Oceanic Trace Gas Measurements by Membrane Inlet Mass Spectrometry (MIMS)

A Sensitive, New Age Approach

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Outline

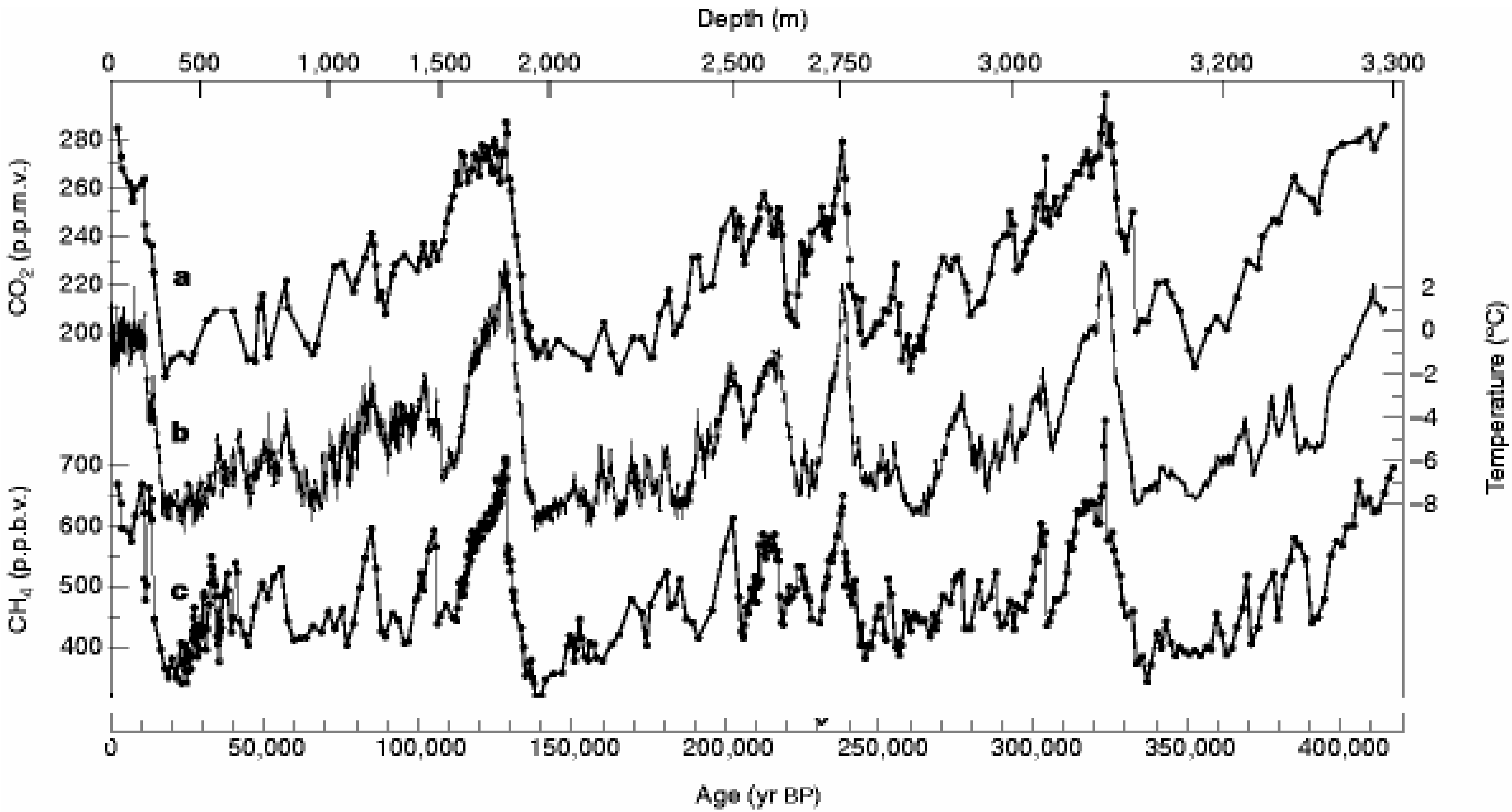
- Motivation: Why oceanic trace gases?

- Instrument development and assessment

- Field measurements in the Subarctic Pacific Ocean / Bering Sea: Spatial distribution of CO_2, O_2, DMS, and N_2.

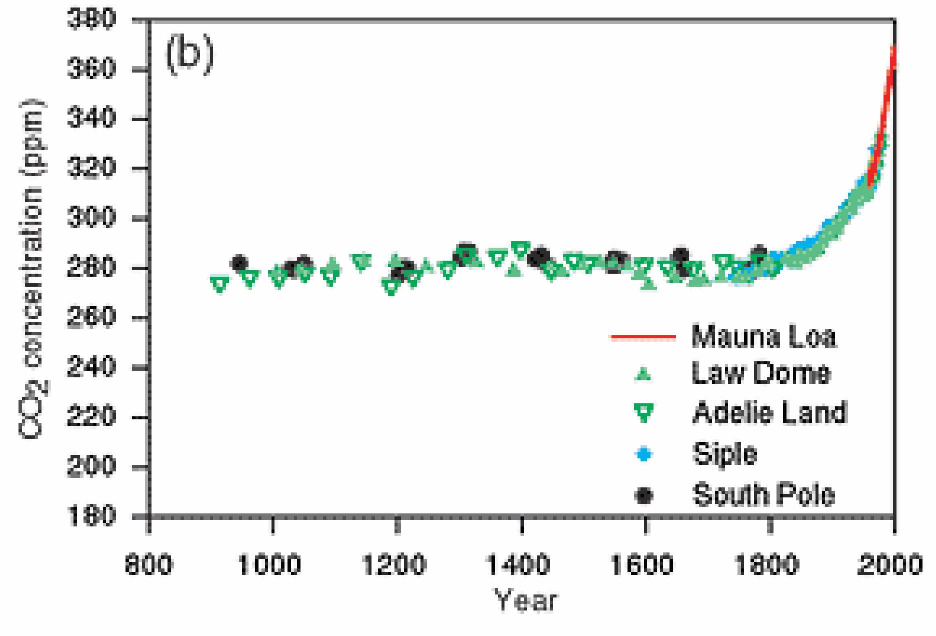
- Future directions

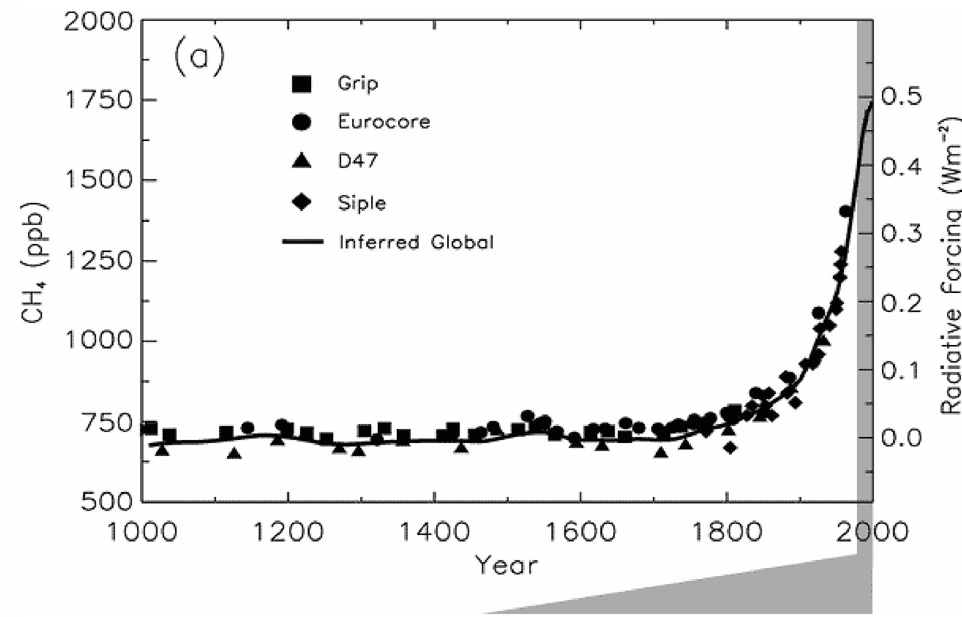
Greenhouse gases co-vary with temperature over glacial cycles



Petit et al. (1997) Nature

Anthropogenic Perturbations of Greenhouse Gases

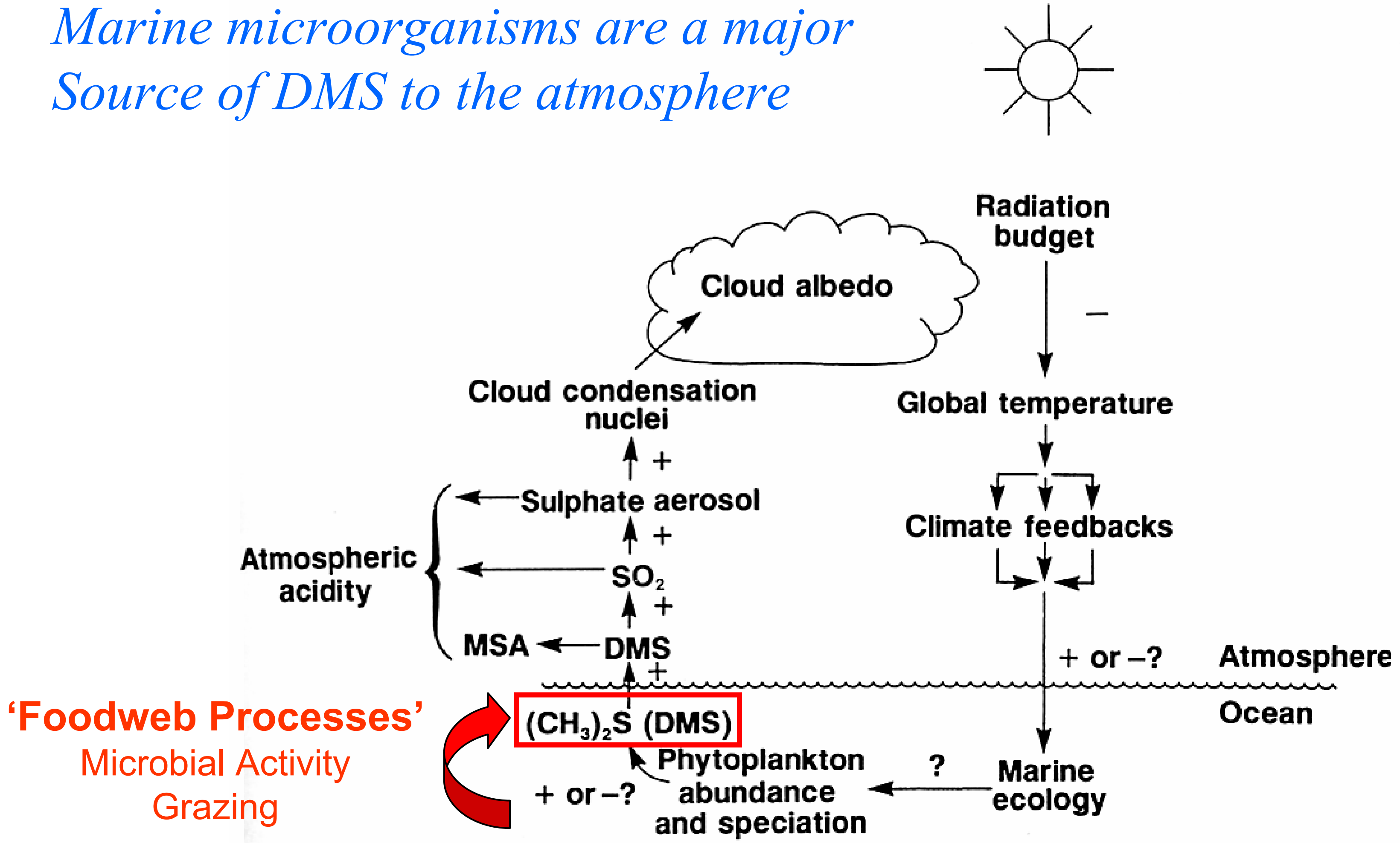




IPCC 2001

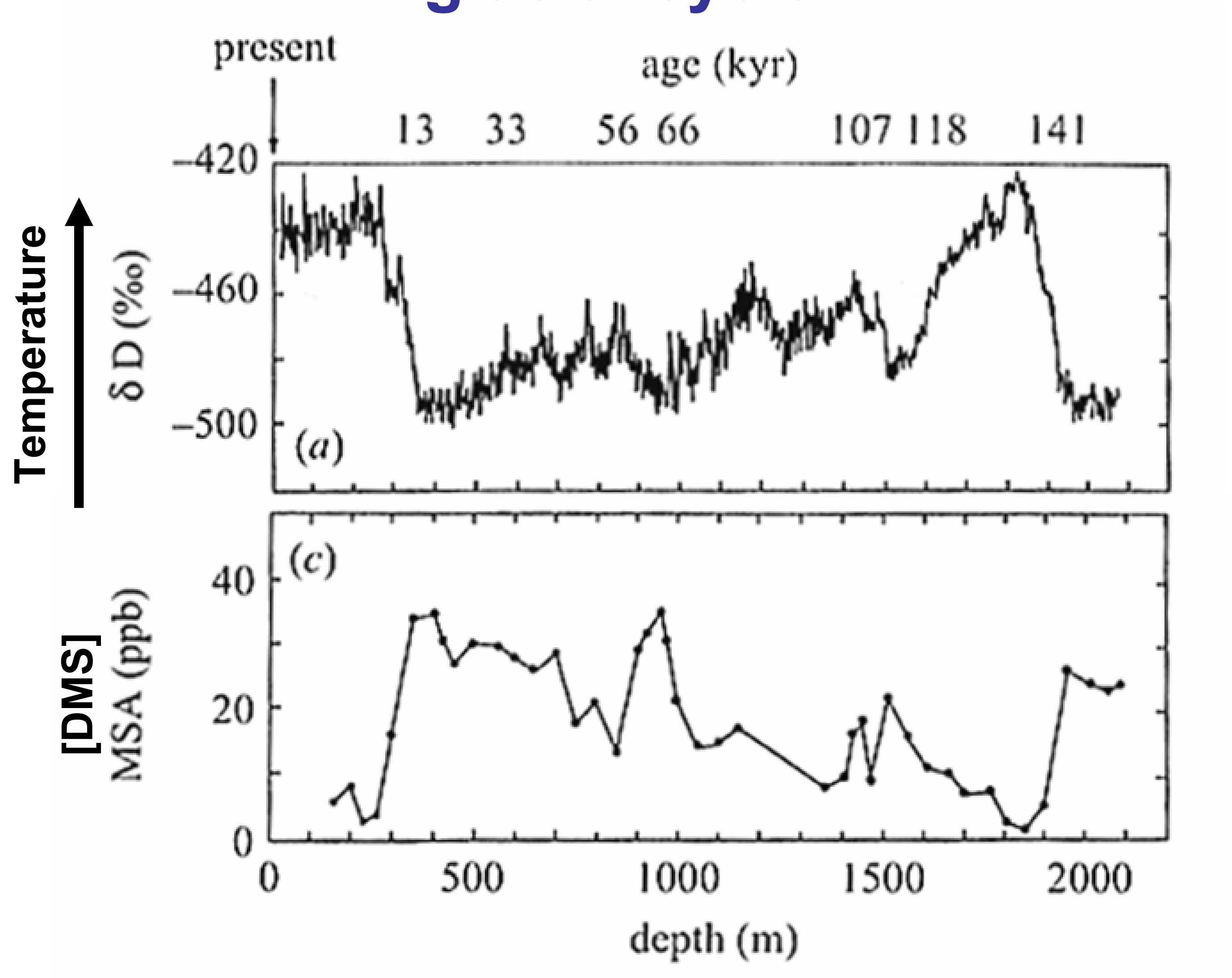
Dimethylsulfide (DMS) Increases Energy Reflectance in the Atmosphere

Marine microorganisms are a major Source of DMS to the atmosphere



Watson and Liss (1998) Trans. Roy Soc. London

Dimethylsulfide fluctuations over the last glacial cycle



Lerand et al. (1991) Nature 350: 144-146

Oceanic processes are critically important in the cycling of ‘climatologically active’ trace gases

