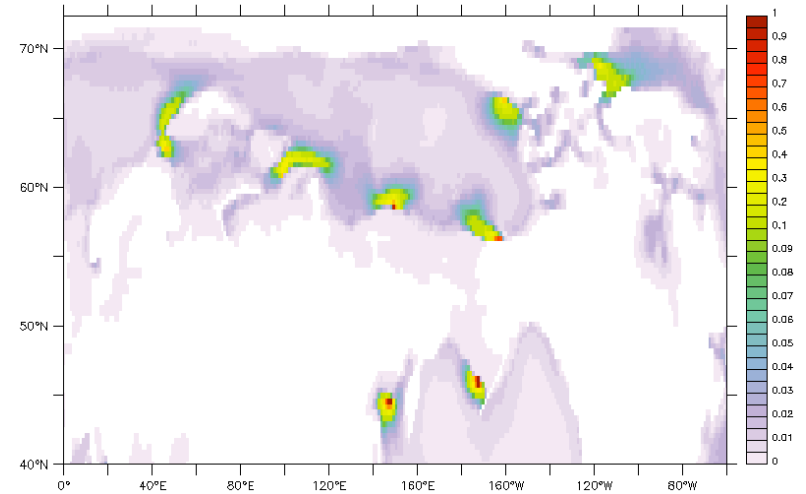


# Vertically integrated concentration (normalized by maximum)

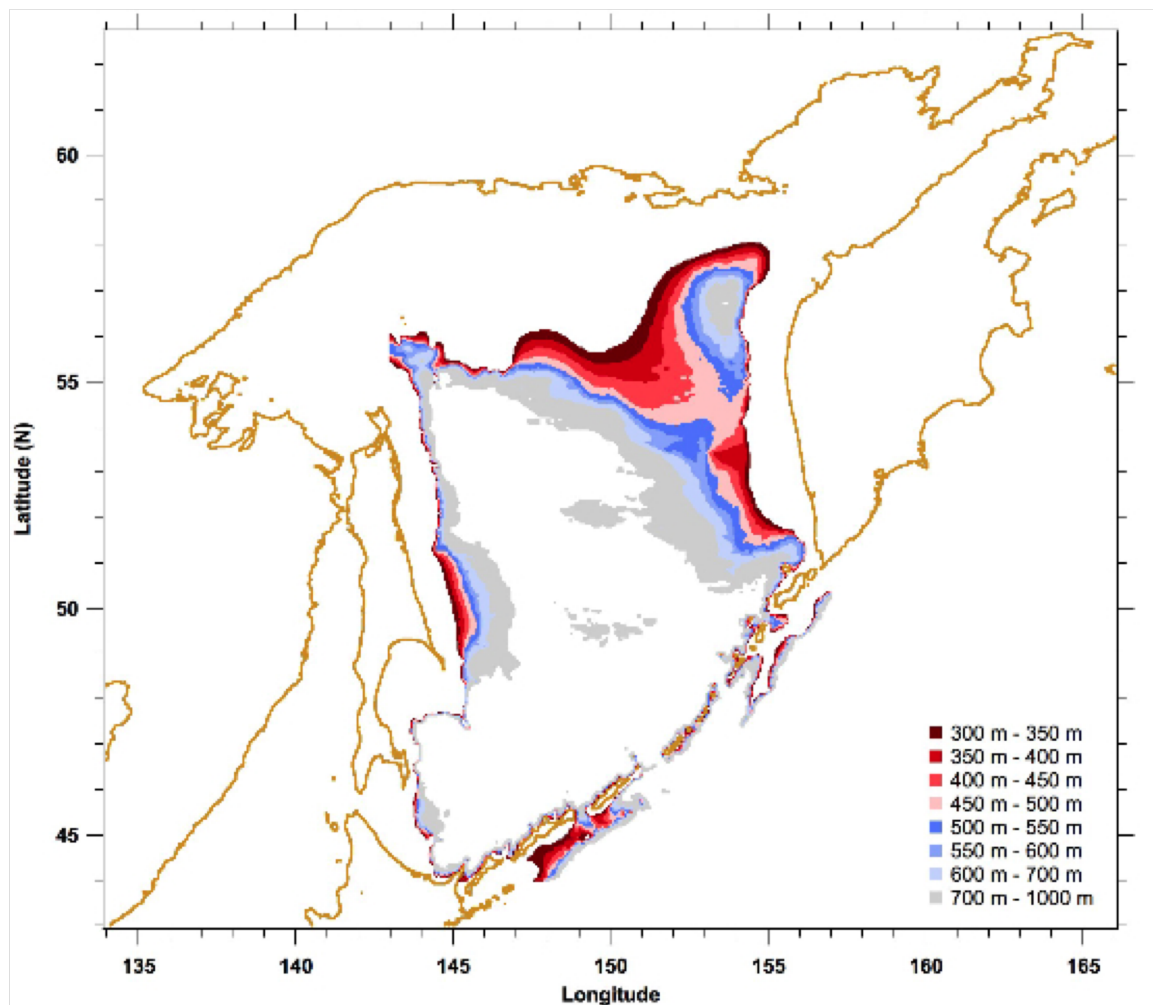
1/10° after 6 months



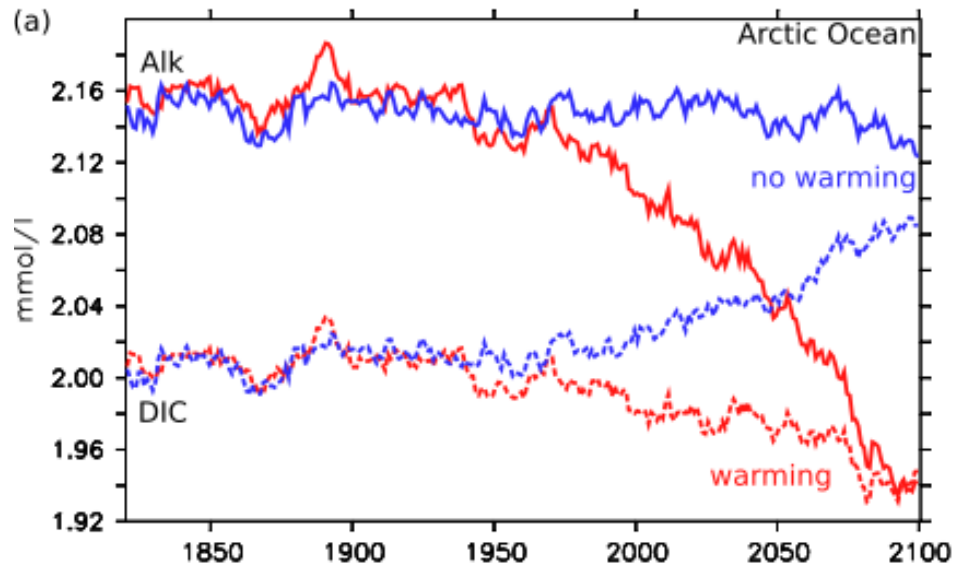
1° after 12 months



(The Okhotsk is going to light up like a candle, dudes



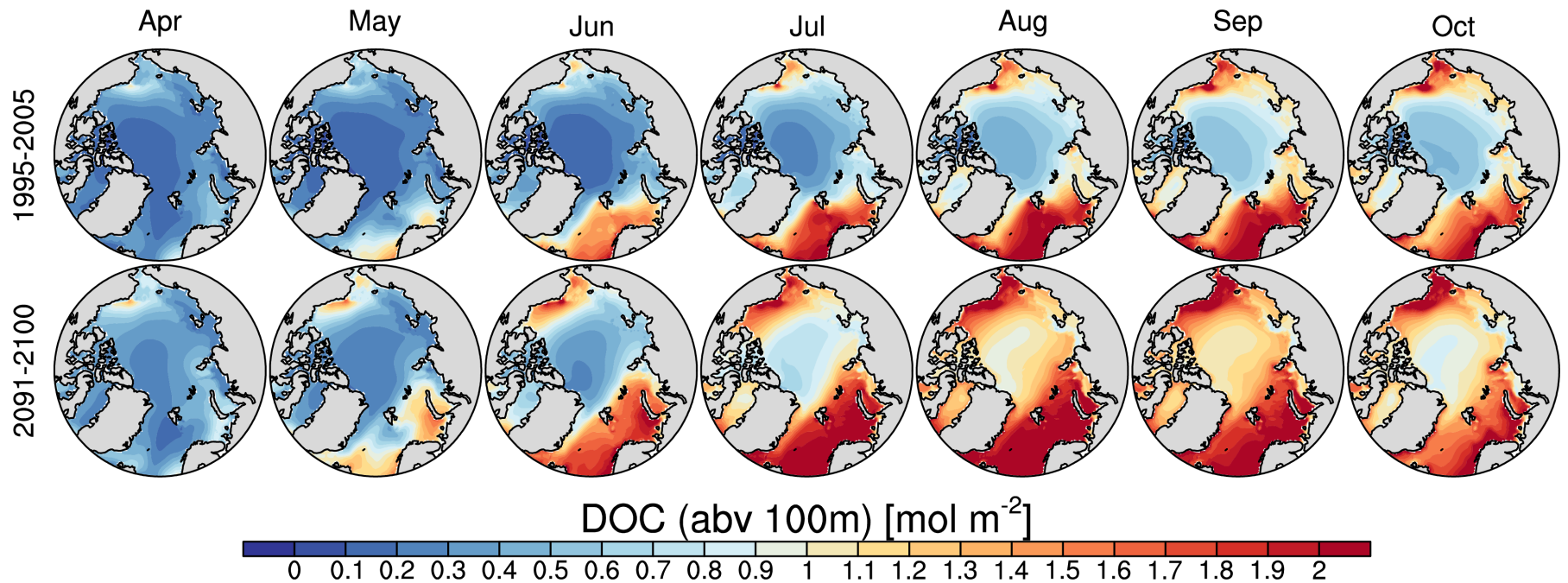
Reagan 2011  
Sea of Okhotsk Methane Budget