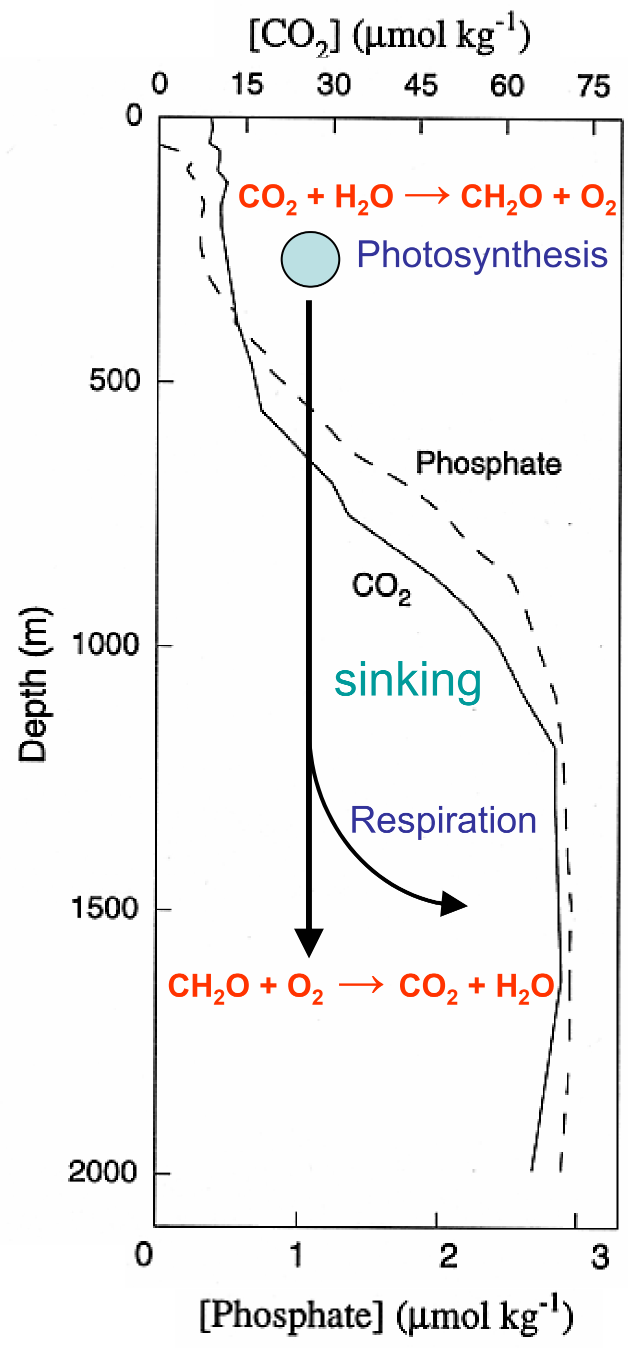
Additionally, gas measurements reveal a wealth of information about how the oceans function

Gases as Biogeochemical Tracers

CO_2 / O_2: Photosynthesis / Respiration
N_2: Denitrification
N_2O: Denitrification, Nitrification
H_2S: SO_4^{2-} oxidation
CH_4: Methanogenesis, Methane oxidation

Gases as Physical Tracers

CFC's, / He: Ocean circulation
N_2 / Ar / O_2: Bubble injection



Gas Measurement in seawater

- Many highly sensitive, accurate, and precise techniques exist:
  Gas Chromatography (N_2, Ar, CH_4, N_2O, DMS etc.)
  Infrared Absorbance (IR) / coulometry (CO_2), polarography (O_2)
  Isotope Ratio Mass Spectrometry (N_2, O_2, Ar, CO_2, N_2O etc.)

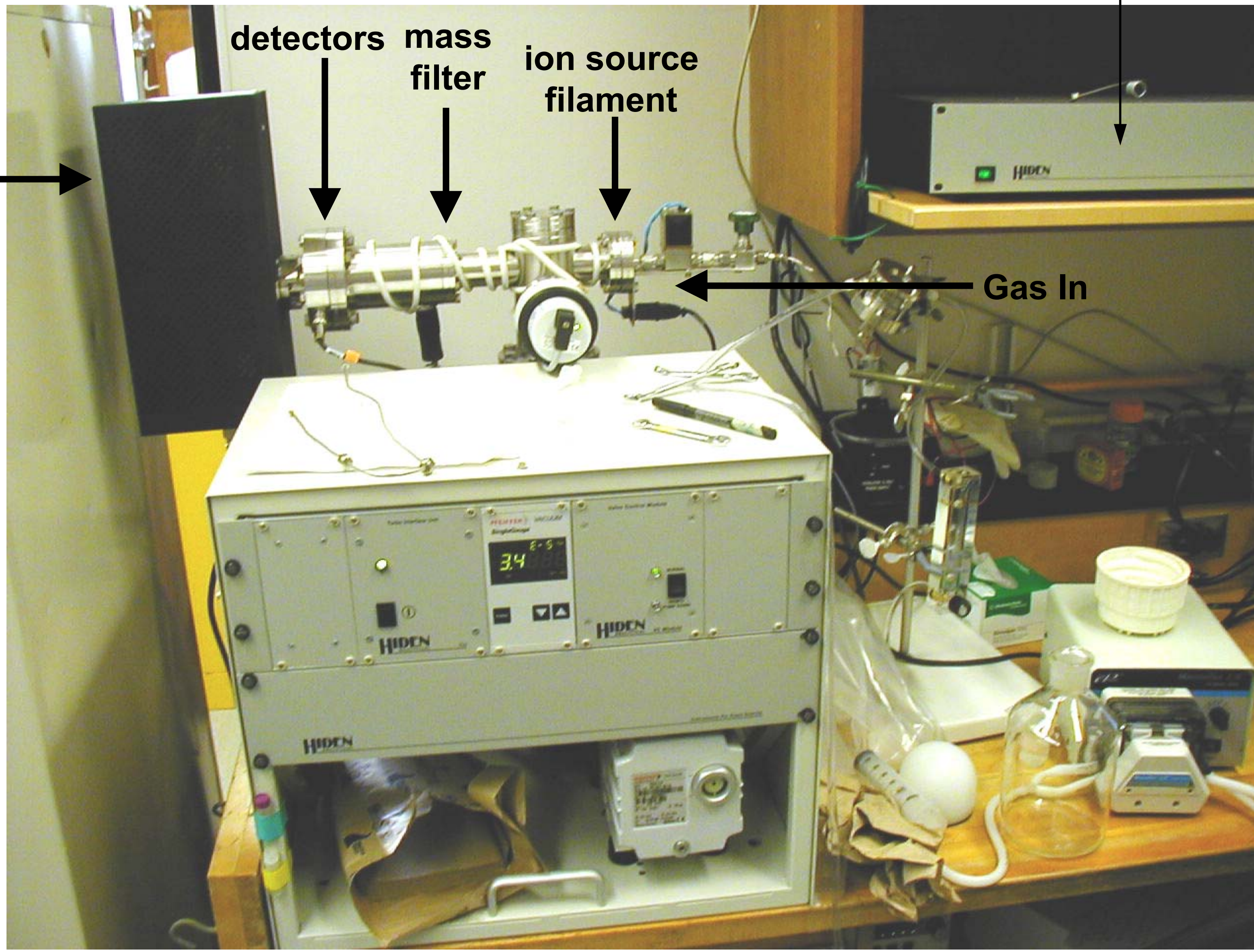
- Some of these methods are specific for single gases, while others are costly, laborious, and not well suited to in-situ measurements at sea.

- **Looking for a single method to easily/rapidly measure many gases simultaneously in real-time.**

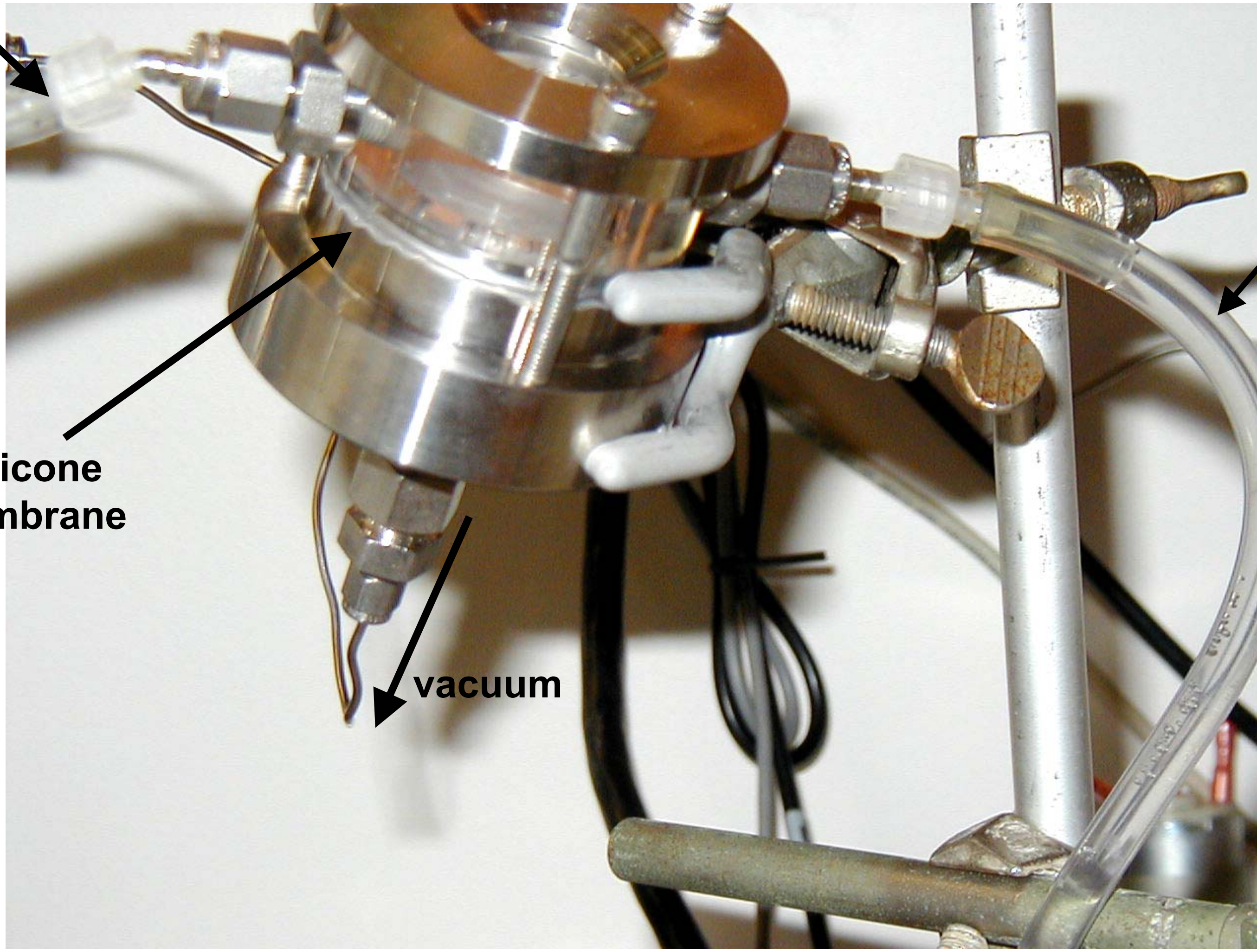
- **Membrane Inlet Mass Spectrometry**
  - Developed in the late 60's, subsequently applied to a variety of environmental problems: (volatile organics, soil /sediment gas fluxes).
    Oceanographic work has been largely restricted to laboratory analysis of major gases (N_2, O_2, CO_2, Ar) in coastal waters.

Application to ship-board open ocean studies

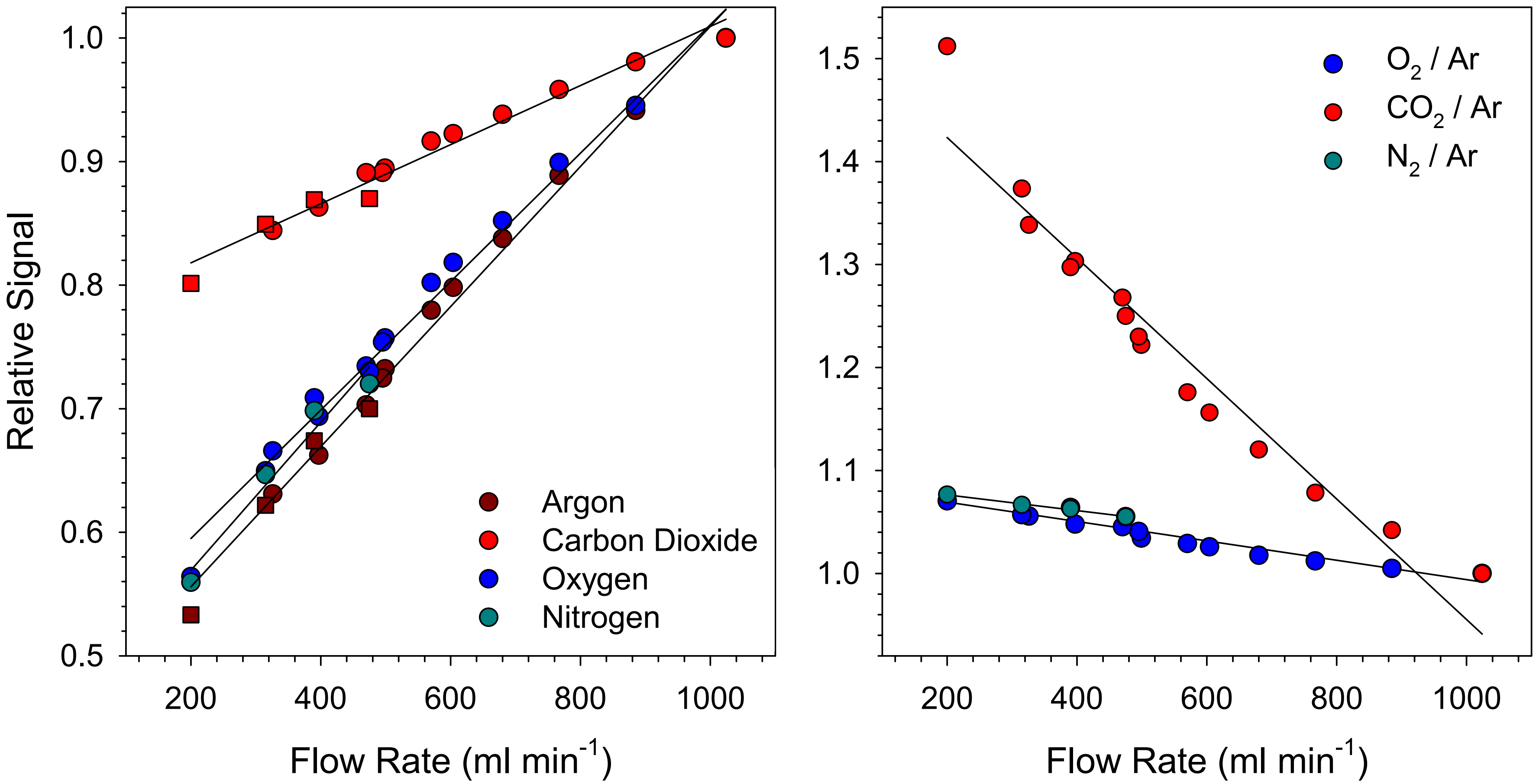
Instrumentation I: Hiden Analytical
Triple filter quadropole mass spectrometer



Instrumentation II:
Large Area Membrane Inlet System



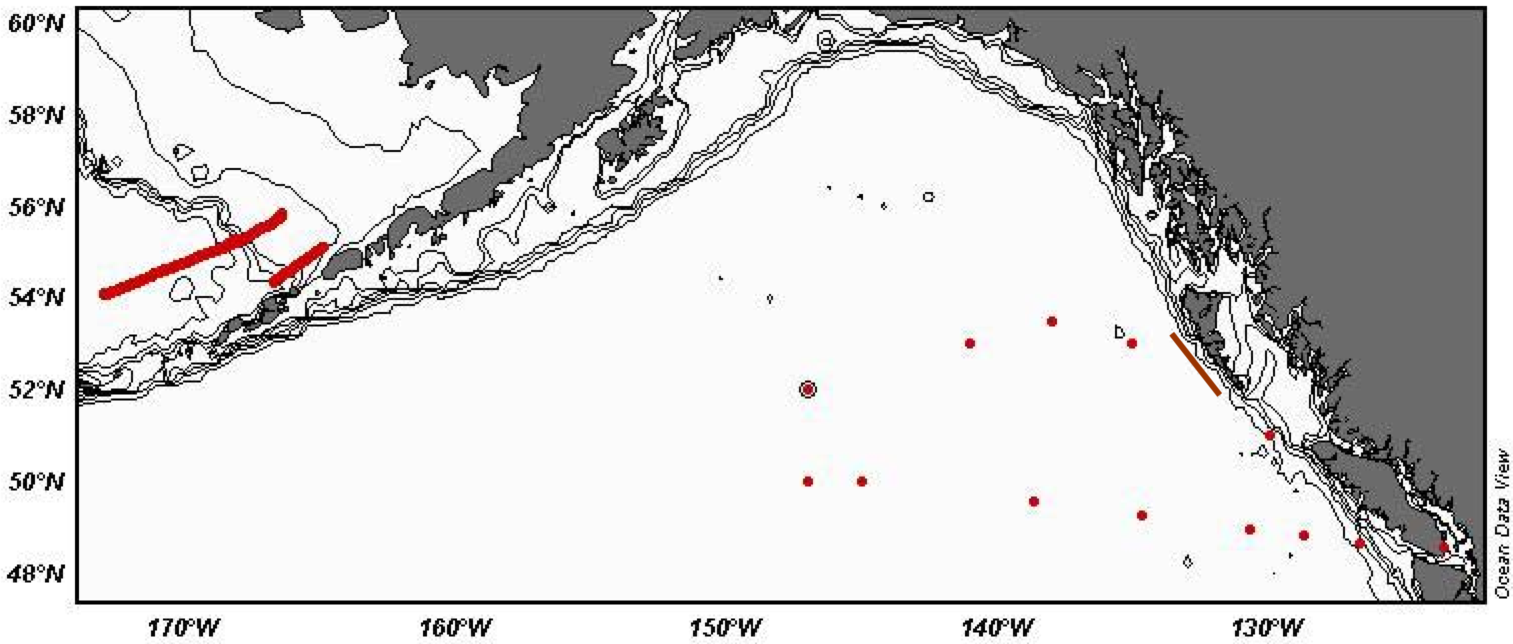
Flow Rate Effects



Temperature effects…..