## Arctic pH, C storage

C anions balance Alkalinity

Convert to DOC, POC



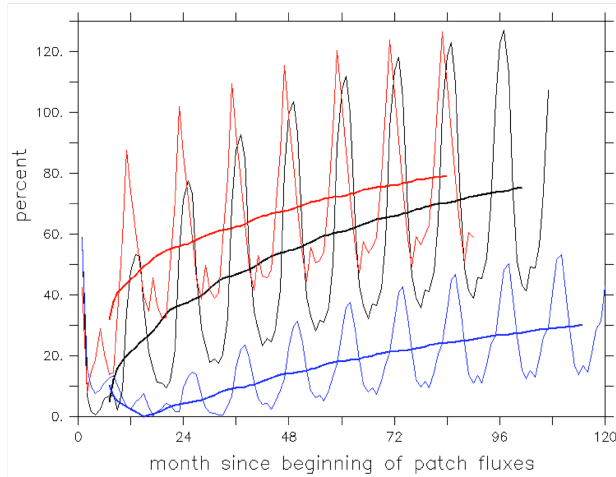
# Bubbles, Matrices, CH<sub>4</sub> Futures

Enter mixed layer from:

50 meters

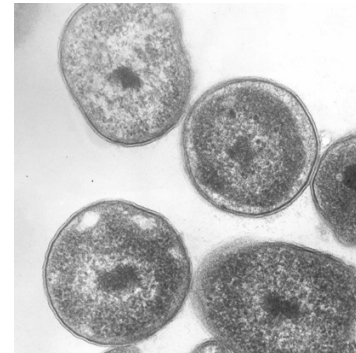
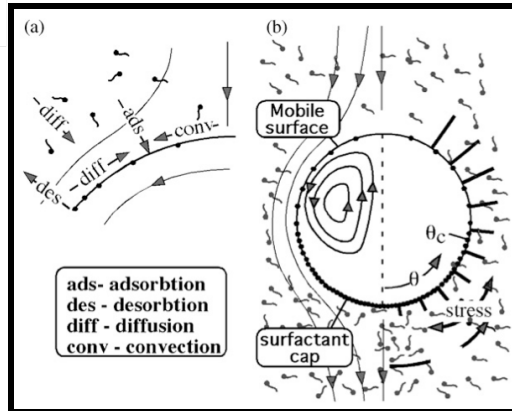
150 meters

300 meters

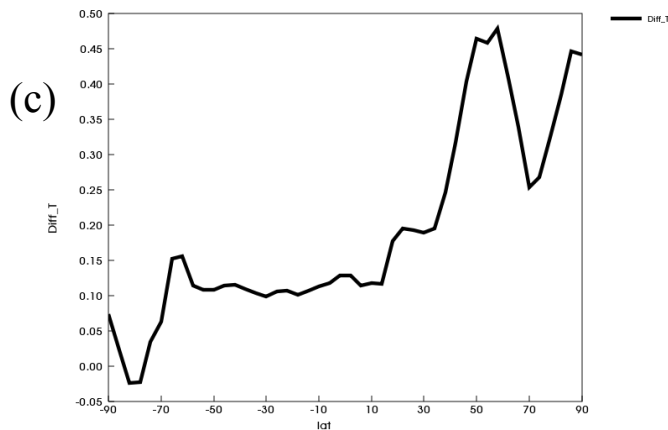
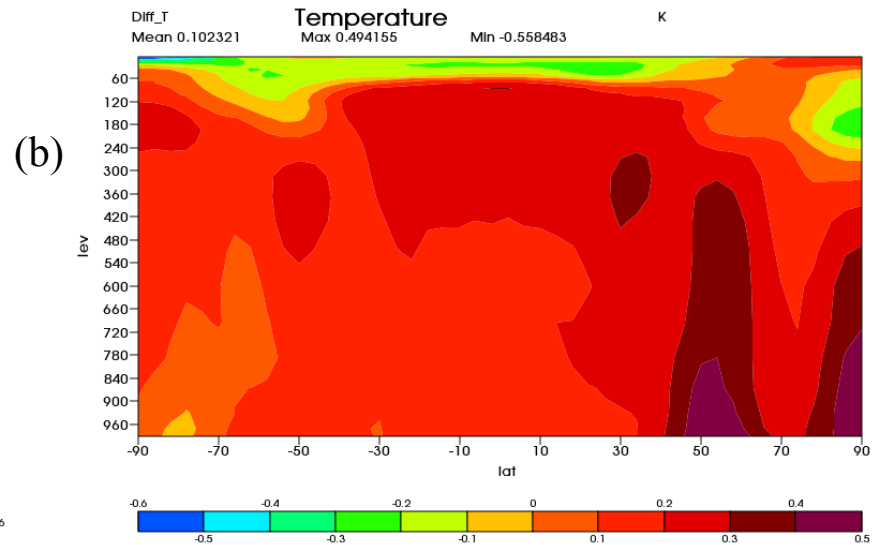
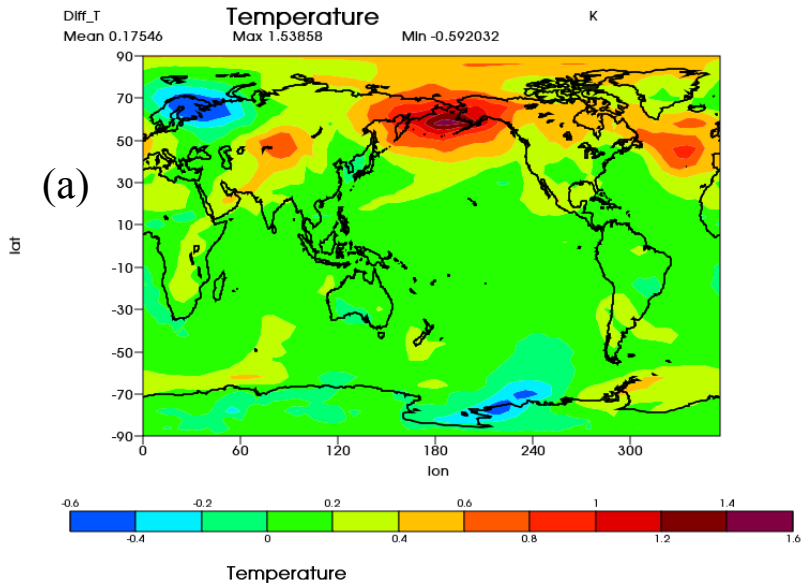


**Percent CH<sub>4</sub>, Atlantic Layer to Arctic Mixed Layer**  
(conservative K<sub>v</sub>)

|                |                | <b>Bubble Rise</b> (vertical from destabilization at 350) |       |            |        |        |
|----------------|----------------|---|-------|------------|--------|--------|
|                |                | 0 m   | 100 m | 300 m      | 300 m  | >300 m |
|                |                |   |       | (floor up) | (Δ100) |        |
| <b>Circuit</b> | <b>Biology</b> |   |       |            |        |        |
| 1,000 km       | on             | 0   | 0     | 0          | 0      | 100    |
|                | off            | 0   | 0     | 10         | 20     | 100    |
| 10,000 km      | on             | 0   | 0     | 0          | 0      | 100    |
|                | off            | 0   | 0     | 20         | 40     | 100    |
| >10,000 km     | on             | 0   | 0     | 0          | 0      | 100    |
|                | (GIN mix)      | off   | 100   | 100        | 100    | 100    |



# Notable Increase in temperature not spatially uniform



- (a) Raw Difference in surface air temperature relative to control
- (b) Raw Difference in Temperature averaged over longitudes
- (c) Zonal Mean of Raw Difference in Surface Air Temperature

# East Siberia falling through Cracks

Shakhova et al. document tens of nM at sea surface  
Likely source is degrading submarine permafrost  
Not covered in *any* CCSM working group

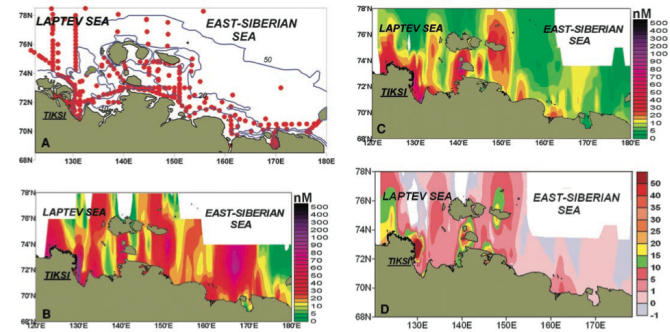
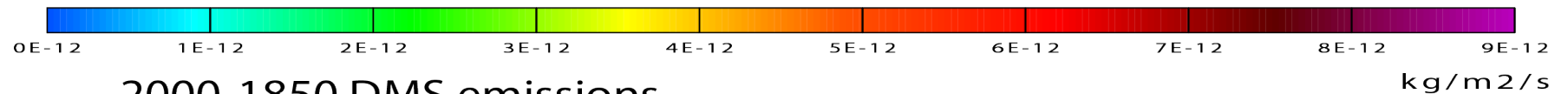
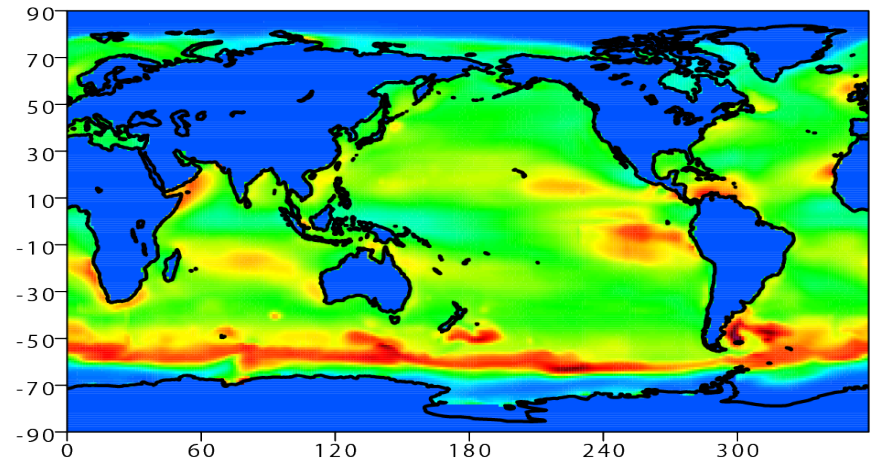
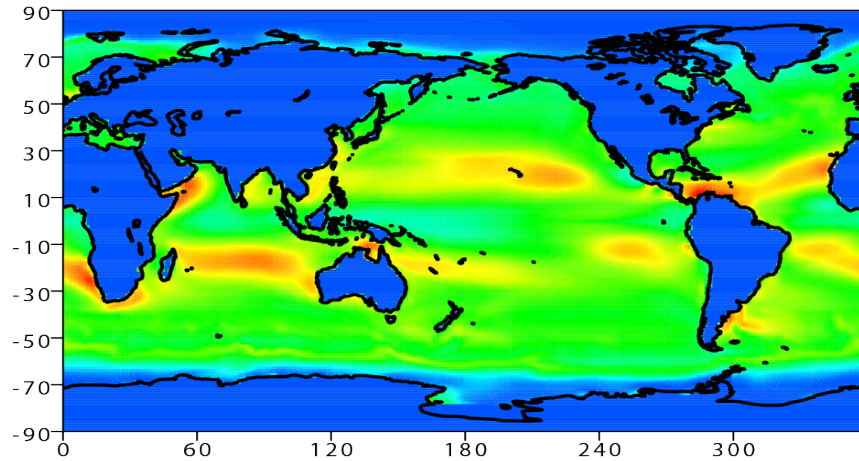


Fig. 1. Summertime observations of dissolved  $\text{CH}_4$  in the ESAS (21). (A) Positions of oceanographic stations in the eastern Laptev Sea and East Siberian Sea; bathymetry lines for 10, 20, and 50 m depth are shown in blue. (B) Dissolved  $\text{CH}_4$  in bottom water. (C) Dissolved  $\text{CH}_4$  in surface water. (D) Fluxes of  $\text{CH}_4$  venting to the atmosphere over the ESAS.

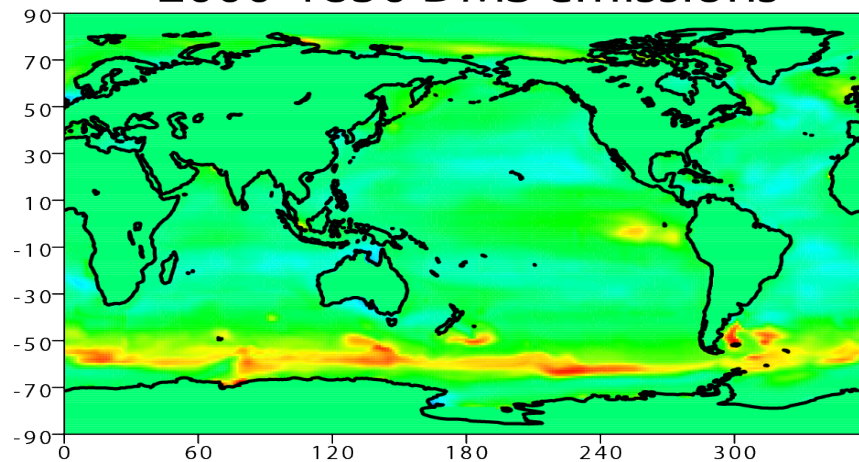
# DMS flux changes dramatically from 1850 to 2000, especially in Southern ocean

1850 DMS emissions

2000 DMS emissions



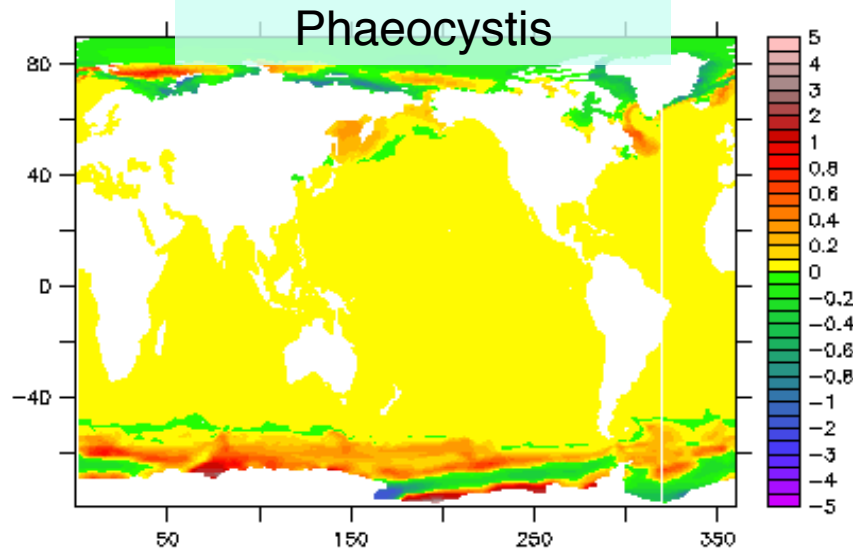
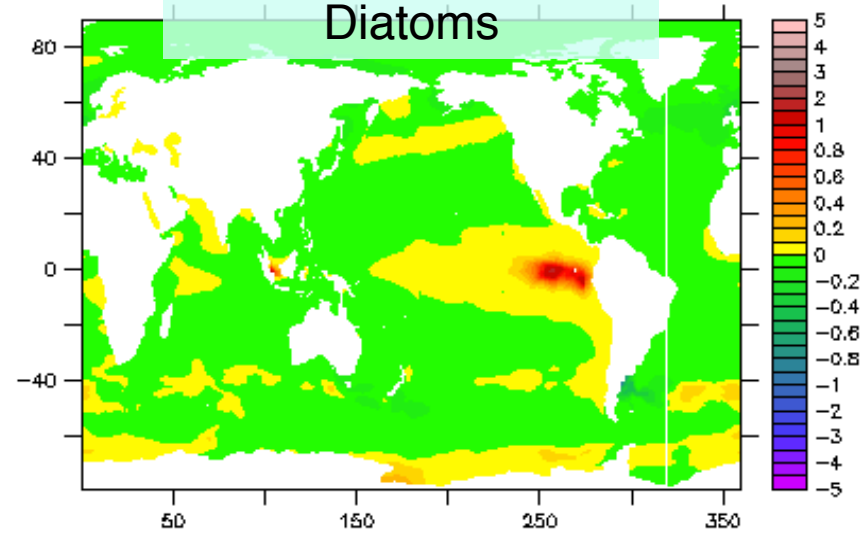
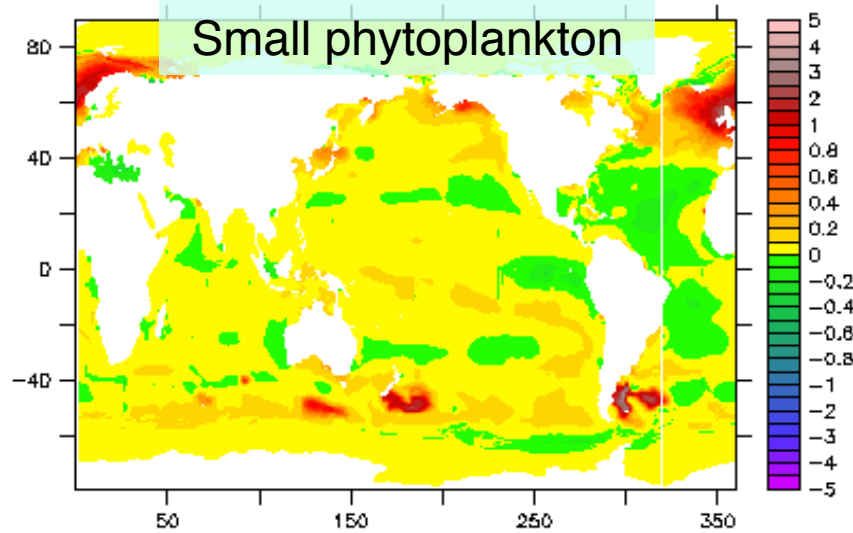
2000-1850 DMS emissions