Field Trials: Summer 2003

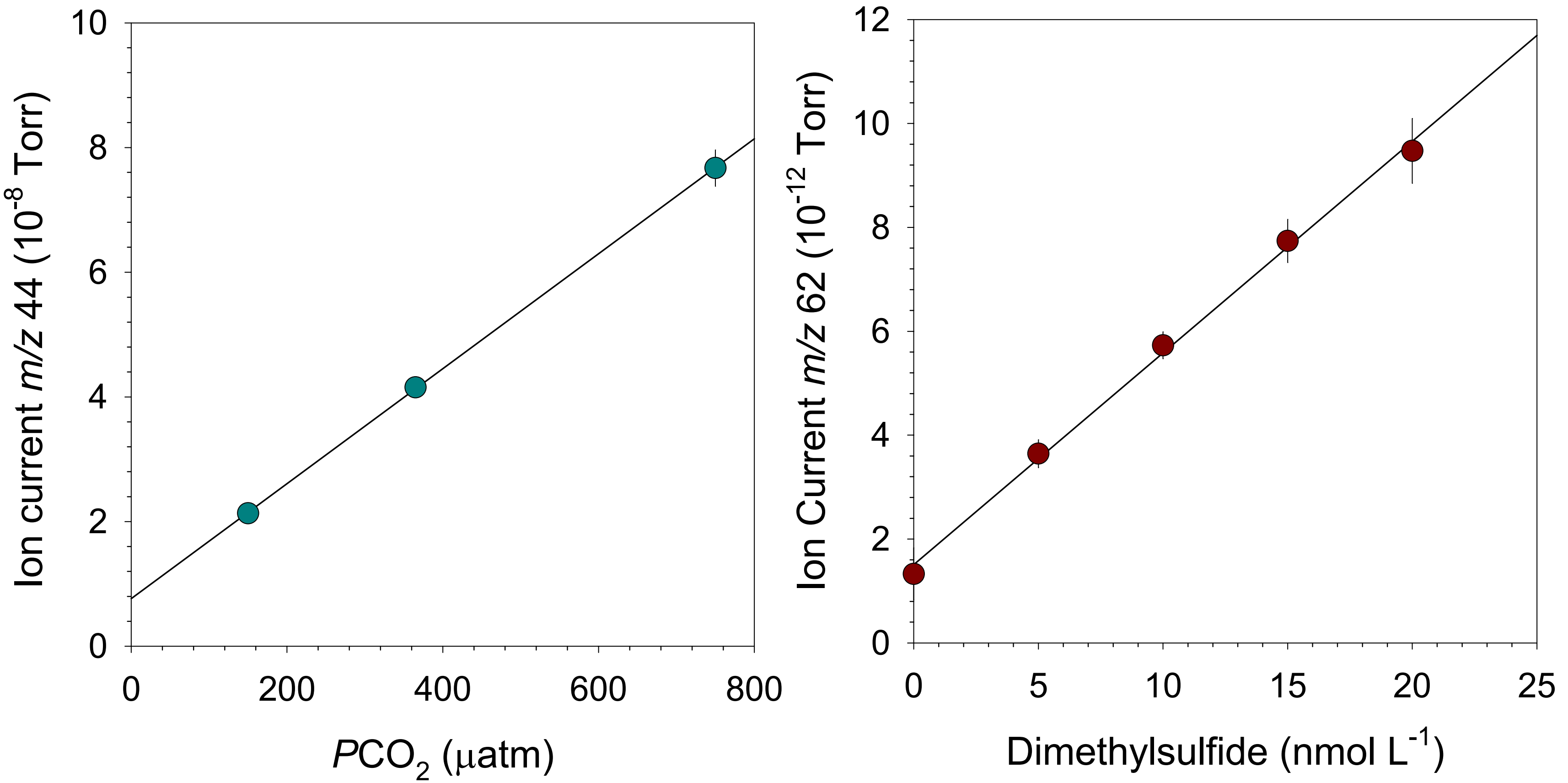
- Trial 1: Subarctic Pacific Ocean (May / June 2003): Coastal – Oceanic transect (Line P + ARGO Stations). Initial field testing
- Trial 2: Bering Sea (Aug. / Sept. 2003): Cross-shelf transects. Underway measurement of O_2 / CO_2 / DMS concentrations across a strong productivity gradient



CCGS John P. Tully

Instrument Calibration

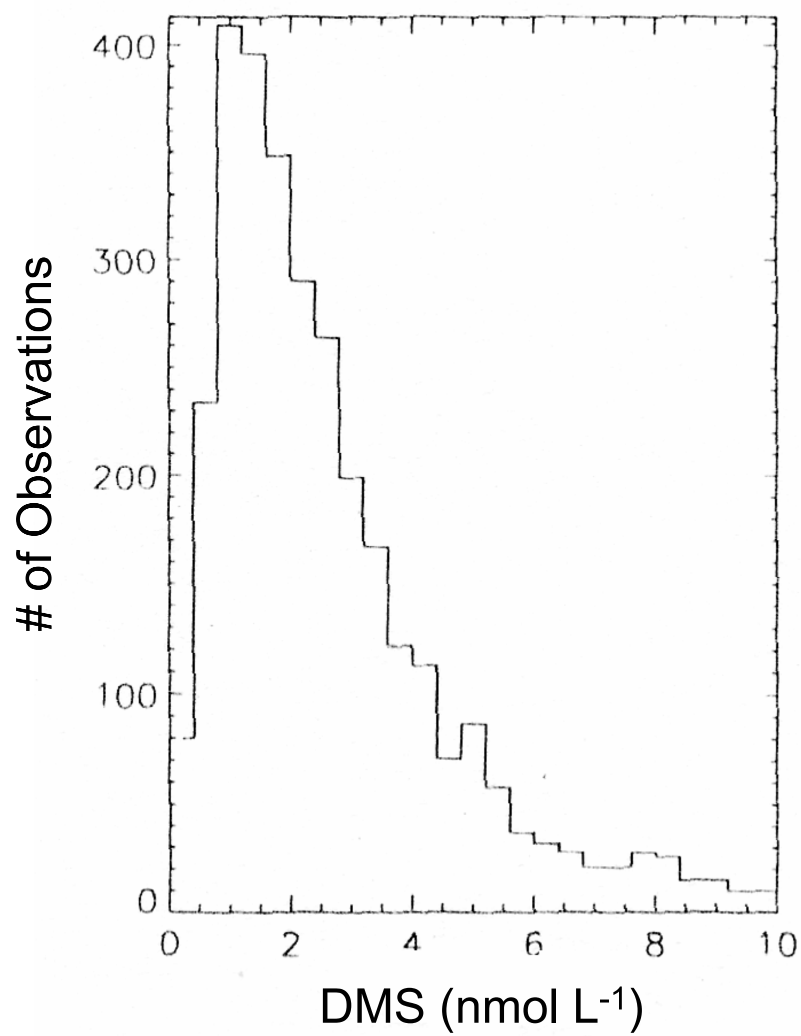
Repeat Calibrations over ~ 3 week period at sea



Current atmospheric CO_2 ~ 375 μatm

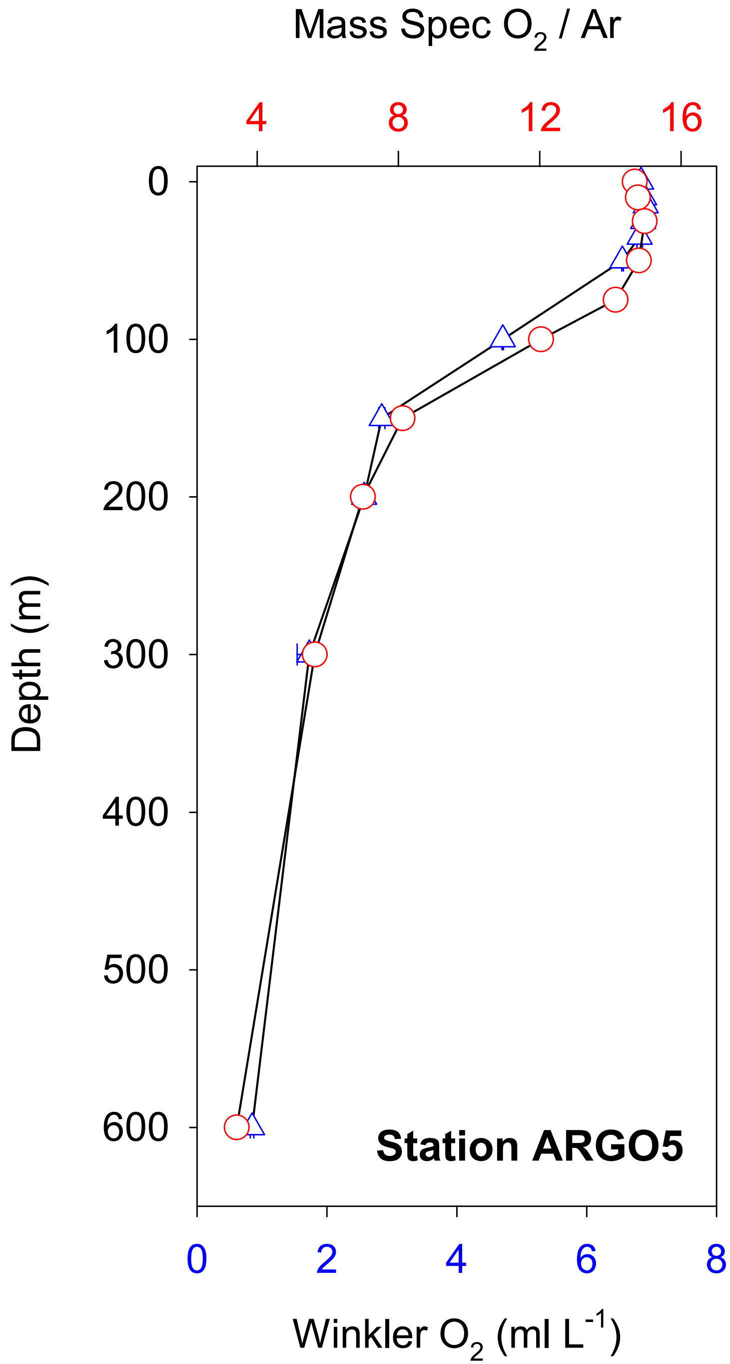
Oceanic DMS Concentrations

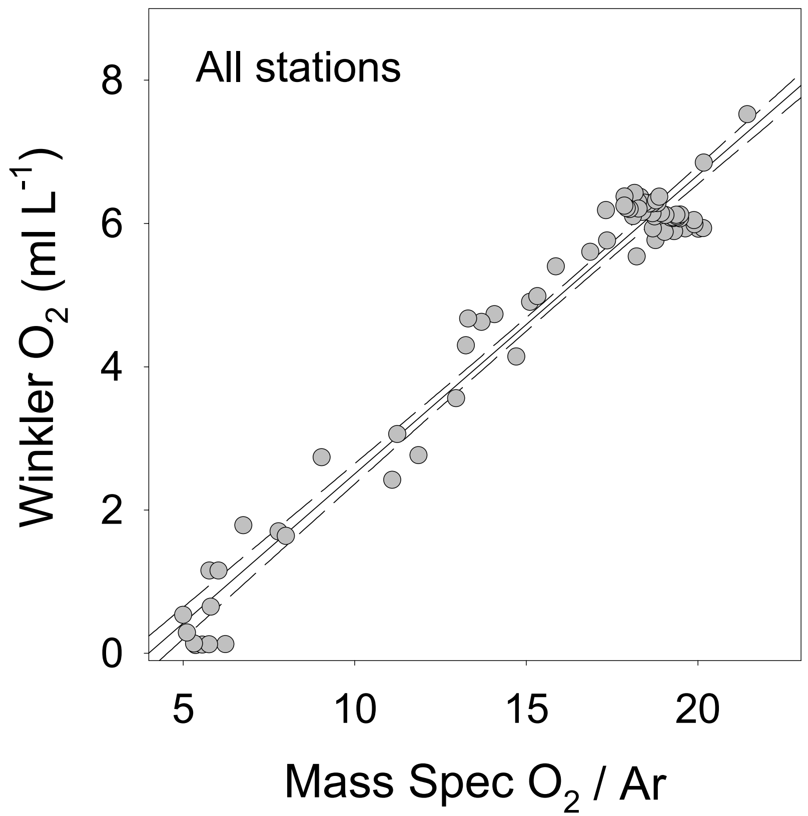
Kettle et al. 1999 GBC



Method Validation I

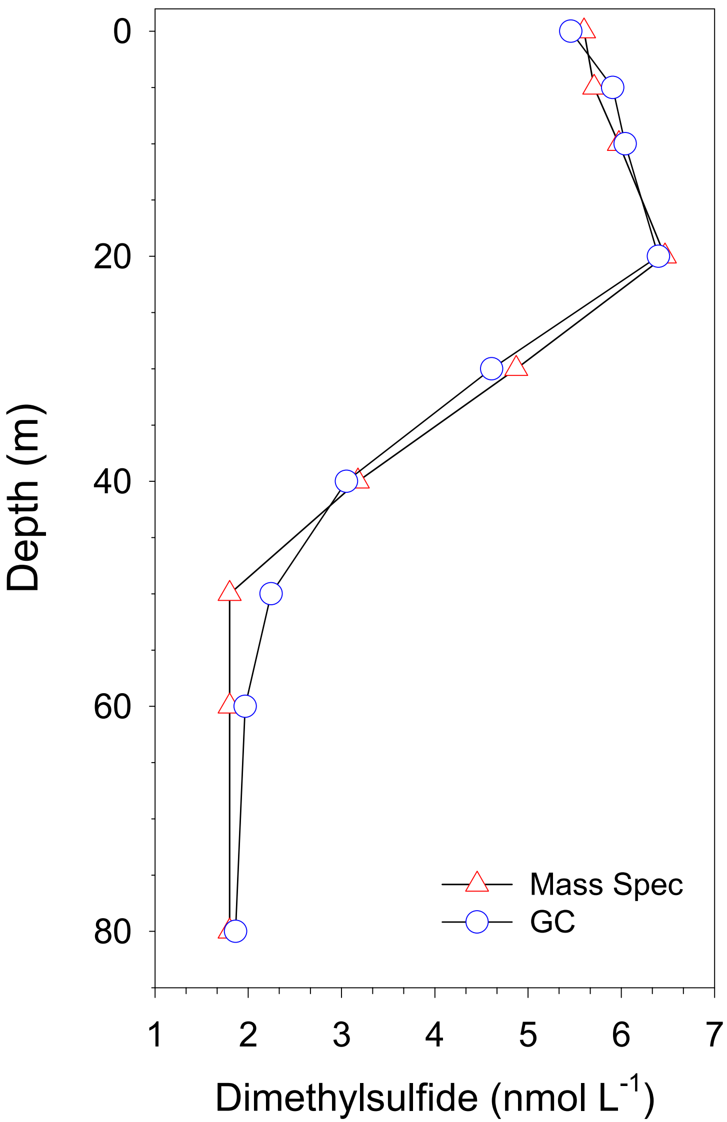
Oxygen Depth Profiles:
Subarctic Pacific: June 2003