Globally averaged increase in DMS emission is 10%



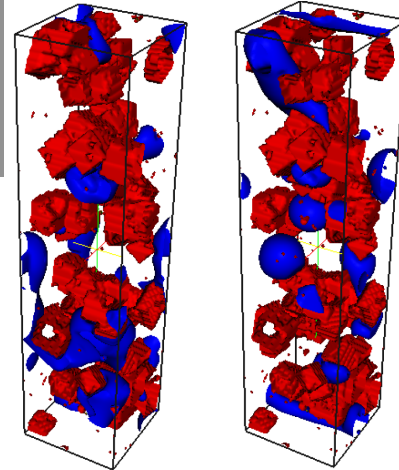
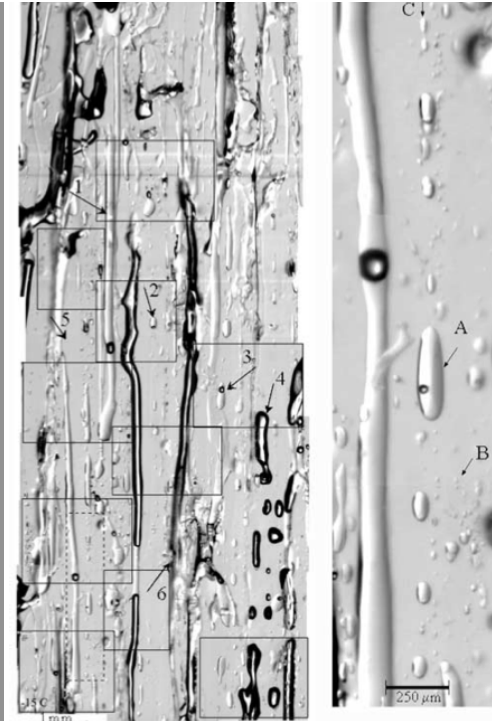
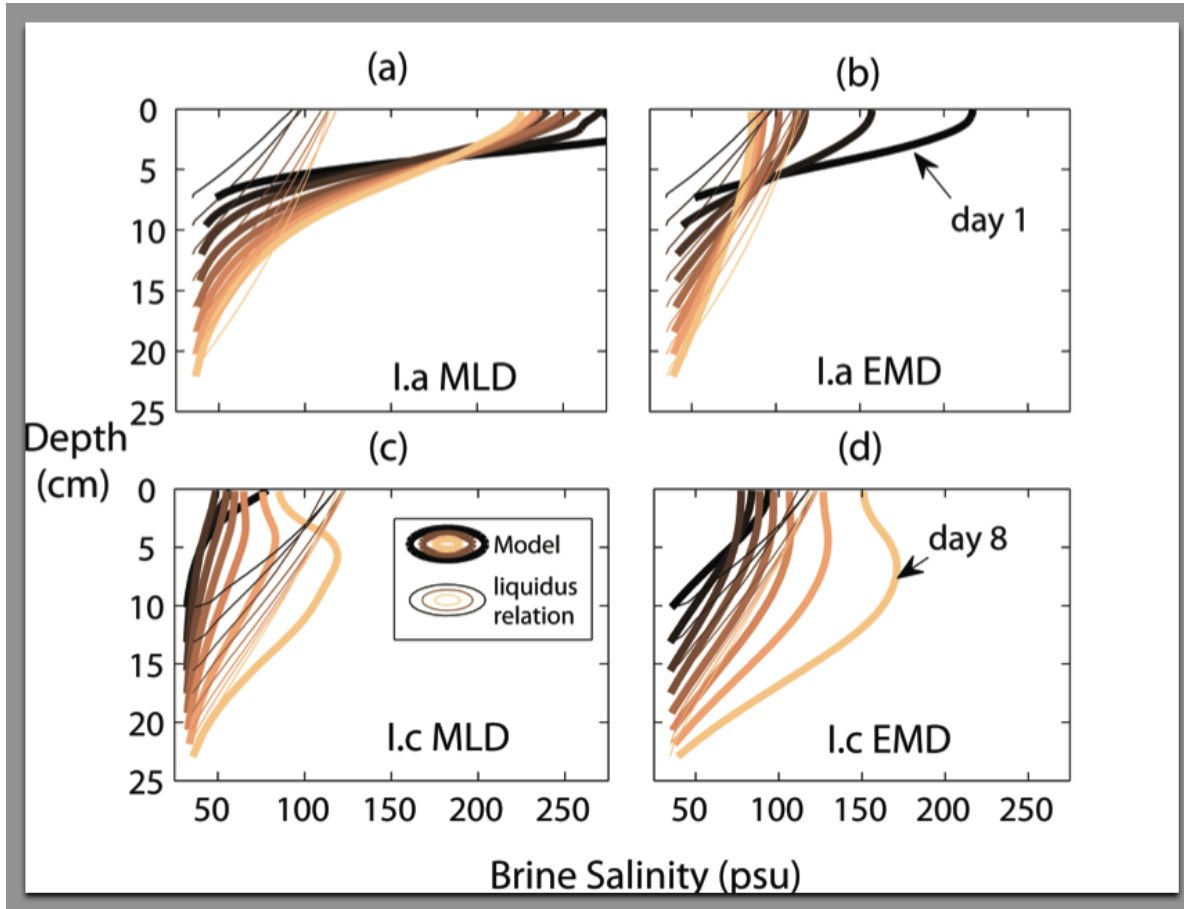
# Changes in DMS are strongly affected by changes in ecosystem structure.



Change in DMS concentration (in seawater) contributed by different phytoplankton types.

Units are normalized DMS concentrations, and are comparable across panels.

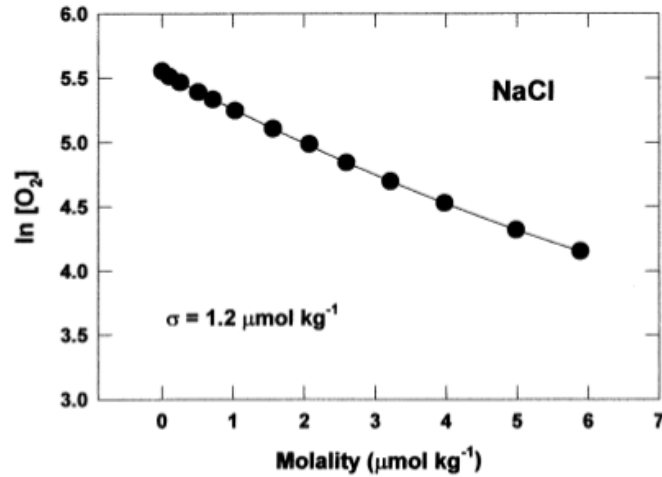
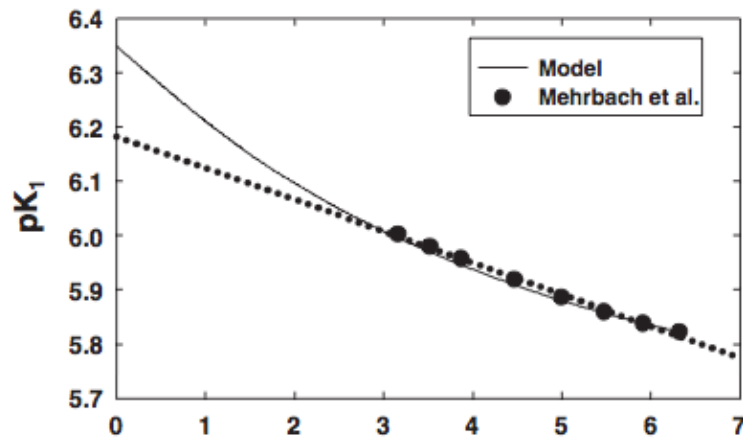
# Through CICE



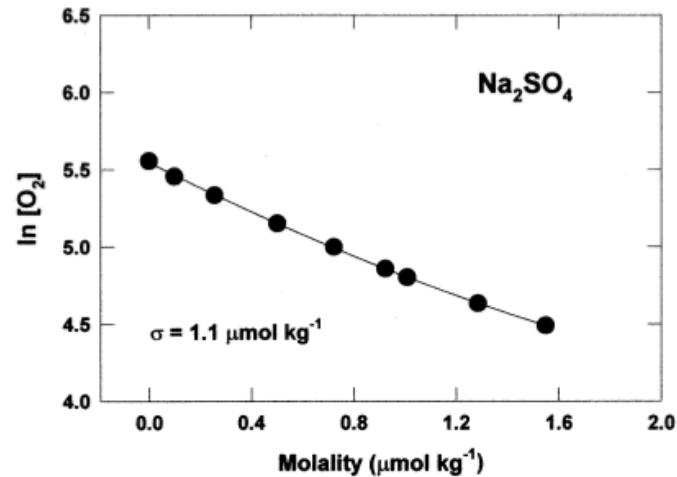
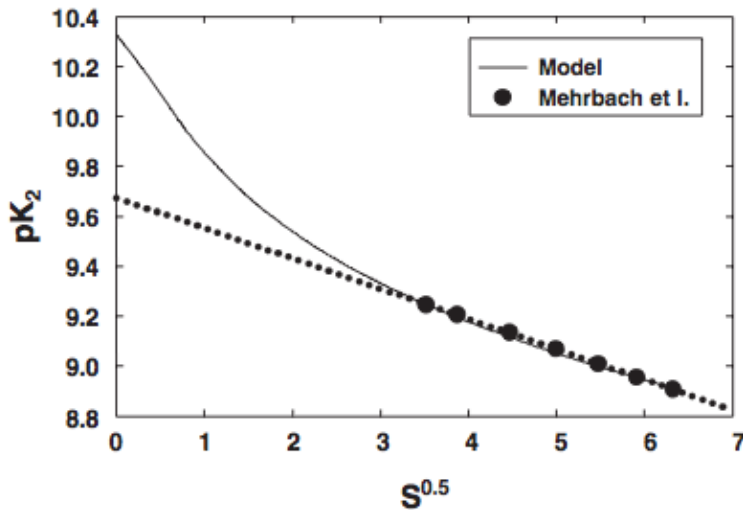
JGR in press

# Extreme Thermochemistry

Carbonic Acid

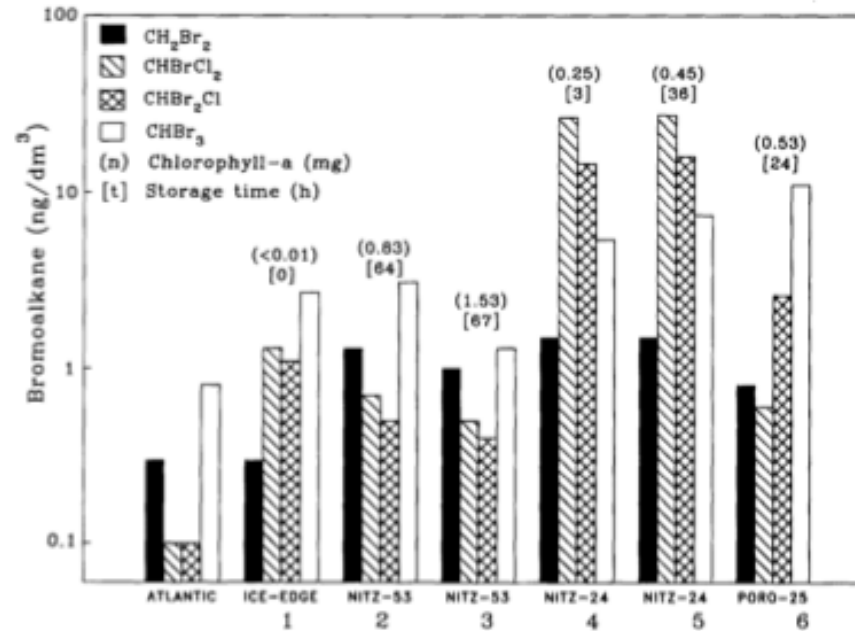
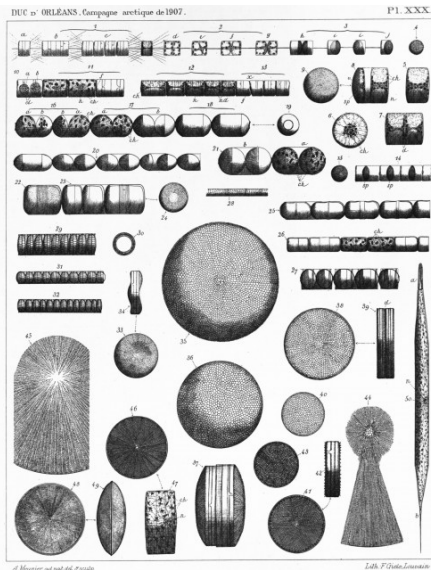
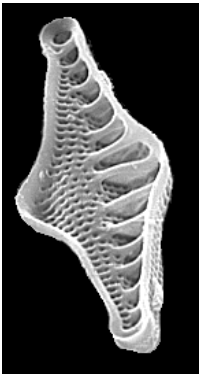
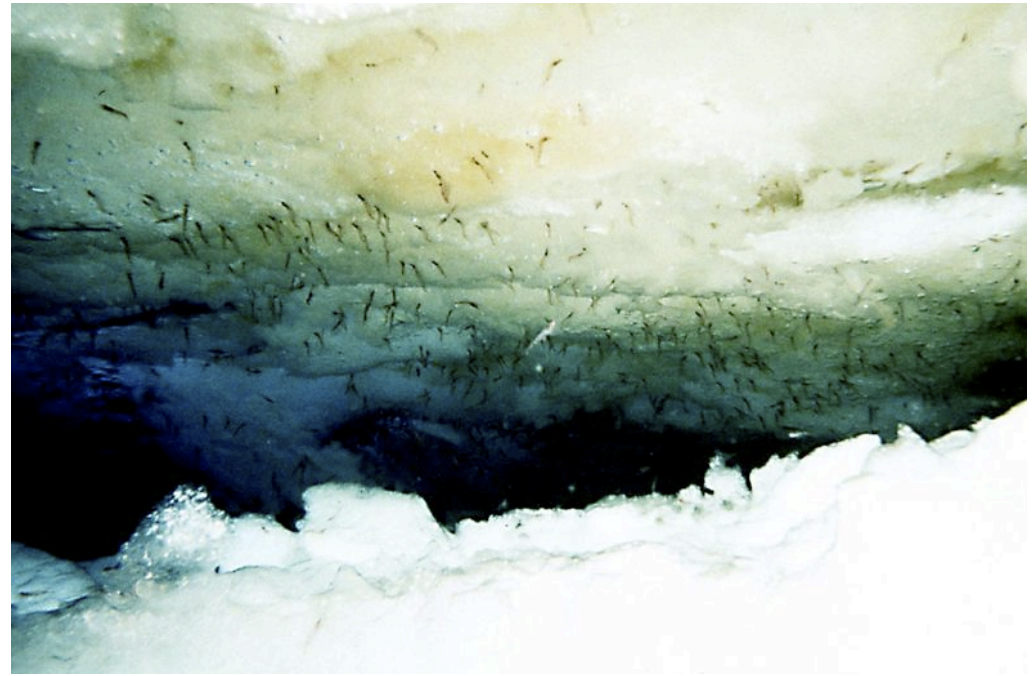
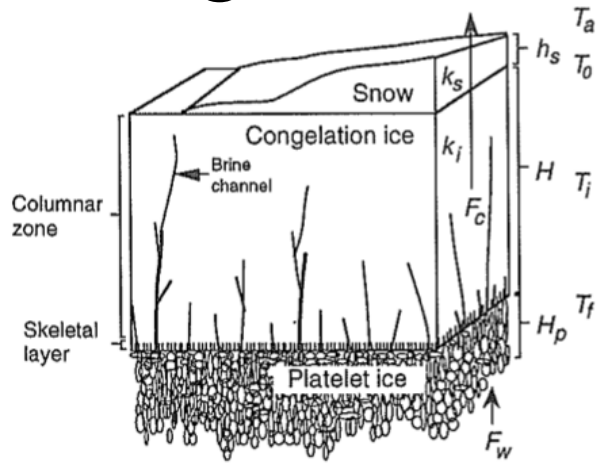


$$\ln \gamma_N = 2 \sum_n \lambda_{Nn} m_n + 2 \sum_c \lambda_{Nc} m_c + 2 \sum_a \lambda_{Na} m_a + 3 \sum_n \mu_{Nnn} m_n + 6 \sum_n \sum_n' m_n m_n' \mu_{Nnn'} + 6 \sum_n m_n \mu_{Nnn} + 6 \sum_n \sum_c m_n m_c \mu_{Nnc} + 6 \sum_n \sum_a m_n m_a \mu_{Nna} + 6 \sum_c \sum_a m_c m_a \zeta_{Nca} + \sum_{c < c'} m_c m_{c'} \eta_{Ncc'} + \sum_{a < a'} m_a m_{a'} \eta_{Naa'}$$