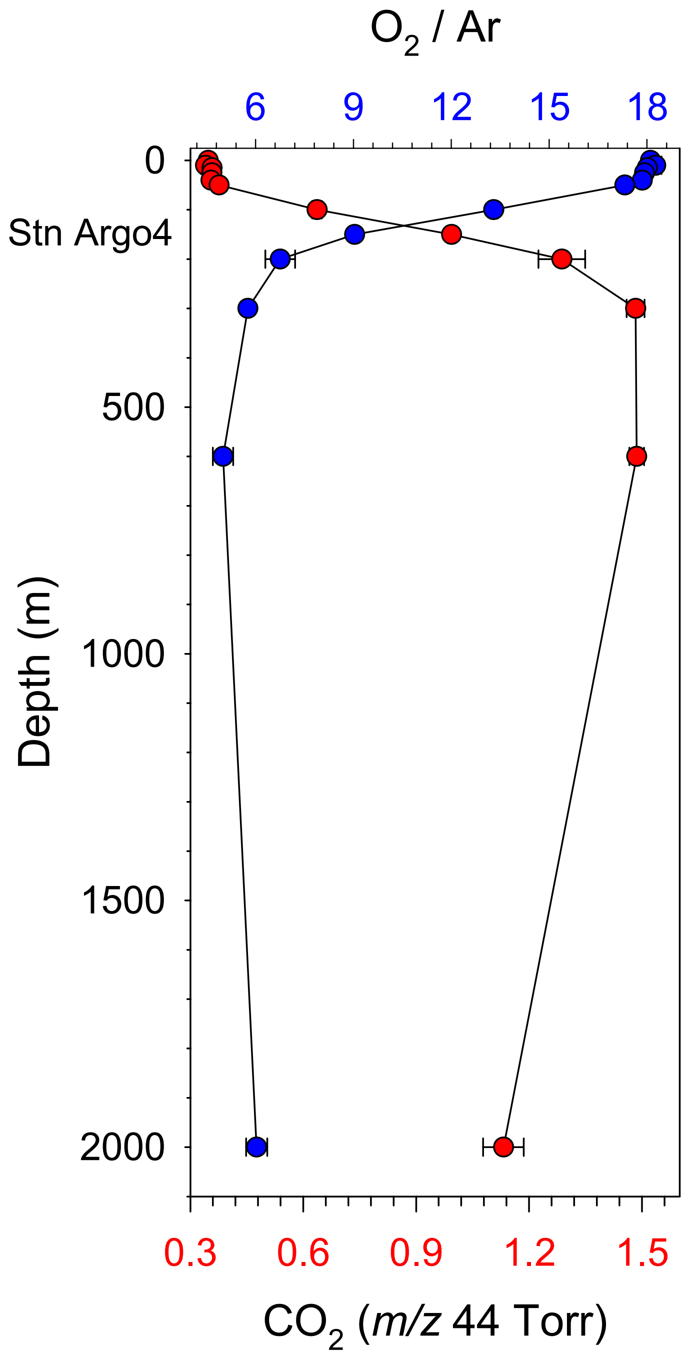
Method Validation II

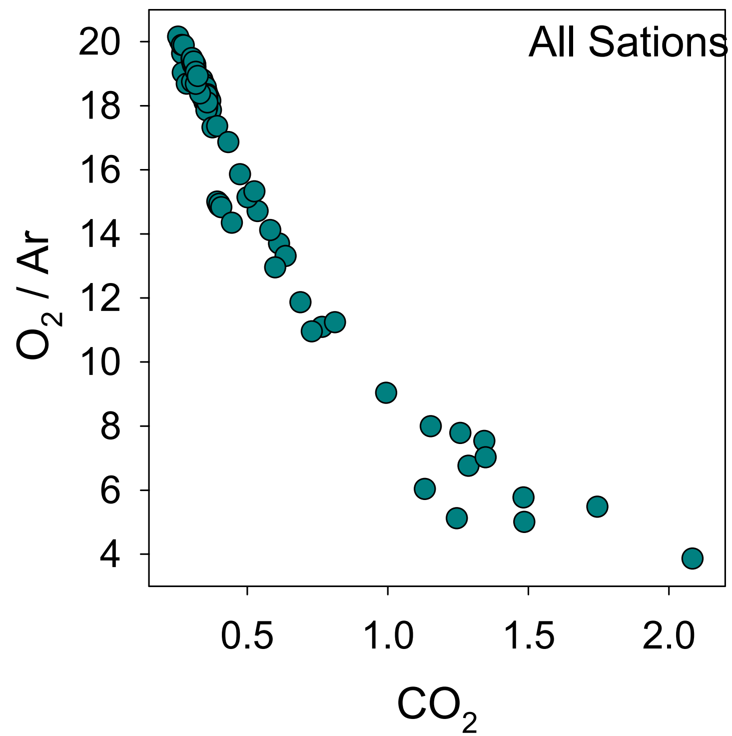
DMS Depth Profile; Bering Sea Aug. 2003



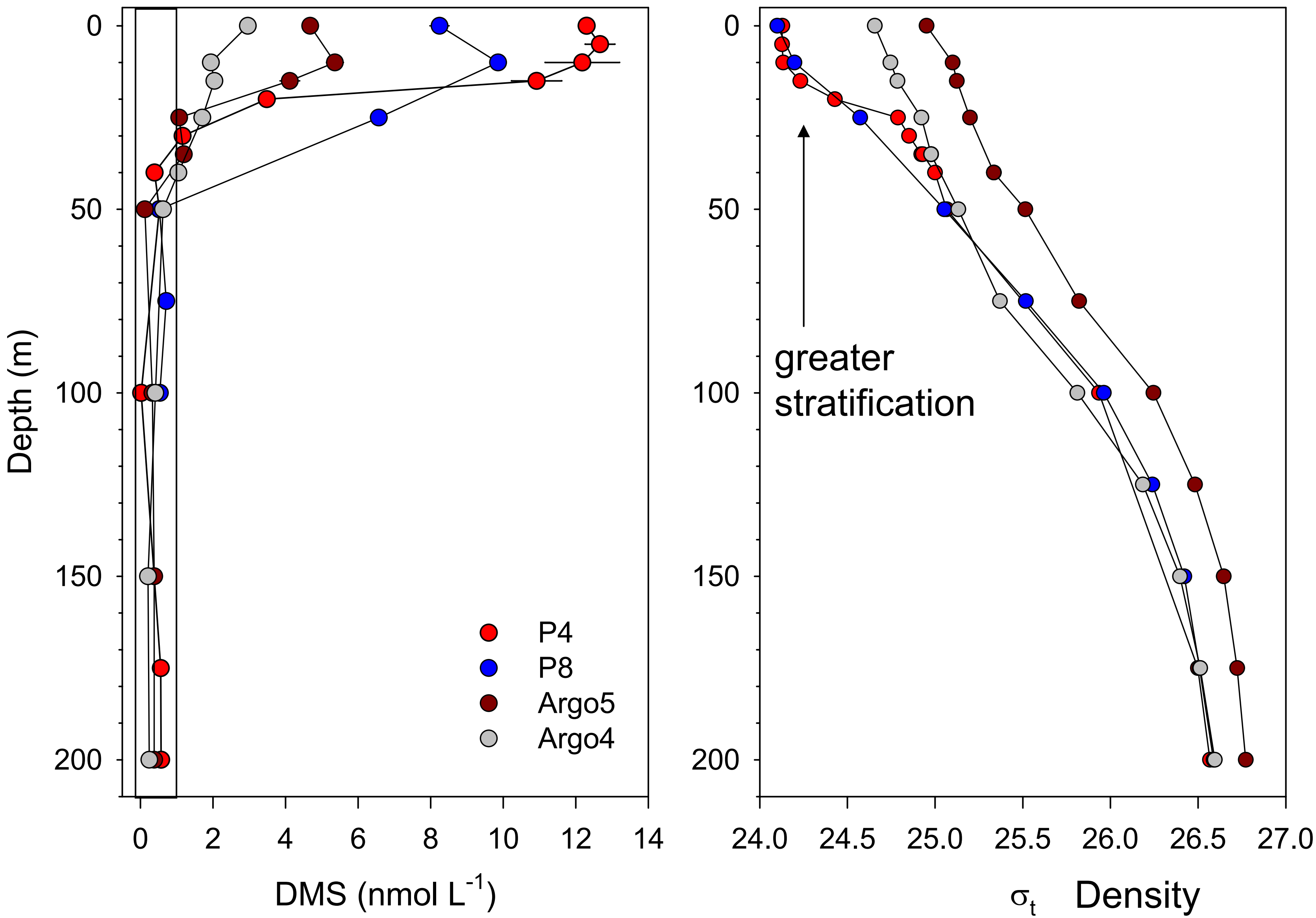
GC Data from Peter Lee
Univ. of Charleston

Typical Depth Profiles Subarctic Pacific





DMS Profiles



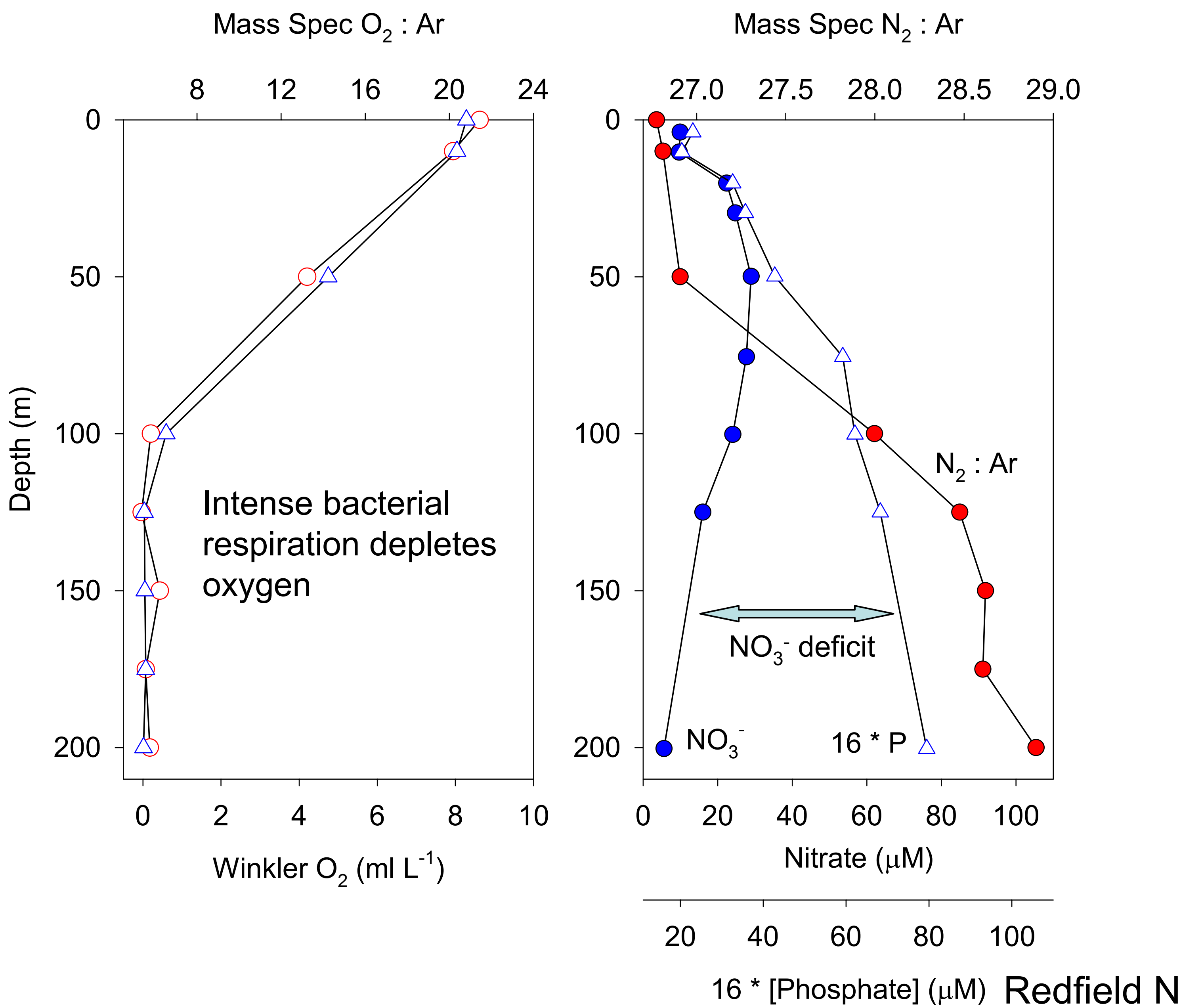
Application of MIMS in denitrification studies

- Denitrification: The use of NO_3^- as an alternative electron acceptor in respiration by heterotrophic bacteria.

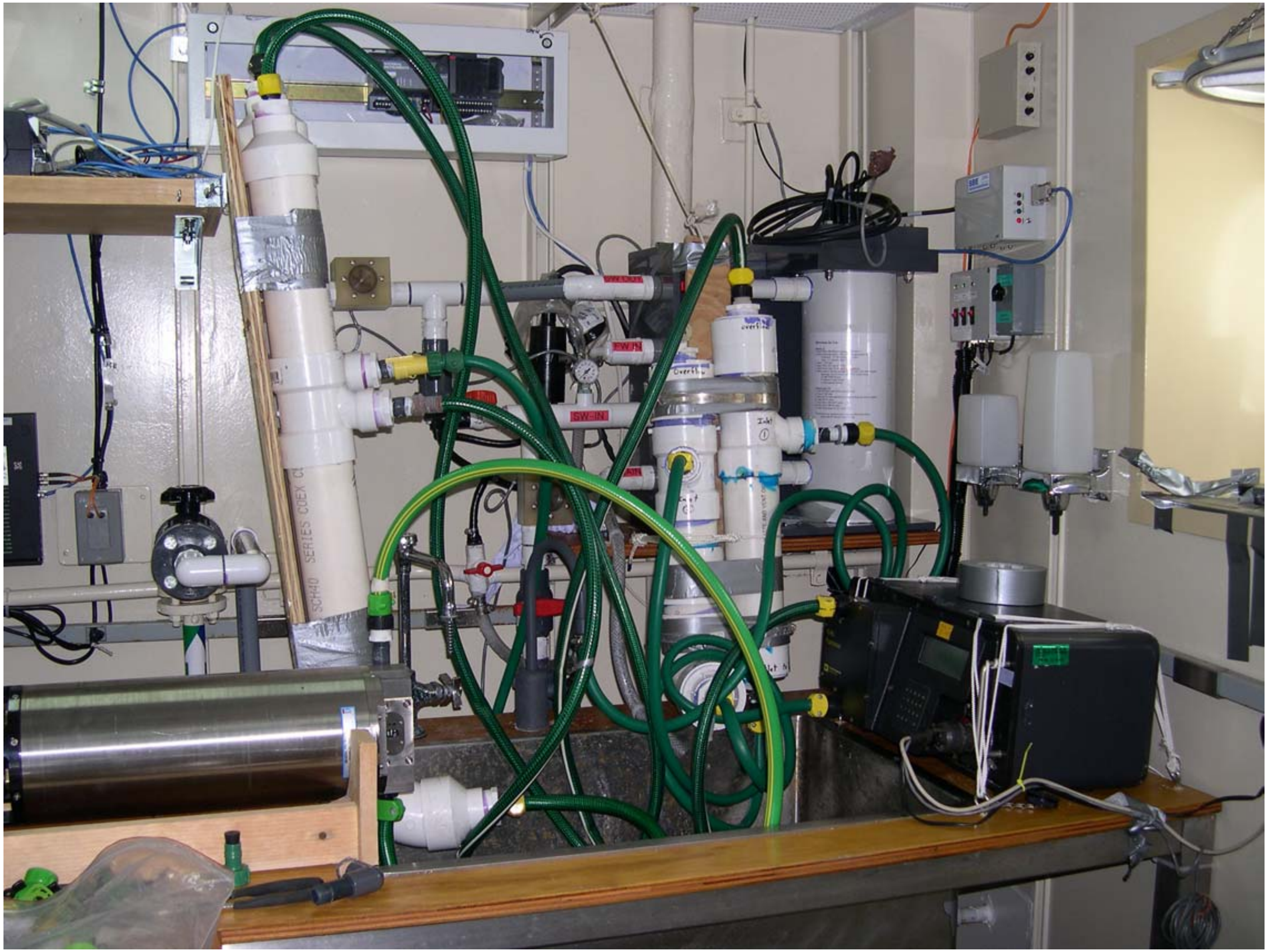
- $NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$

- Major loss term for fixed N_2 in the biosphere (only occurs under low O_2)