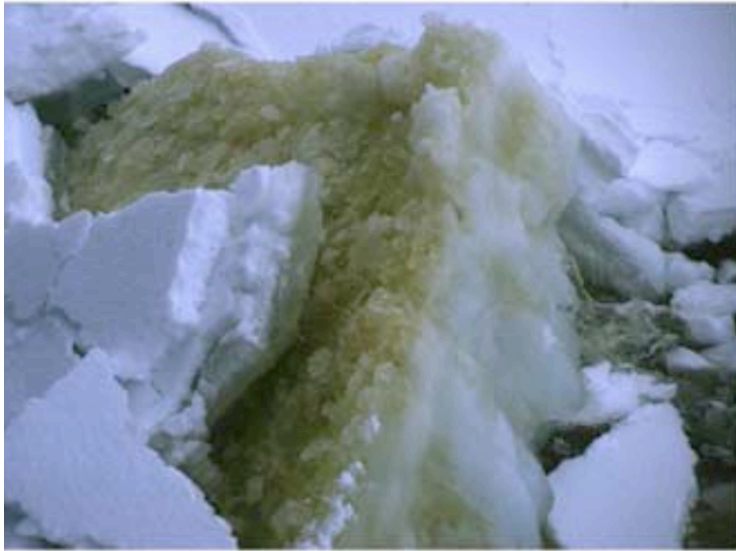


Millero et al., several ? No, CRREL as usual  
Pitzer equations -just Debye-Huckel on steroids

# A Halogen Tale

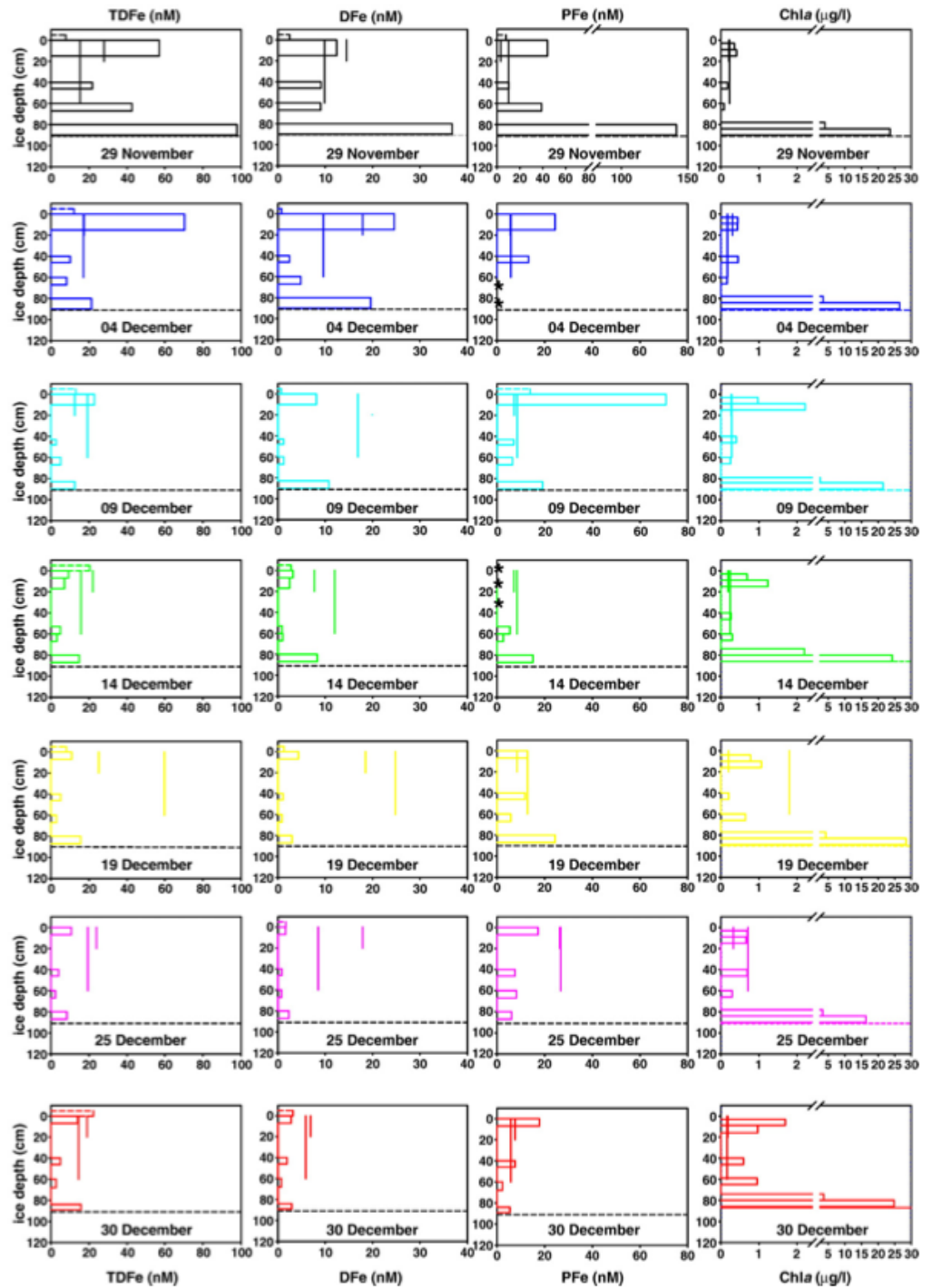


(Southern Ocean Alert)



Ackley et al. 2008  
 gap layer GRL  
 vs.  
 Lannuzel et al. 2008  
 Fe retained in sea ice...  
 By EPS substances

(Southern Ocean Alert)

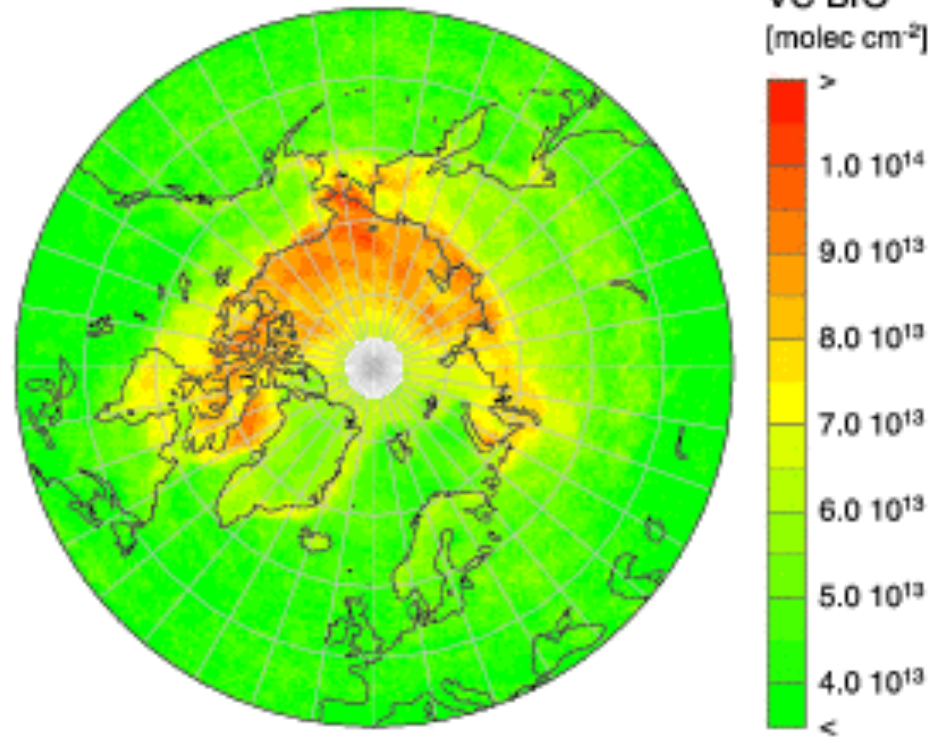


EXTRA EXTRA EXTRAS

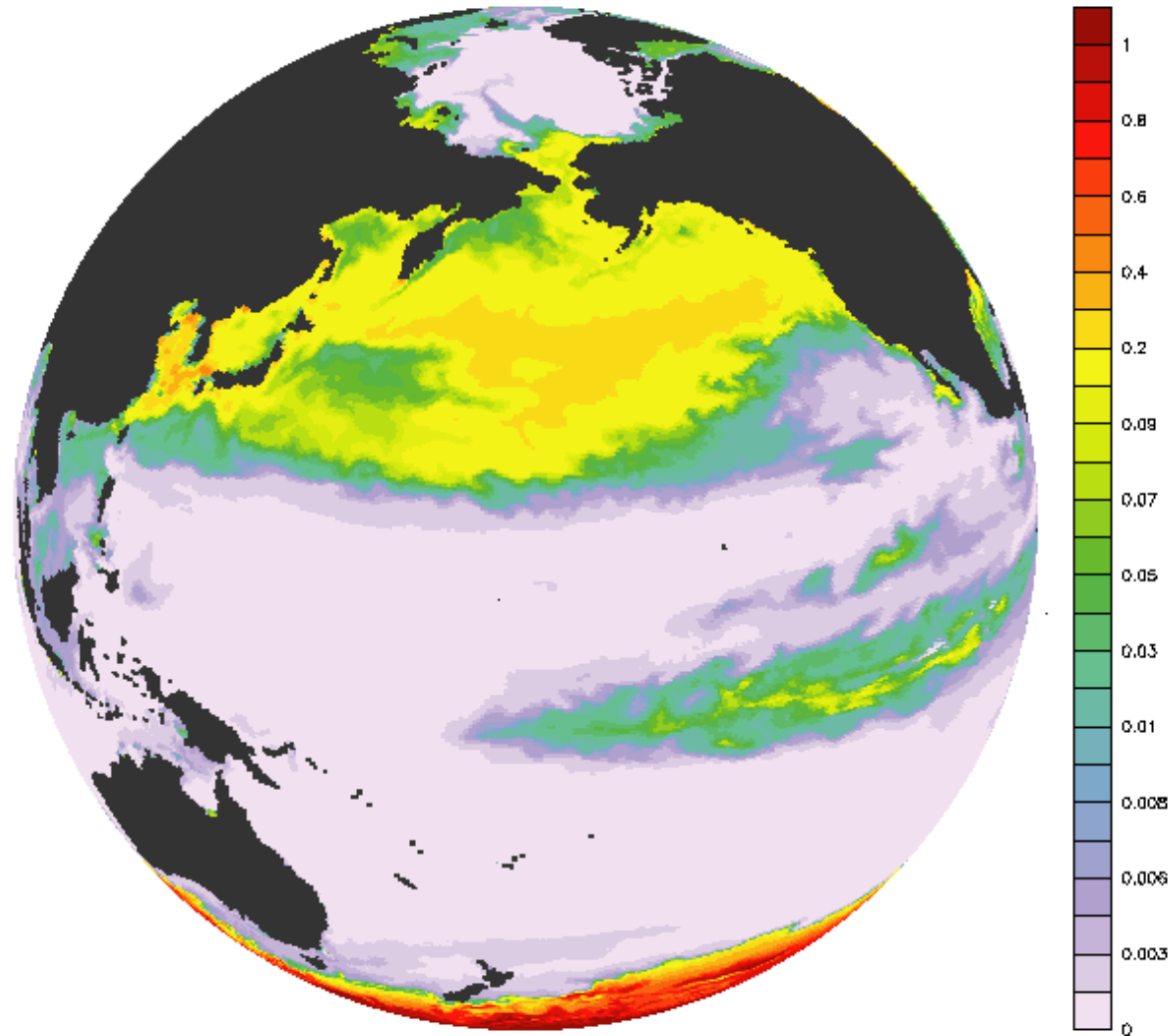
*Methane*

# ~~Bromine~~ Explosion

SCIAMACHY BrO APR 2006



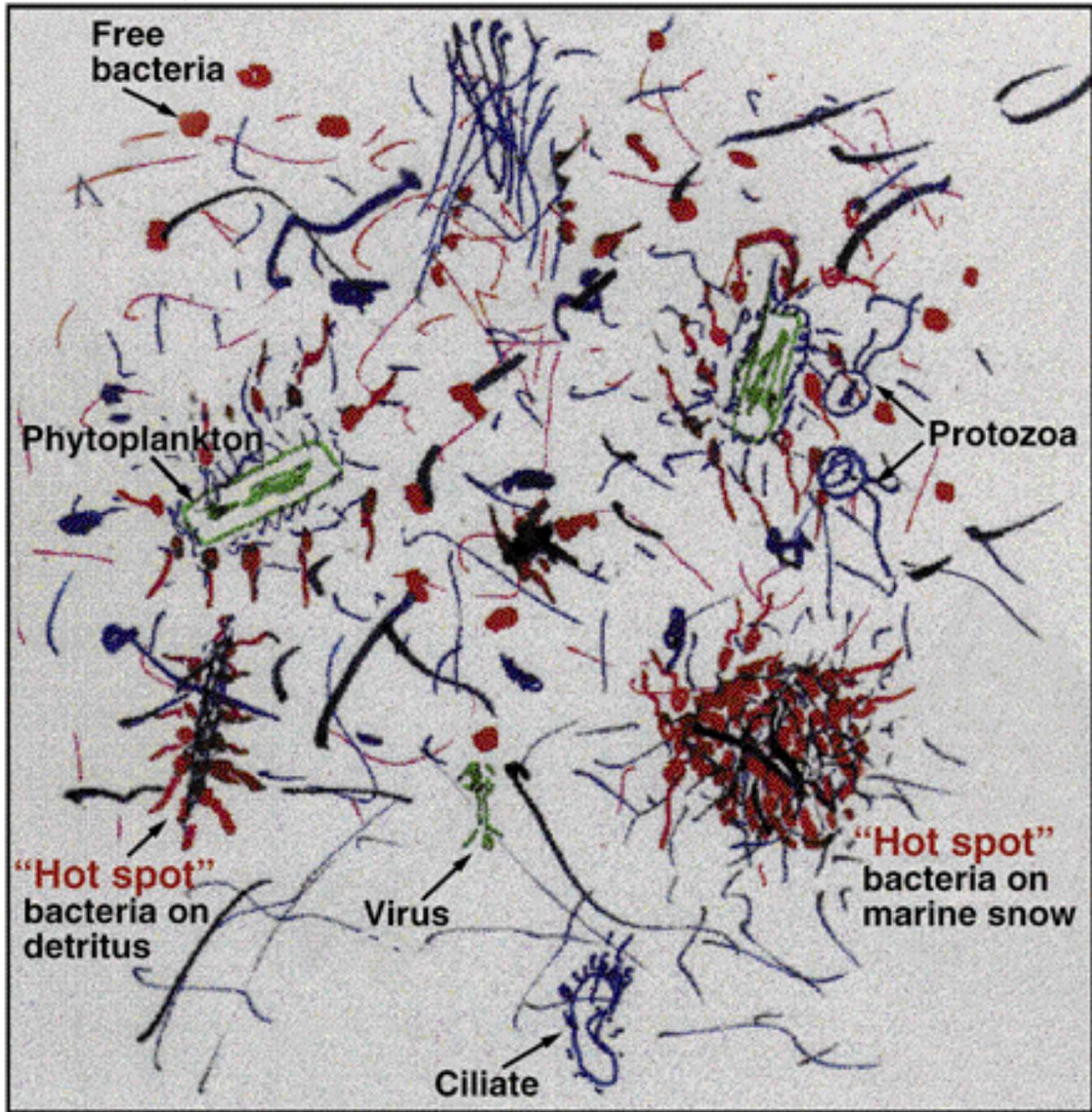
# Pacific Ammonium Distribution

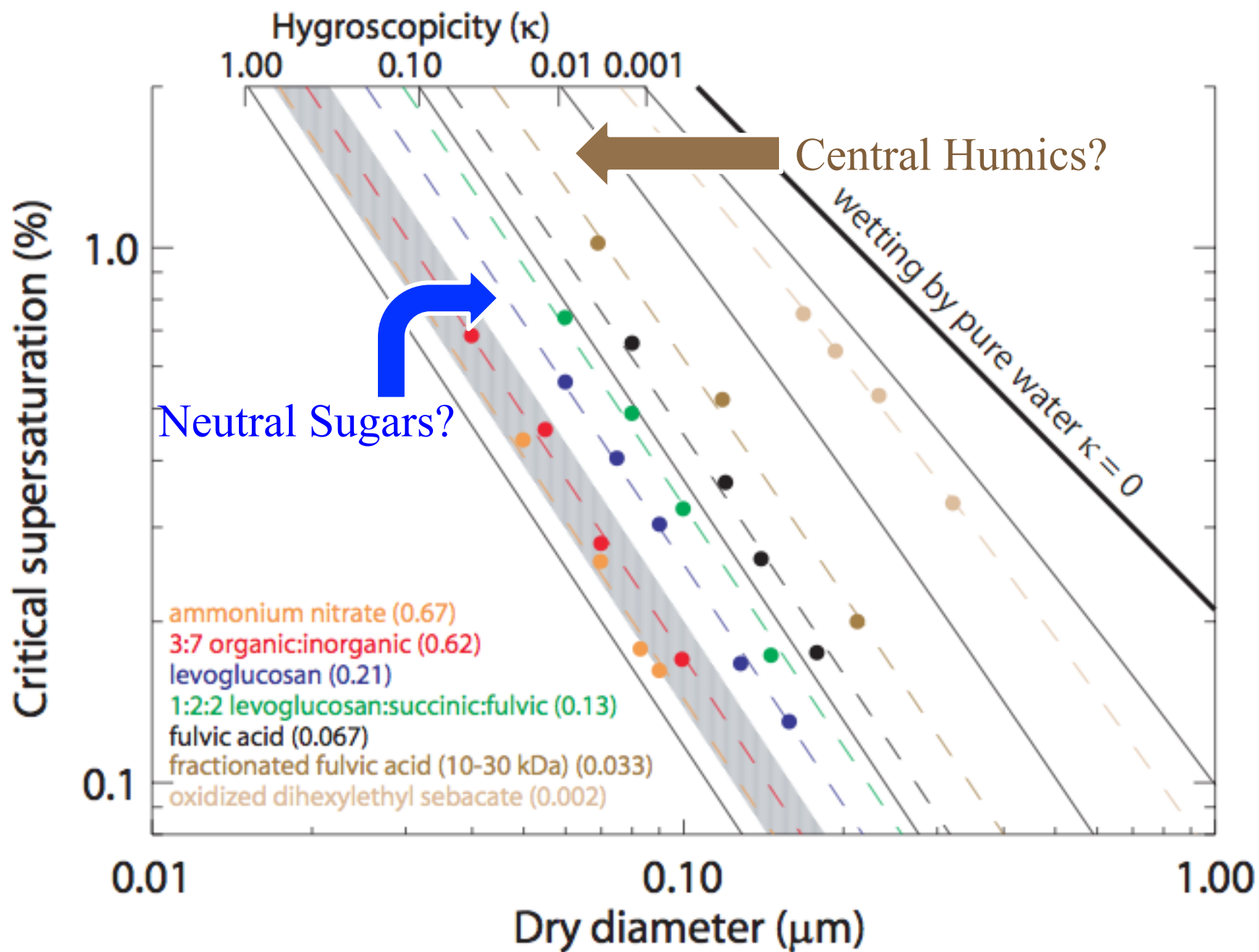


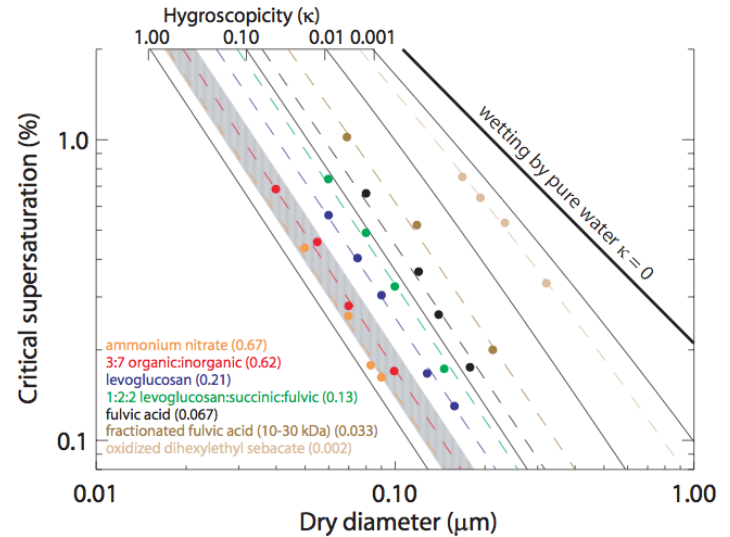
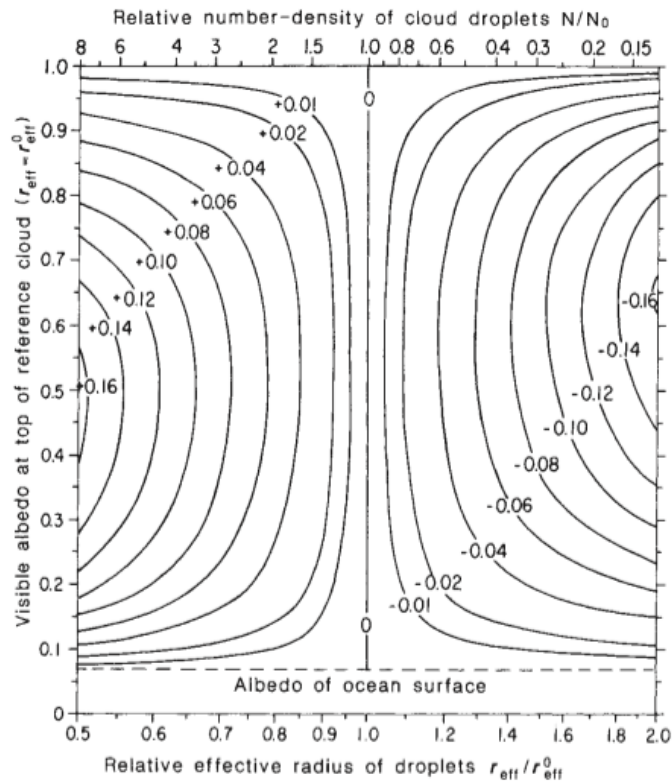
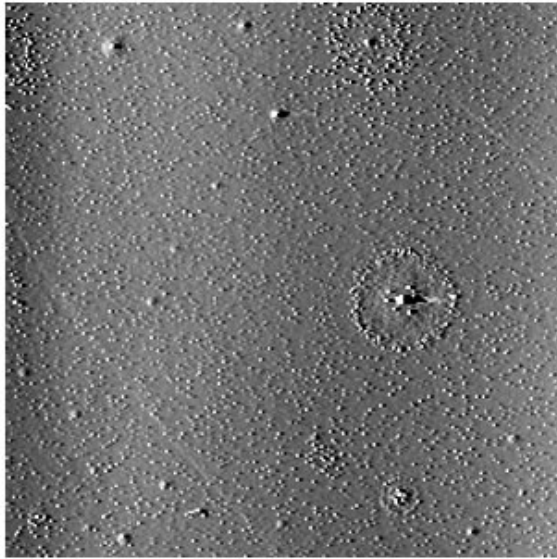
SHADE: LAND

February 1996









*Map:*  
Organic chemistry onto  
Aerosol hygroscopicity onto  
Cloud brightness onto  
Global climate

**GENERAL**

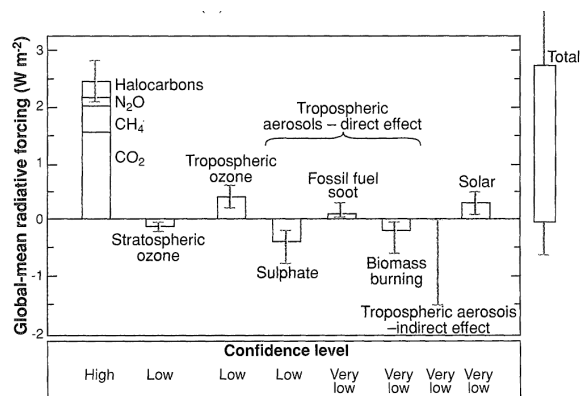
Purgatory

The High Latitude  
Biosphere Responds

(+3° C)  
CO<sub>2</sub>+H<sub>2</sub>O<sub>1,c</sub>

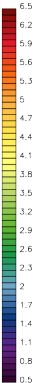