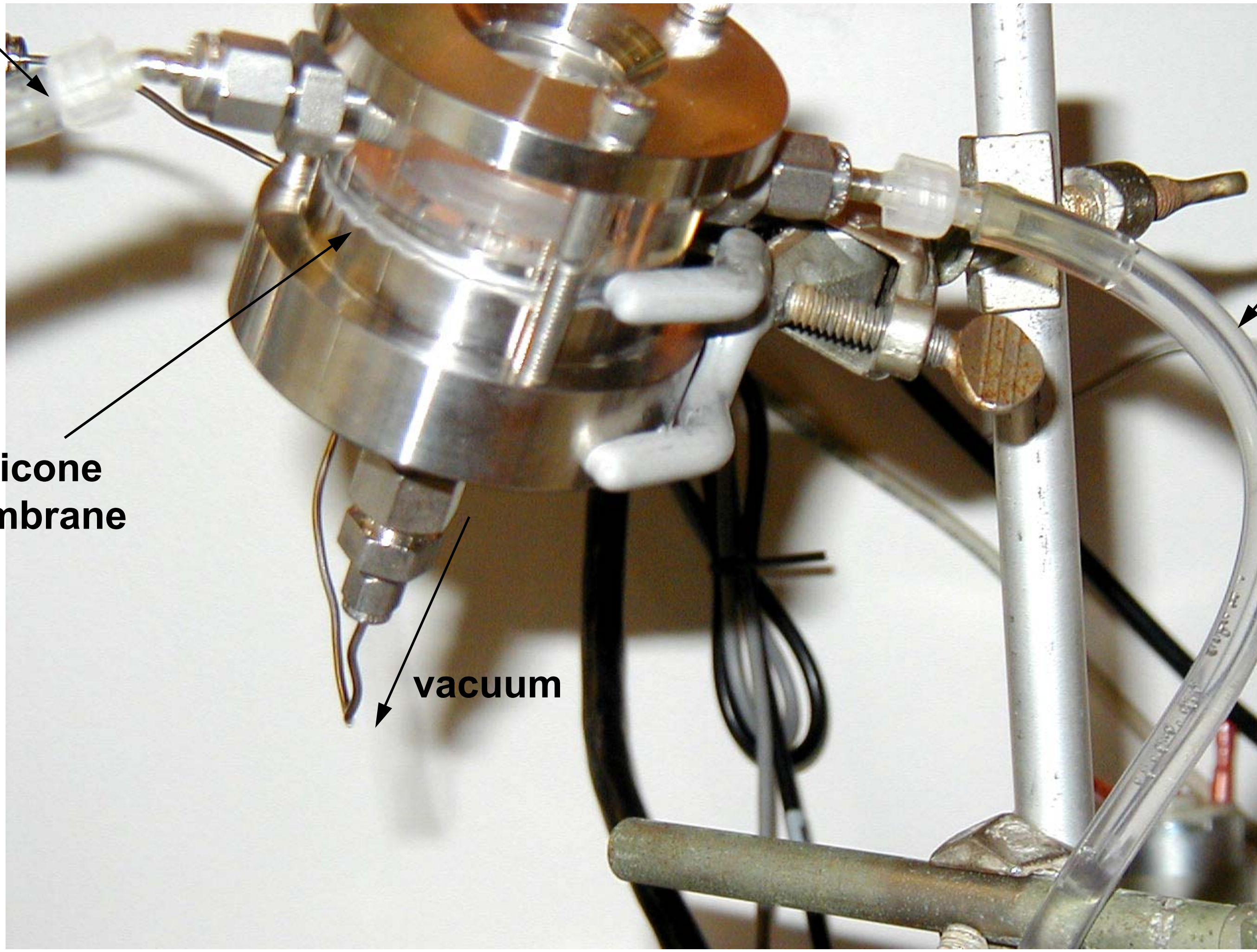
Denitrification in Saanich Inlet



Underway Data Collection

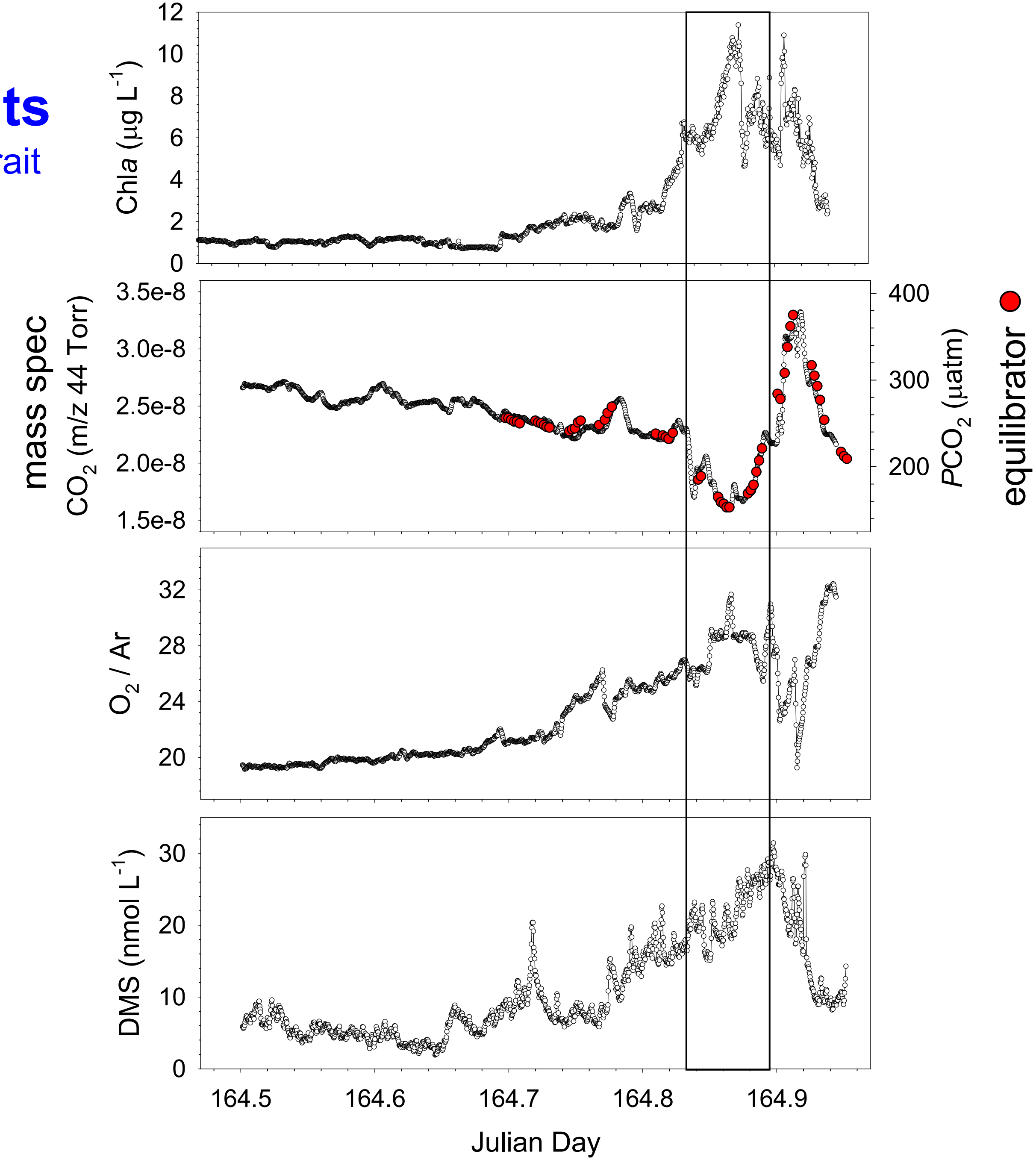


Continuous Flow-Through Operation



Underway Measurements

Queen Charlotte Strait
June 2003

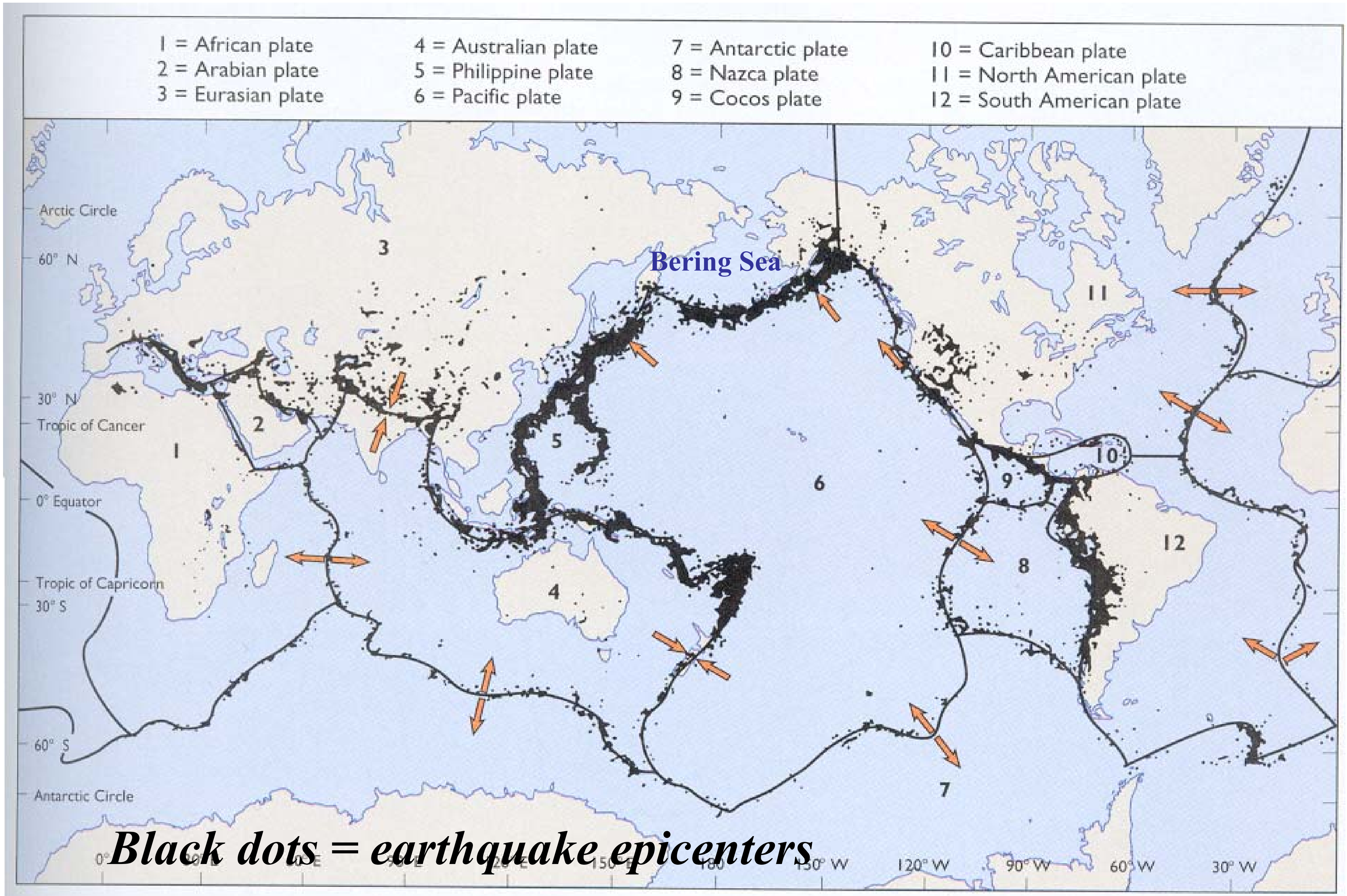


Field Trial #2 Bering Sea

Aug. – Sept. 2003

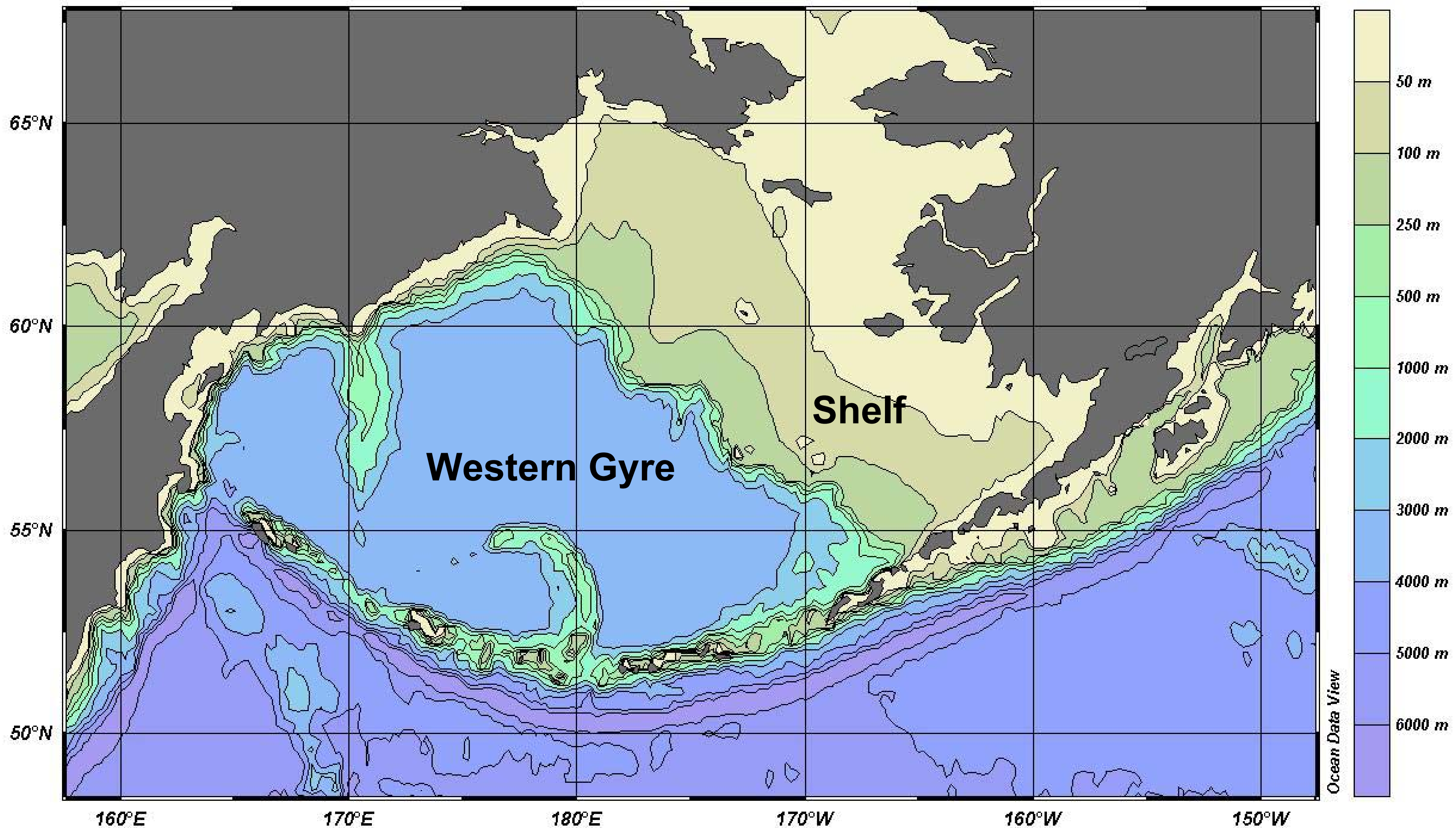
R/V Kilo Moana – University of Hawaii

The Bering Sea is separated from the N. Pacific by the Aleutian Island arc

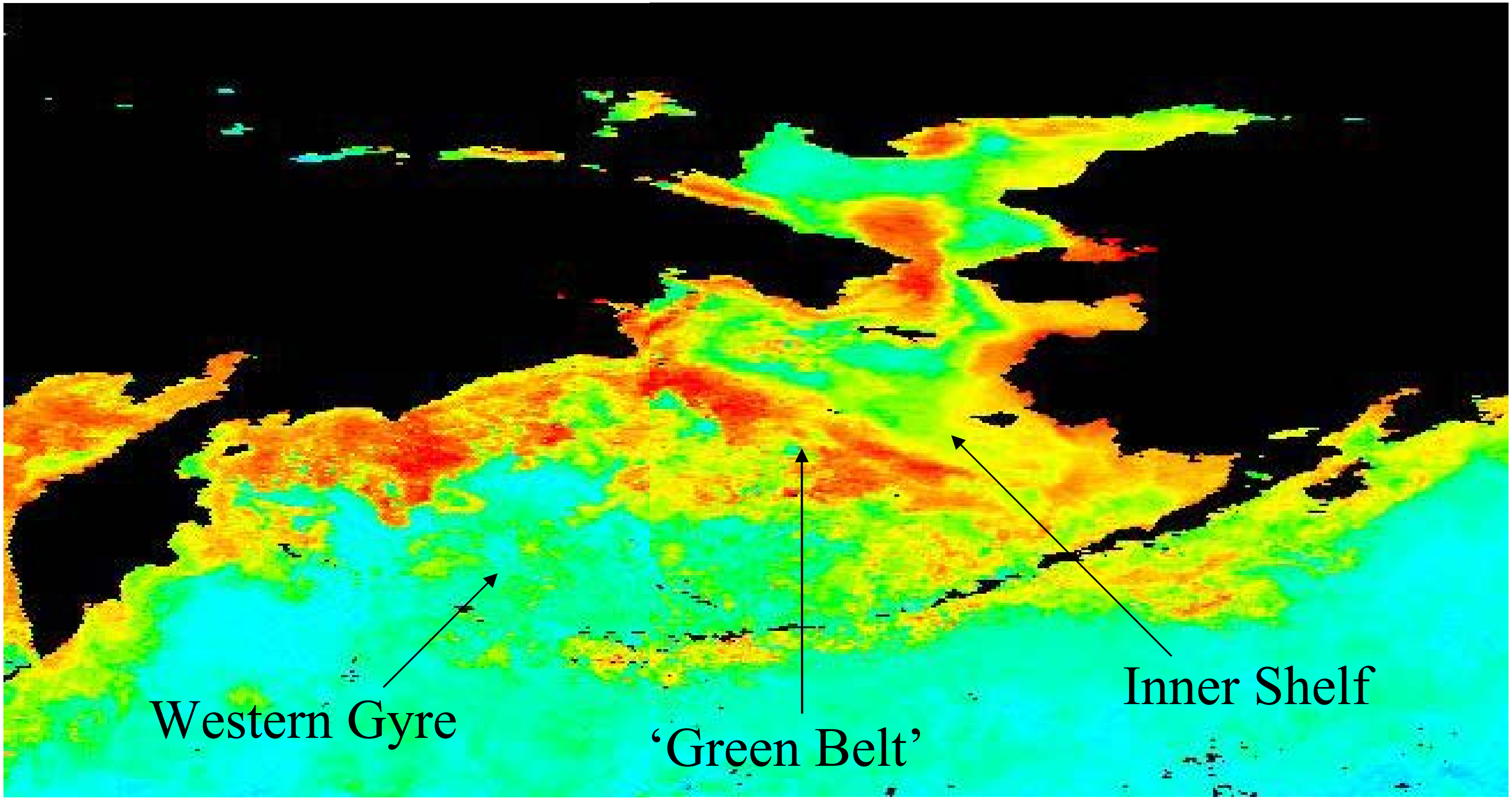


Black dots = earthquake epicenters

Bering Sea Bathymetry

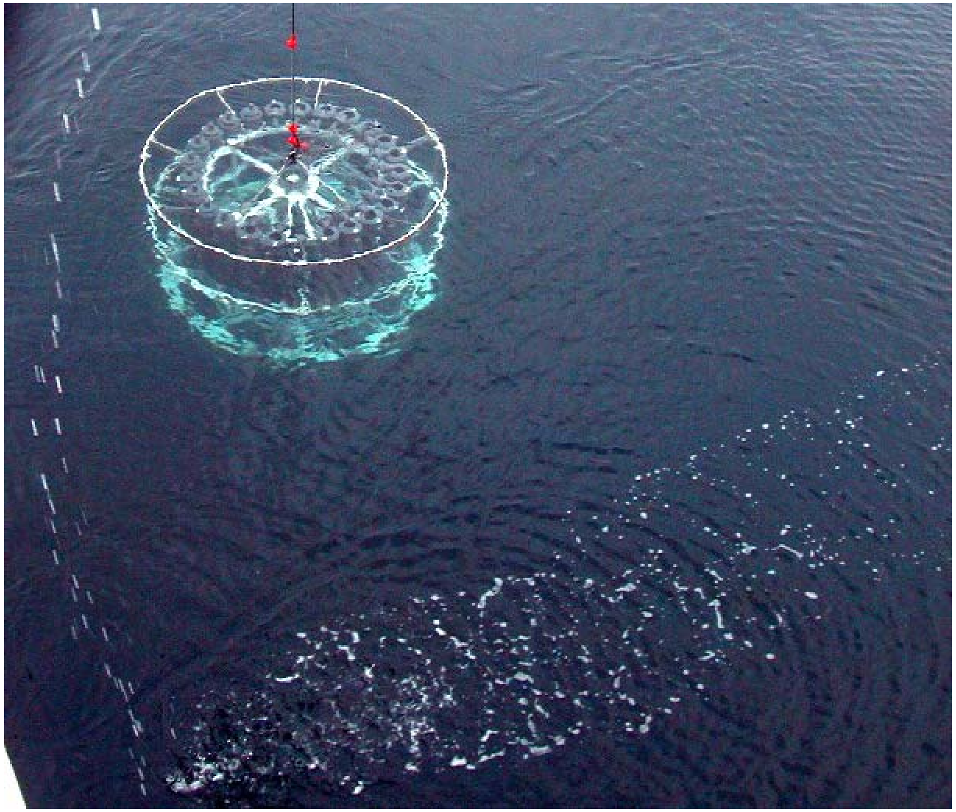


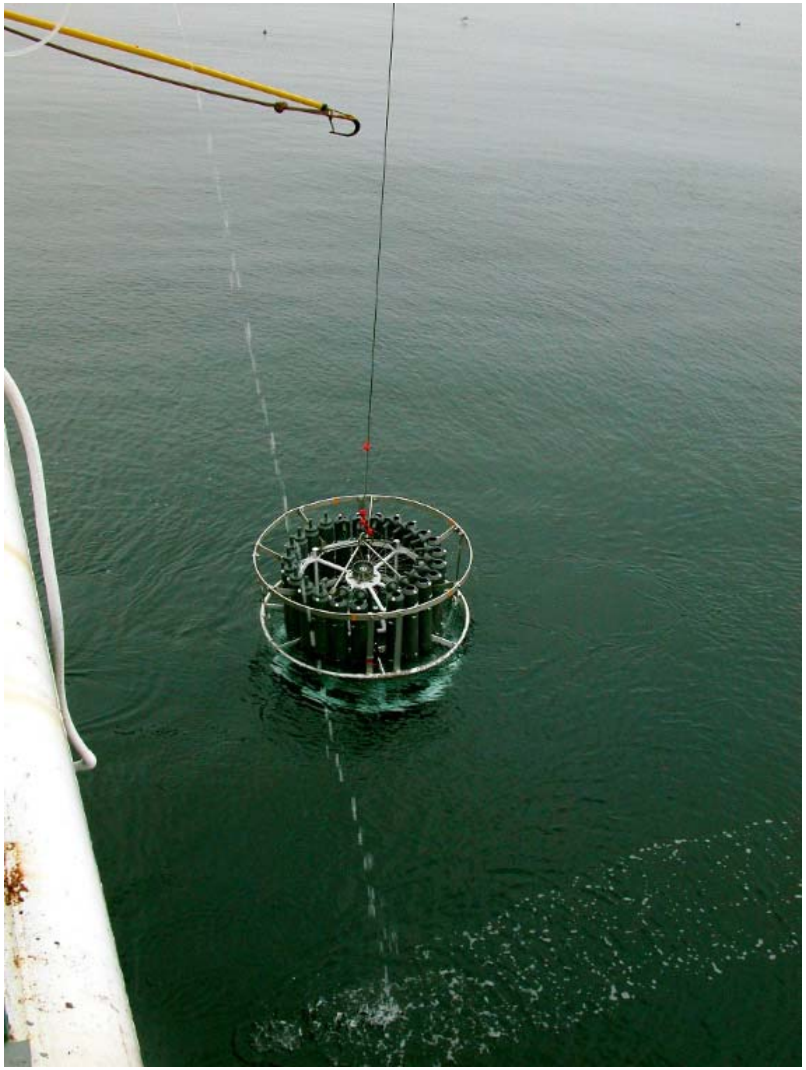
Chlorophyll a Distribution (SeaWiFS)
Spring 2003



Shelf Break

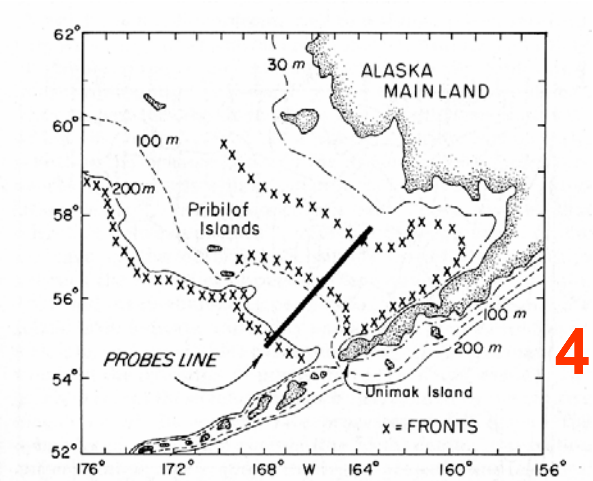
Western Gyre

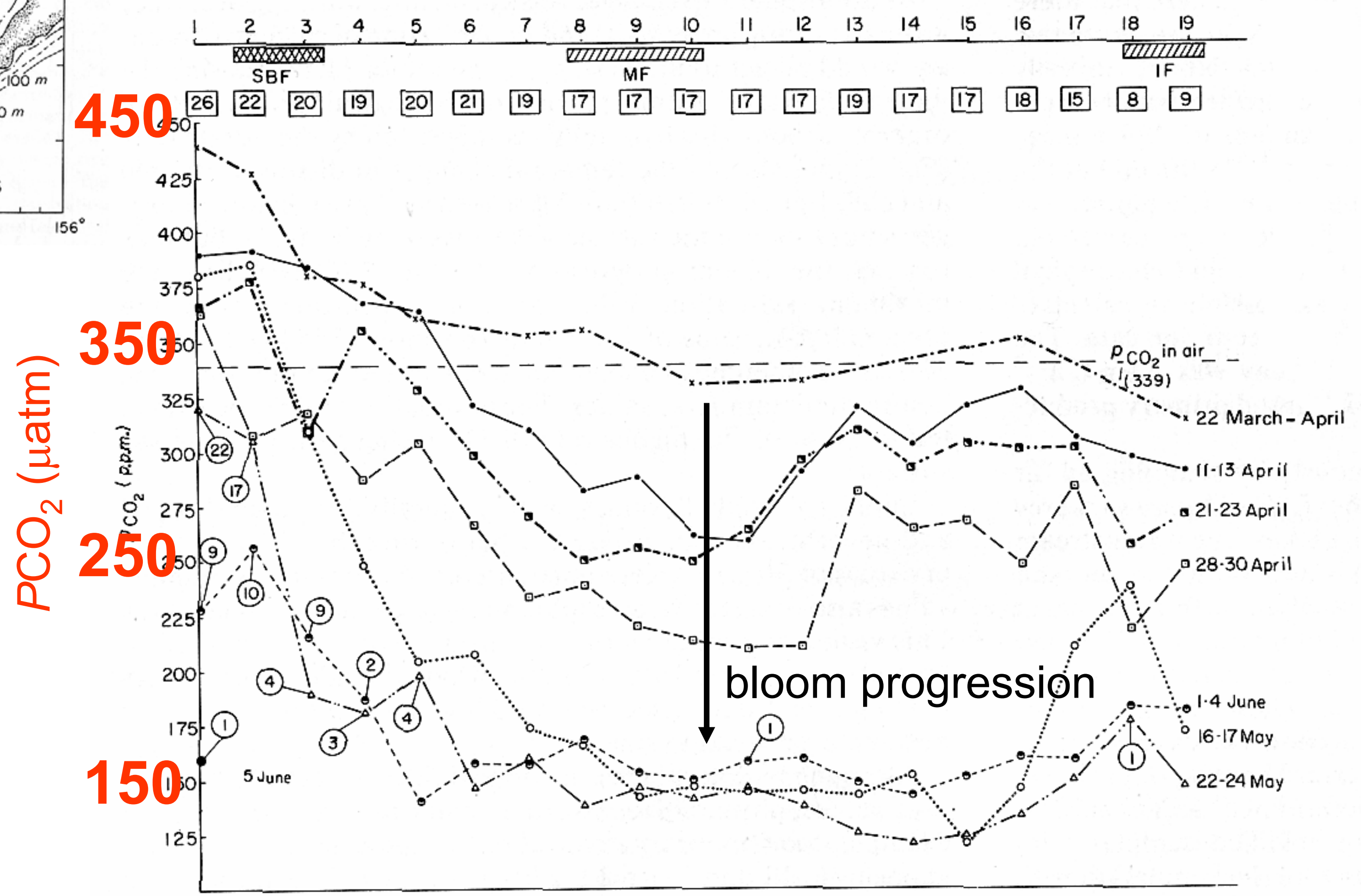




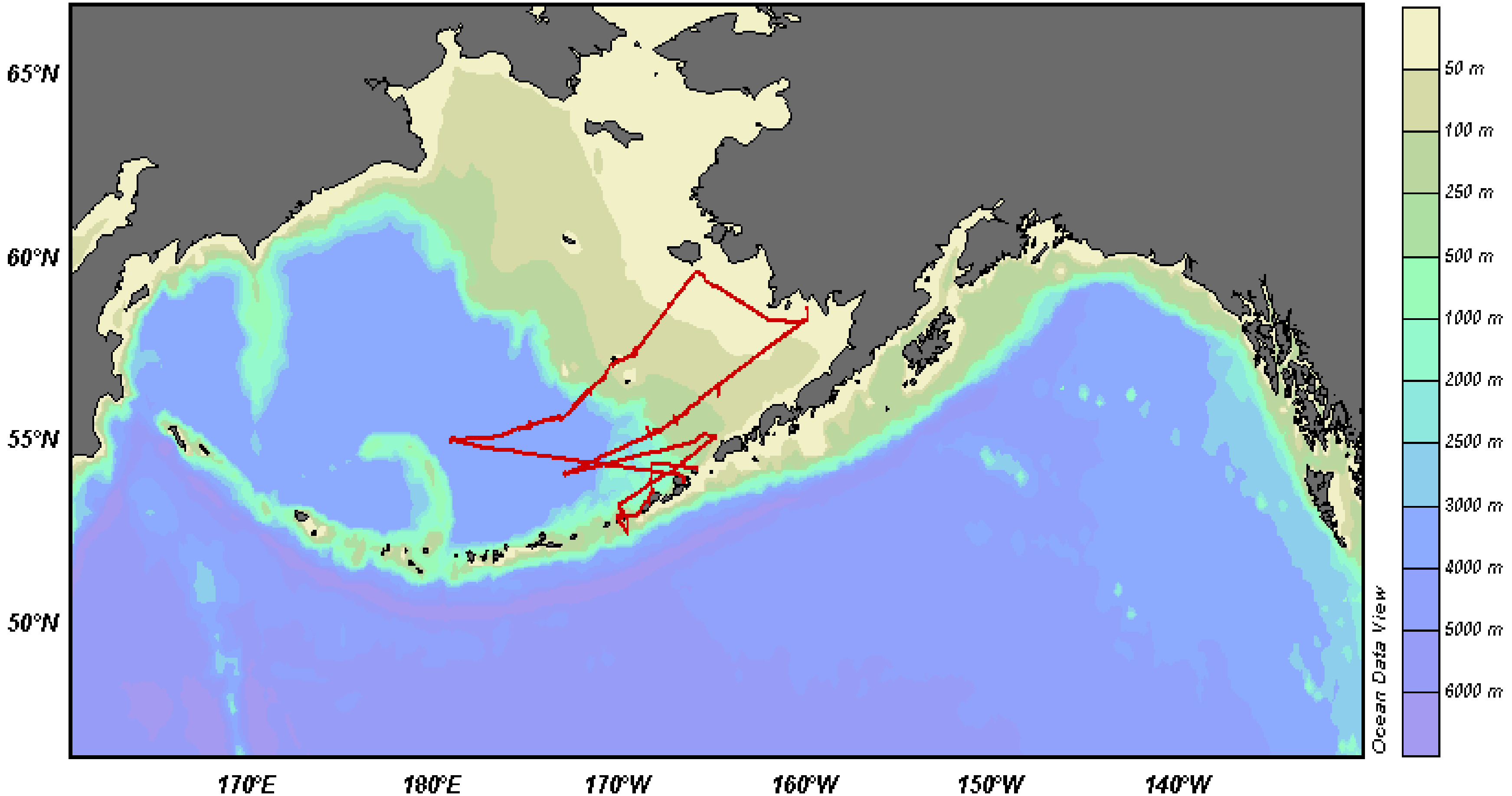
Large CO_2 Gradients in the Bering Sea

Codispoti *et al*. 1982 Nature 296: p 242- 245

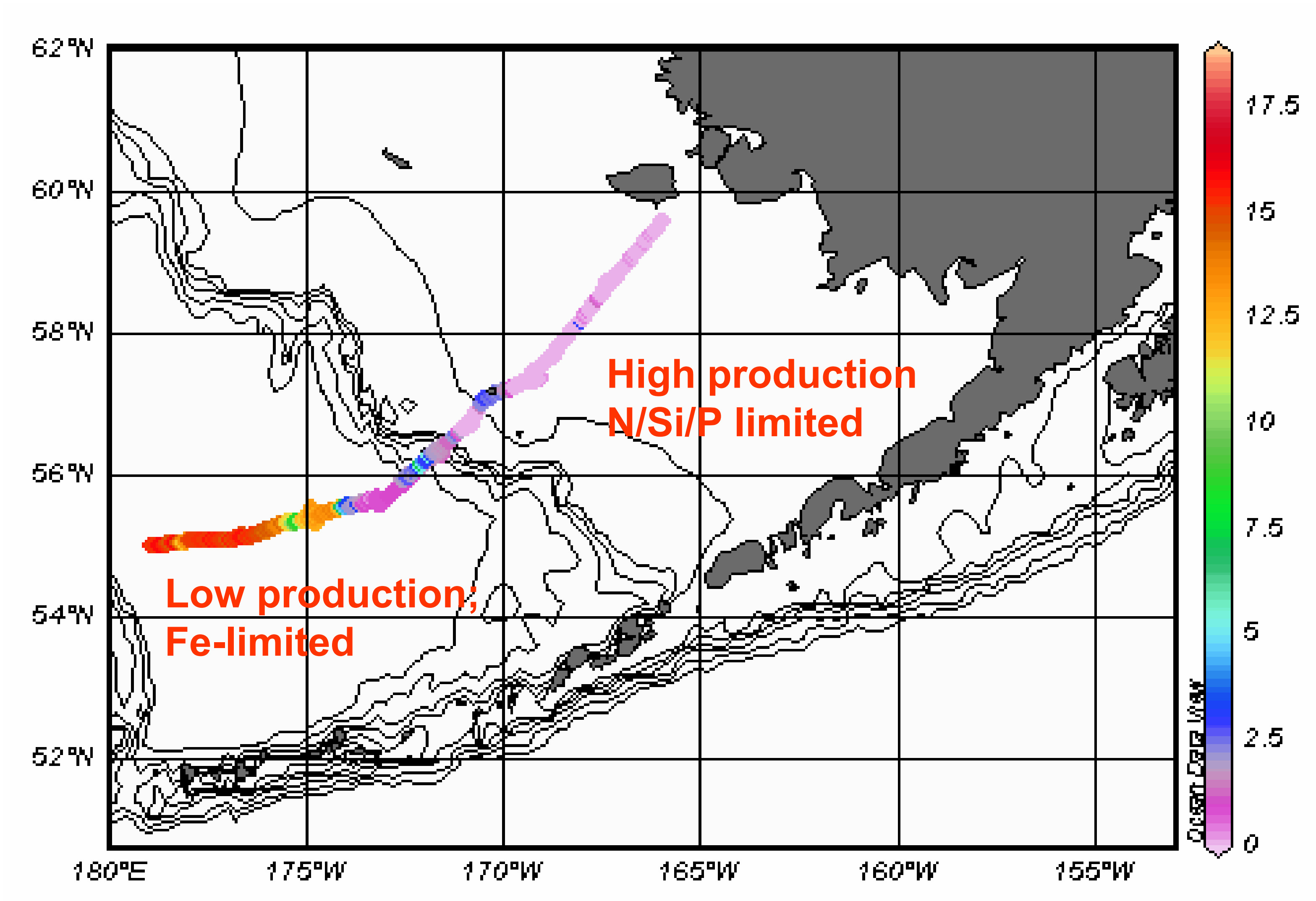




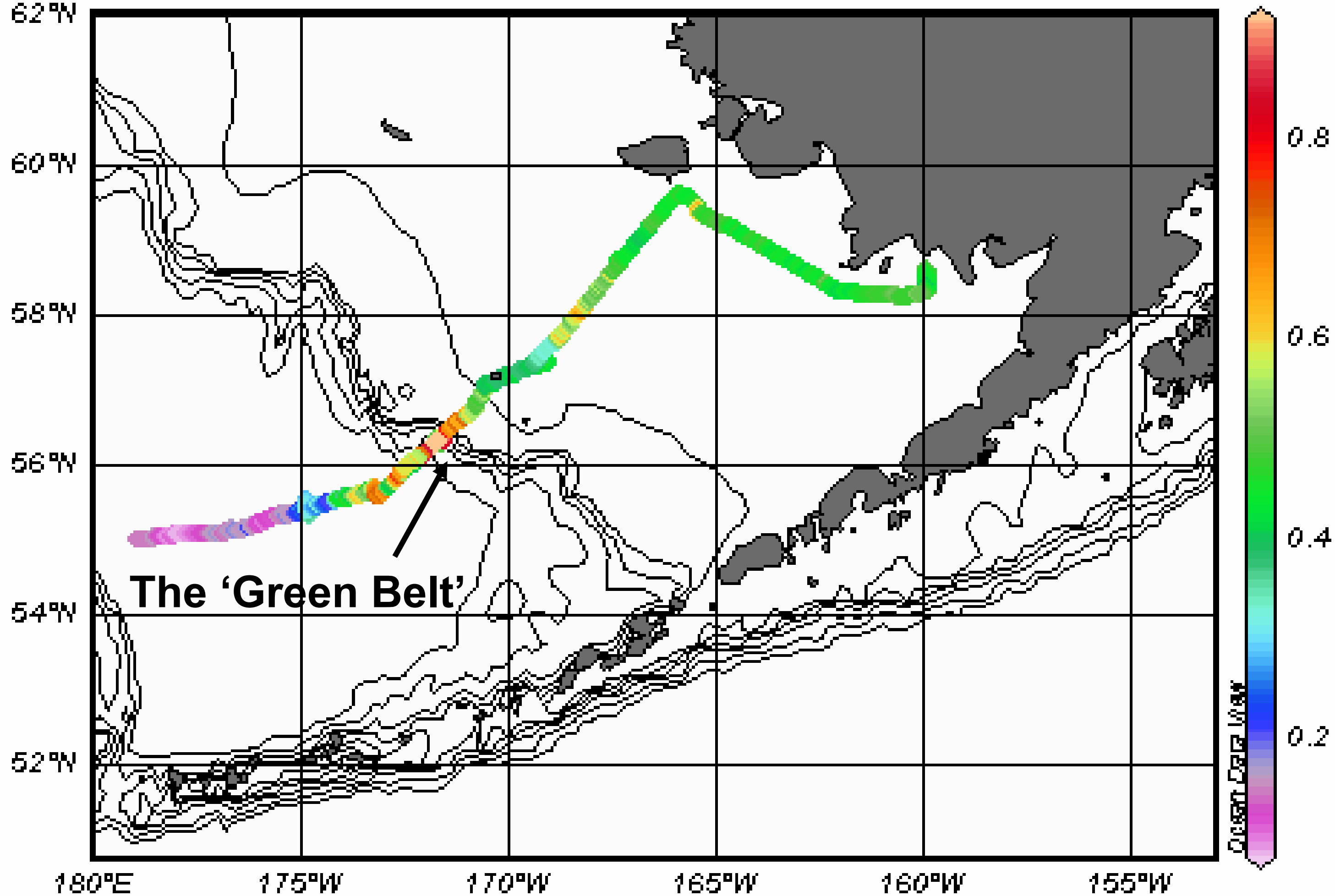
Cruise Track

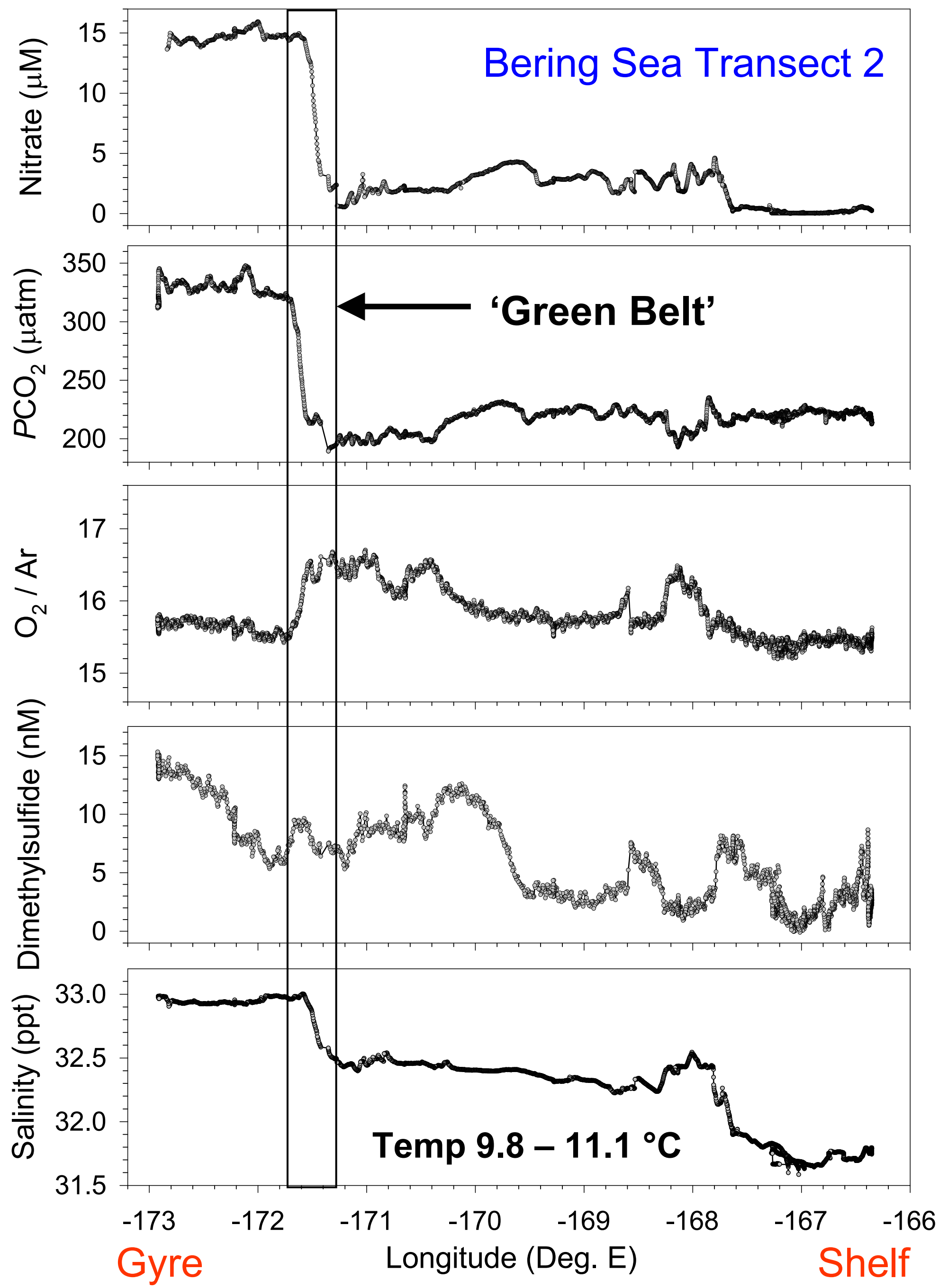


Nitrate Concentration



Chlorophyll Fluorescence

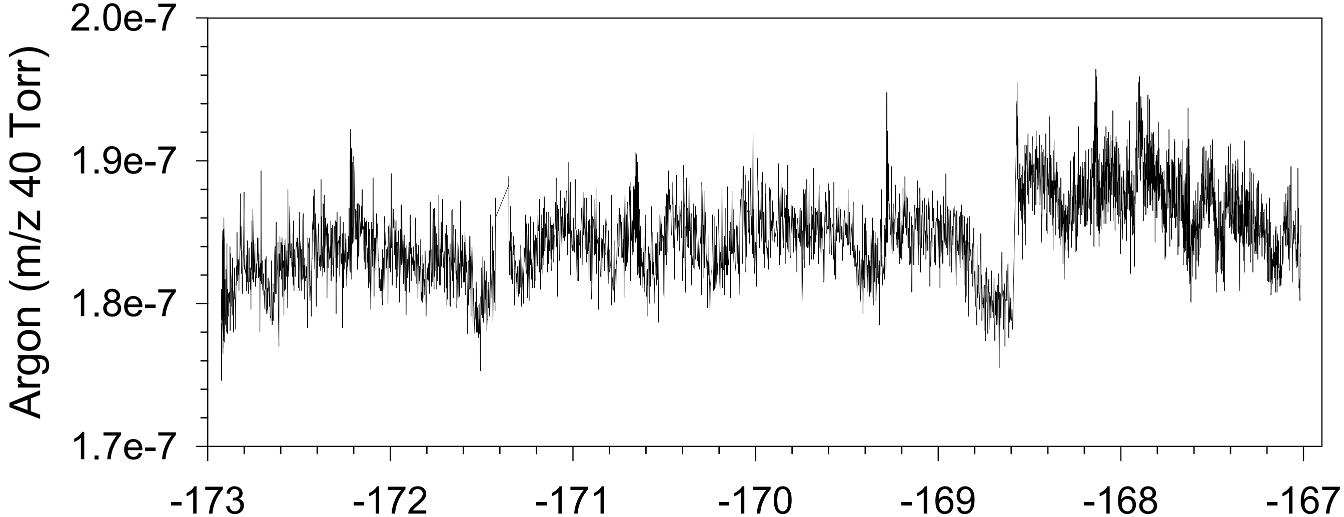


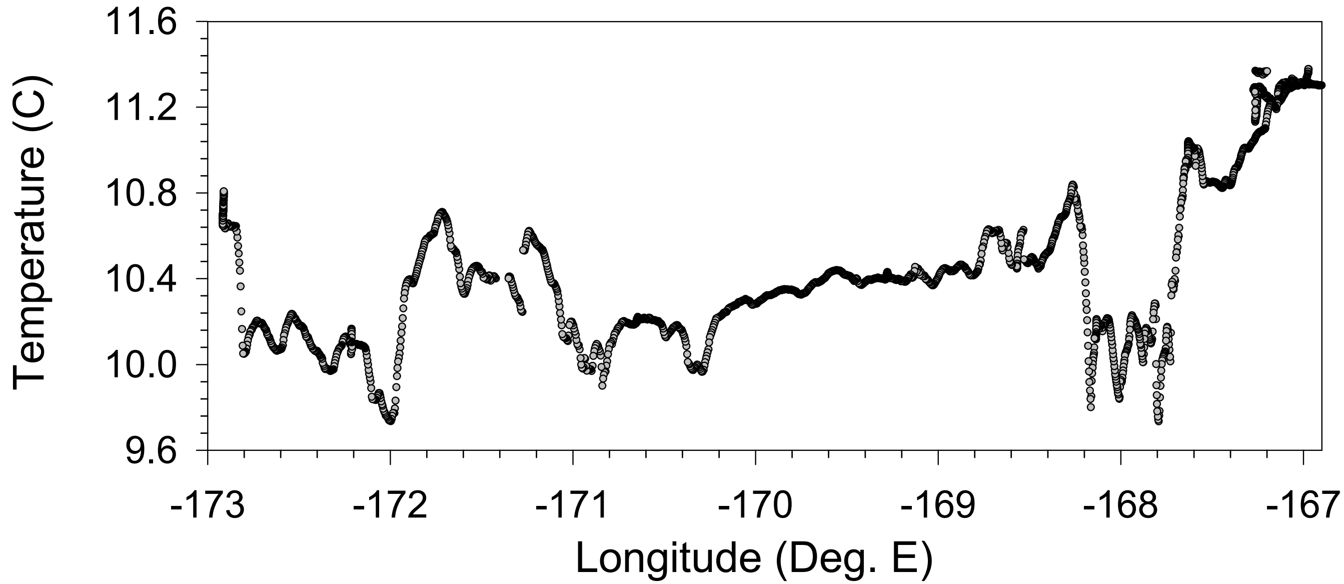


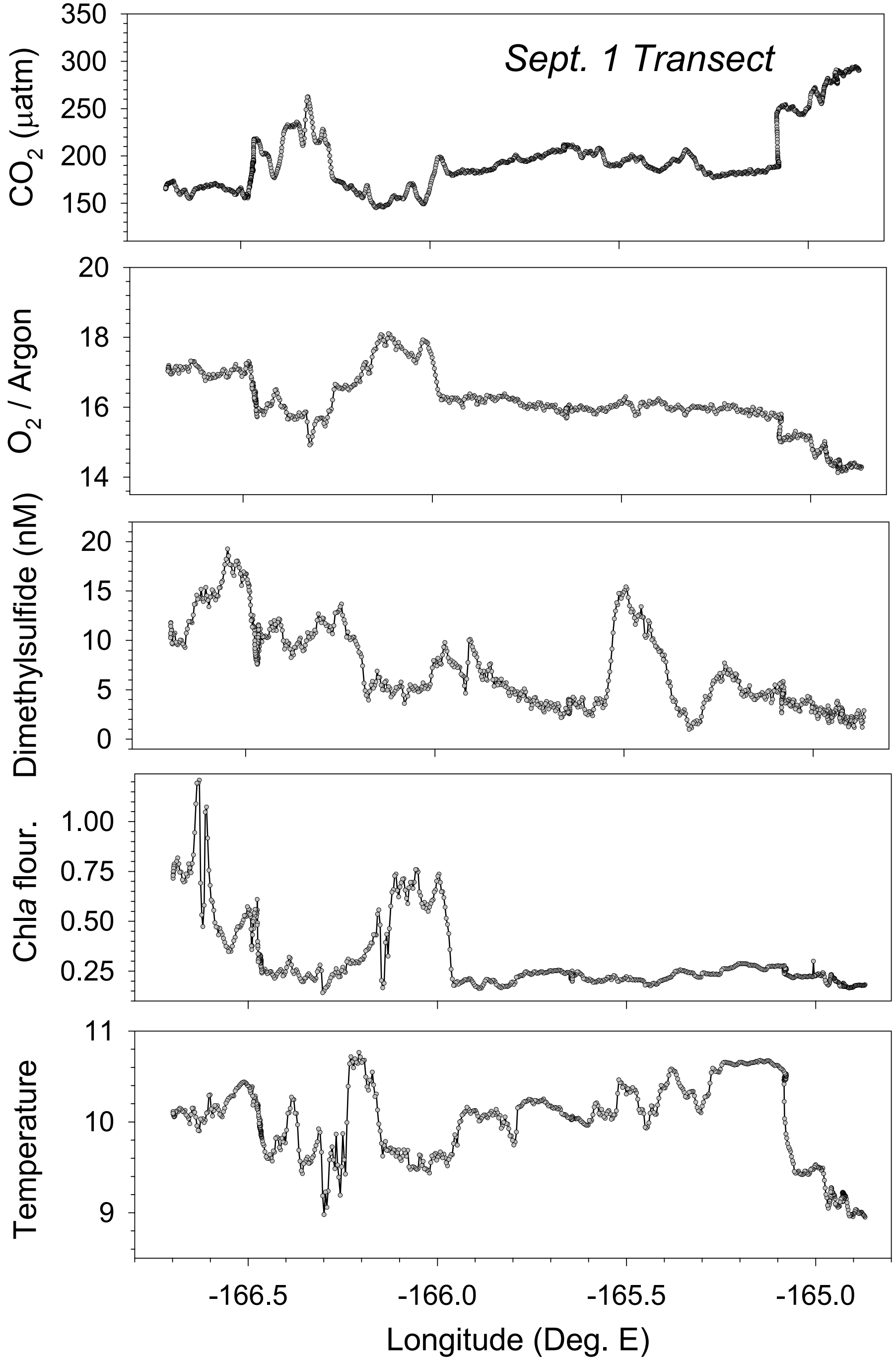
Bering Sea Transect 2
'Green Belt'
Nitrate (μM)
PCO2 (μatm)
O2 / Ar
Dimethylsulfide (nM)
Salinity (ppt)
Temp 9.8 – 11.1 °C
Longitude (Deg. E)
Gyre
Shelf

Argon / Temperature Signal:

Transect 2

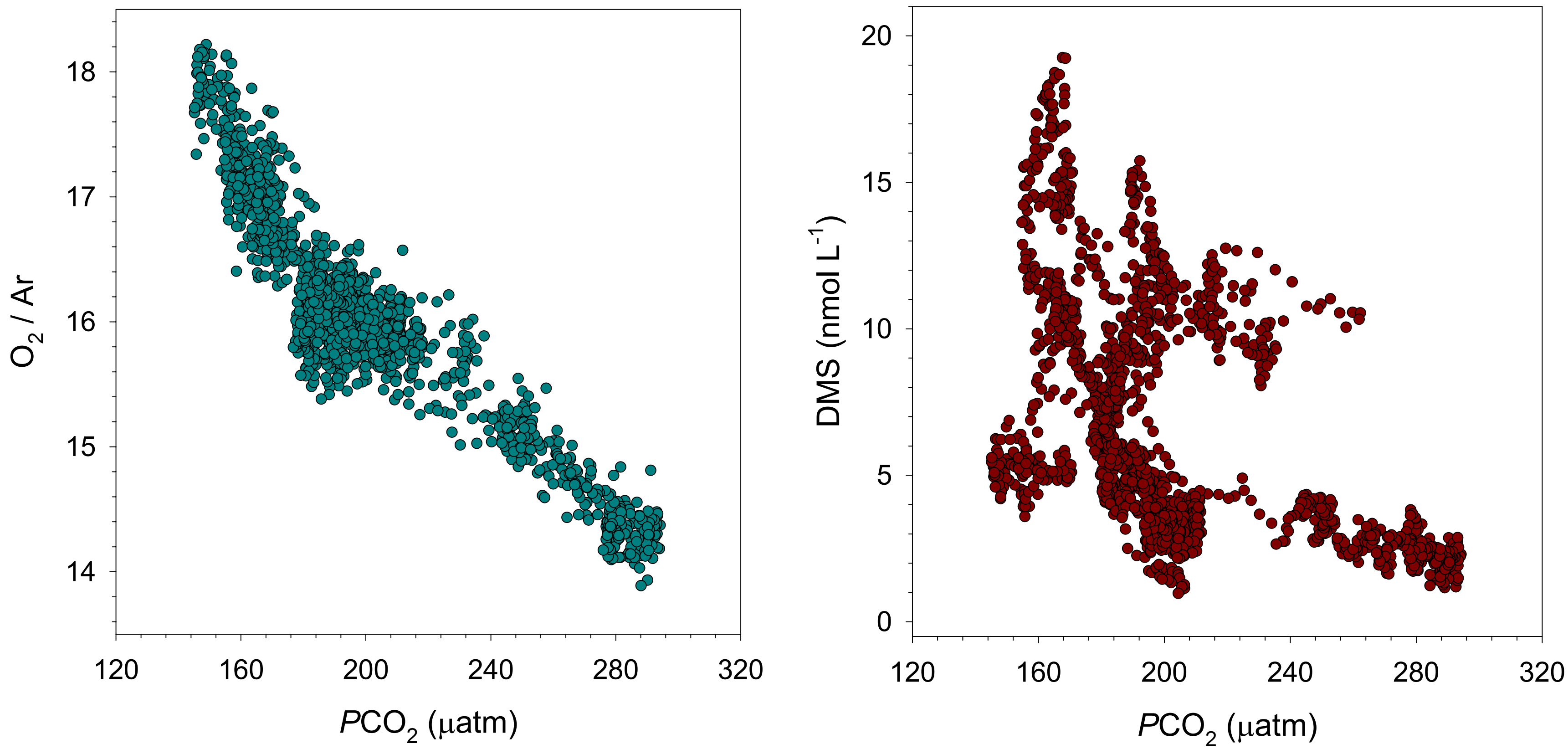




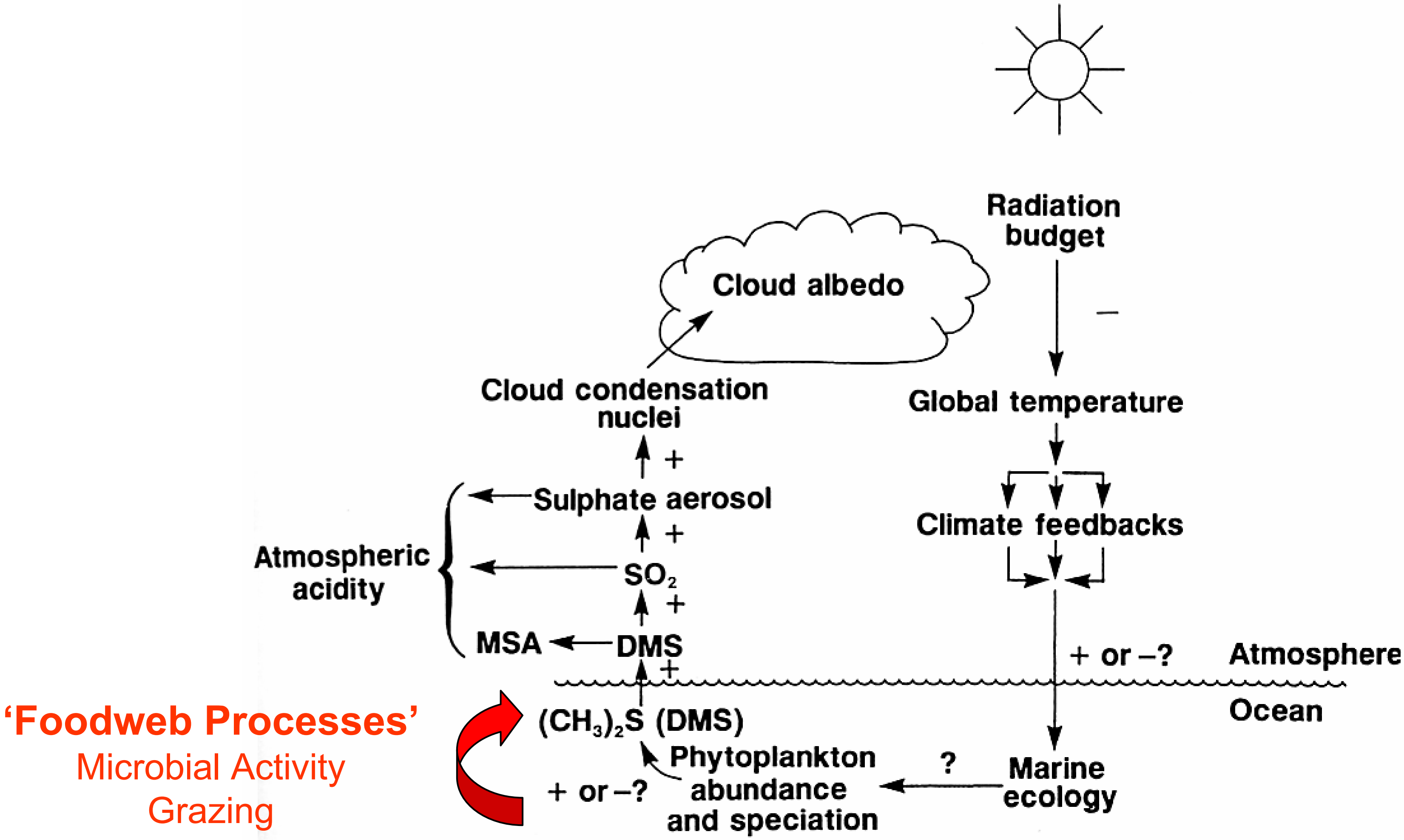


Sept. 1 Transect
CO_2 (µatm)
350
300
250
200
150
O_2 / Argon
20
18
16
14
Dimethylsulfide (nM)
20
15
10
5
0
Chl*a* flour.
1.00
0.75
0.50
0.25
Temperature
11
10