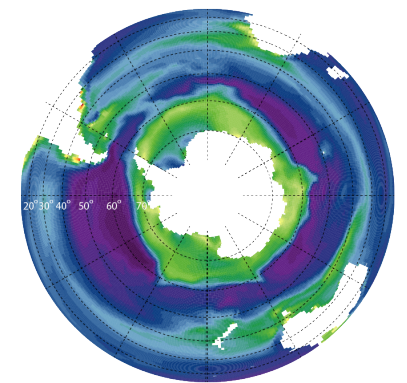
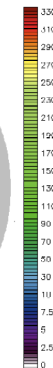
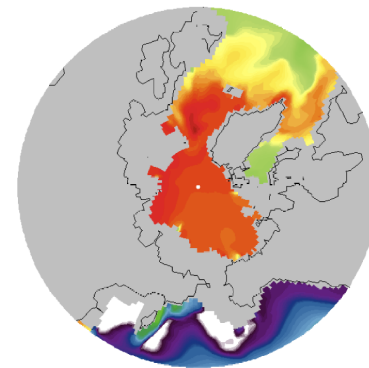
A cozy +1.7°

*So shouldn't we dig into  
these issues a bit?*



High

Abysmal



# *The envelope please...*

By these criteria, rank order for high latitude cycles:

- Ice chlorophyll (surface darkening)  $\text{CO}_2, \text{O}_2$
- DMS
- Organics tweak sea-air transfer All
- $\text{CH}_4$
- Organics tweak aerosol
- Seeding tweaks sea-air transfer
- Open, brine, skeletal C cycles  $\text{CO}_2$
- Aerosol/ice iron cycle
- Ice nitrogen ( $\text{NH}_3/4^+, \text{N}_2\text{O}$ )
- $\text{O}_2$  and radical photochemistry

Note: Order  $10^2$  characters –IPCC does same job in  $10^6$

(Follow the Methane