9
-166.5
-166.0
-165.5
-165.0
Longitude (Deg. E)

Sept. 1 Gas Relationship



DMS concentrations affected by a number of ecological factors



Watson and Liss (1998) Trans. Roy Soc. London

Taxonomic Variability in DMSP Production

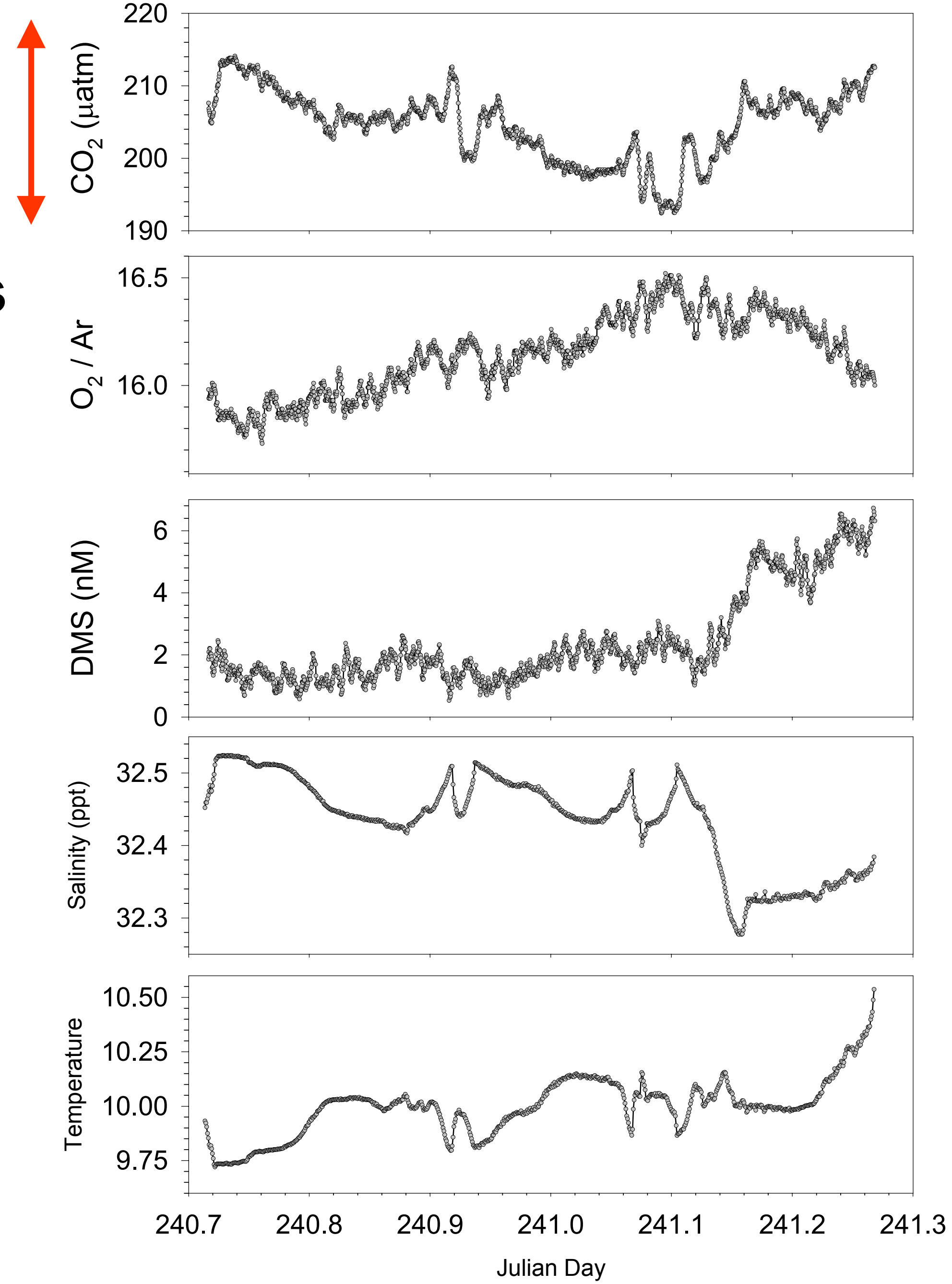
Class/species	DMSPChl *a*:
Bacillariophyceae	
Minidiscus trioculatus	2.59
Chaetoceros simplex	0.26
Cylindrotheca closteriu	1.12
Thalassiosira pseudonana	0.89
Melosira nummuloides	13.40
Skeletonema costatum	3.91
Nitzschia laevis	1.33
Dinophyceae	
Prorocentrum minimum	36.74
Amphidinium carterae	42.25
Prorocentrum micans	33.46
Gymnodinium simplex	124.25
Prasinophyceae	
Micromonas pusilla	7.96
Tetraselmis levis	19.76
Prymnesiophyceae	
Coccolithus neohelis	36.19
Emiliania huxleyi	15.41
Emiliania huxleyi	17.88
Chrysochromulina sp.	24.79
Phaeocystis sp.	43.97
Pavlova pinguis	15.21
Prymnesium parvum	17.29

$\chi = 3.4 \pm 4.5$

$\chi = 44.1 \pm 41.2$

$\chi = 24.4 \pm 11.4$

Gas Distributions across The 'Green Belt'



Thus Far

- MIMS is a viable alternative to other methods Lower Precision but higher through put
- Application to traditional gas profiling with discrete samples
- Use for flow-through studies

- New scientific insight? As of yet, just powerful confirmation of what we know already …..

Up next ….

- Further method development:
  - larger area membrane for higher sensitivity;
  - In situ gas calibration system using mass flow controllers;
  - enhanced pumping system to minimize flow disturbance.

- New Scientific Insights likely to come from:

- Systematic underway sampling / monitoring
  - Distribution of DMS related to phytoplankton species composition and foodweb

    Structure
  - Effects of CO_2 concentrations on phytoplankton physiology.

- Isotope studies of trace gas cycling.
  - ^{15}N labeled NH_4^+ and NO_3^- additions look for $^{15}N_2$ and $^{15}N_2O$ production
  - ^{34}S labeling of DMSP to look at DMS foodweb cycling
  - $^{18}O_2$ and $^{13}CO_2$ labeling to measure primary production