Ocean Carbonate Dynamics- "Finding a cure for POC envy"

William "Barney" Balch

Bigelow Laboratory for Ocean Sciences

W. Boothbay Harbor, ME 04575

"POC Envy"

When most people talk about "**carbon cycle science**" and the "**biological pump**", they are usually referring to fixation of particulate organic carbon (POC).

Fixation of particulate inorganic carbon (PIC) is rarely mentioned, even though carbonates dominate over organic matter in the earth's sediments (i.e. carbon sequestration) by a factor of 6-7X and biomineralization is a significant source of CO_2!

Calcium Carbonate and Global Carbon Pools

- Calcium carbonate (particulate inorganic carbon) is one of the major particulate carbon pools on earth, 1/4 of all marine sediments are $CaCO_3$.

Pool	*GT Carbon*
PIC (sediments)	5.7E6
DOC (ocean)	1000
POC(sediments)	0.8E6
Atmos C	700

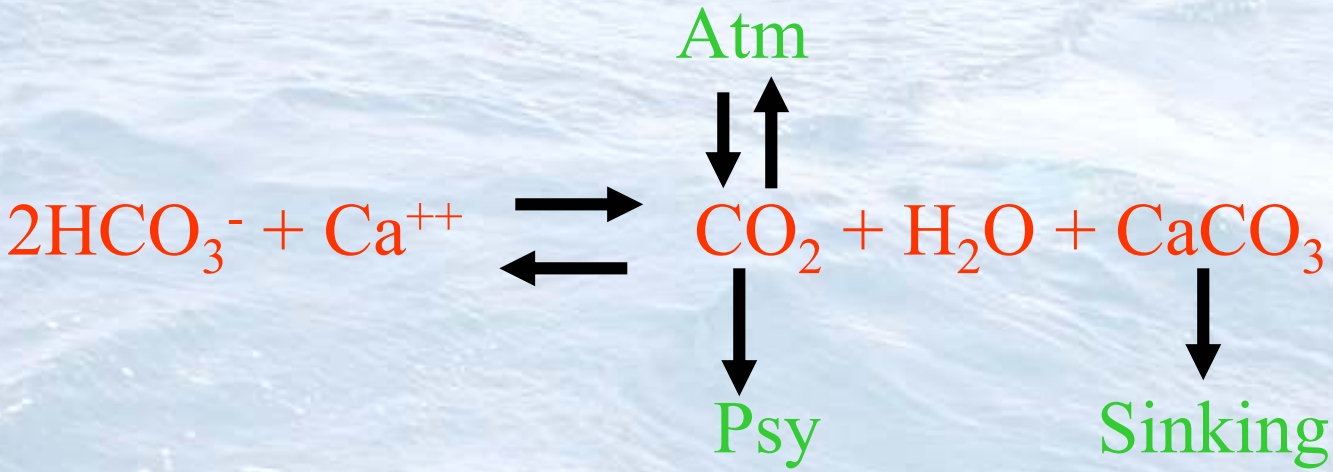
•PIC associates with detrital aggregates, acts as major ballast for POC, increasing sinking rates to sea floor

•Found in several forms, it is stable in surface sea water, dissolving in deeper sea water

•Also absorbs dissolved organic matter and carries it to sea floor as POC/PIC matrix

Biogeochemistry of Calcification

- Stoichiometry of biomineralization of $CaCO_3$:

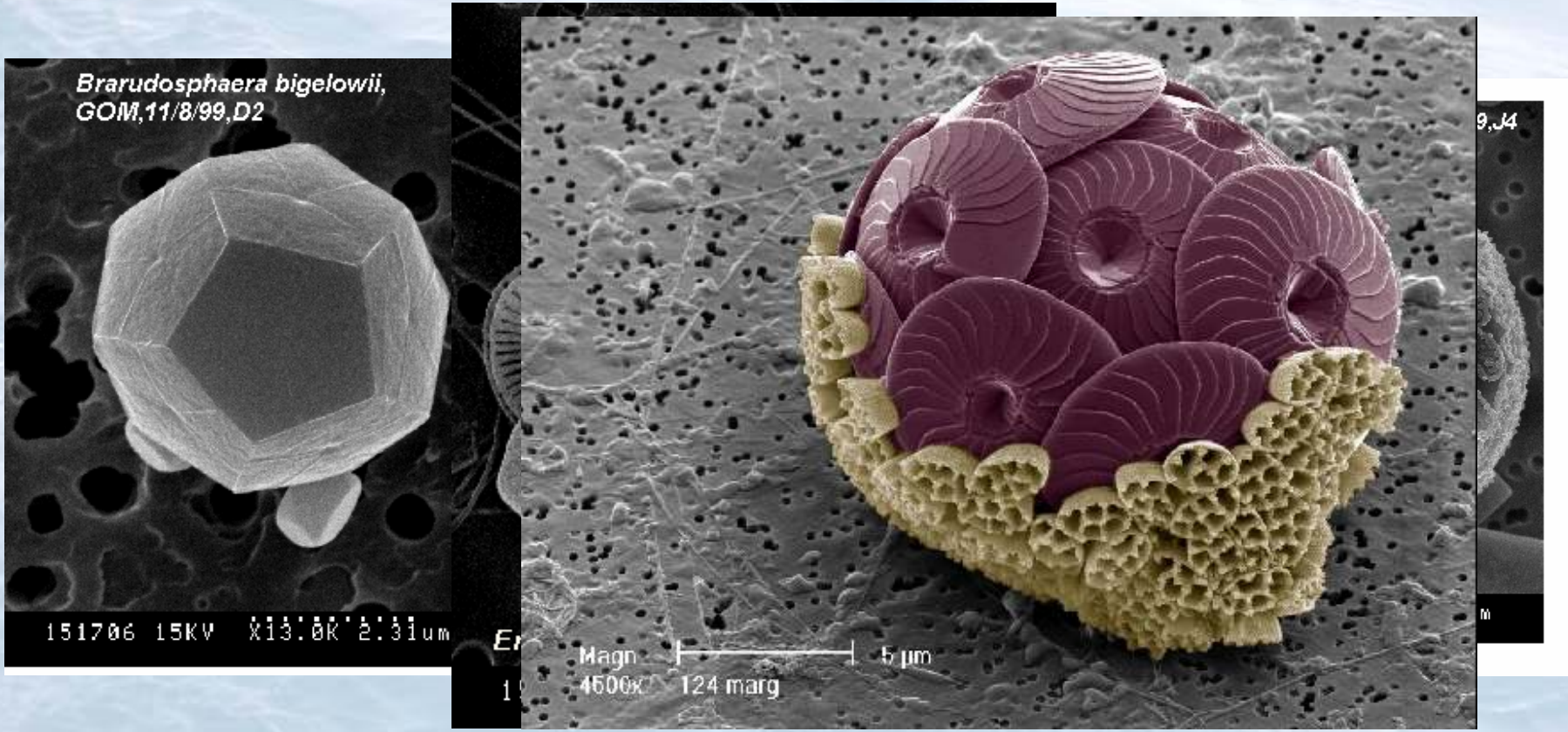


- In top kilometer of ocean, reaction strongly driven to right, but pressure, temperature and pH affect equilibrium
- Marine calcification thought to be about 1GT per year (~1/5 fossil fuel CO_2 generation or ~equivalent to CO_2 production associated with deforestation and agricultural tilling of soils) [Intergovernmental Panel on Carbon Climate]

Global Ocean Acidification

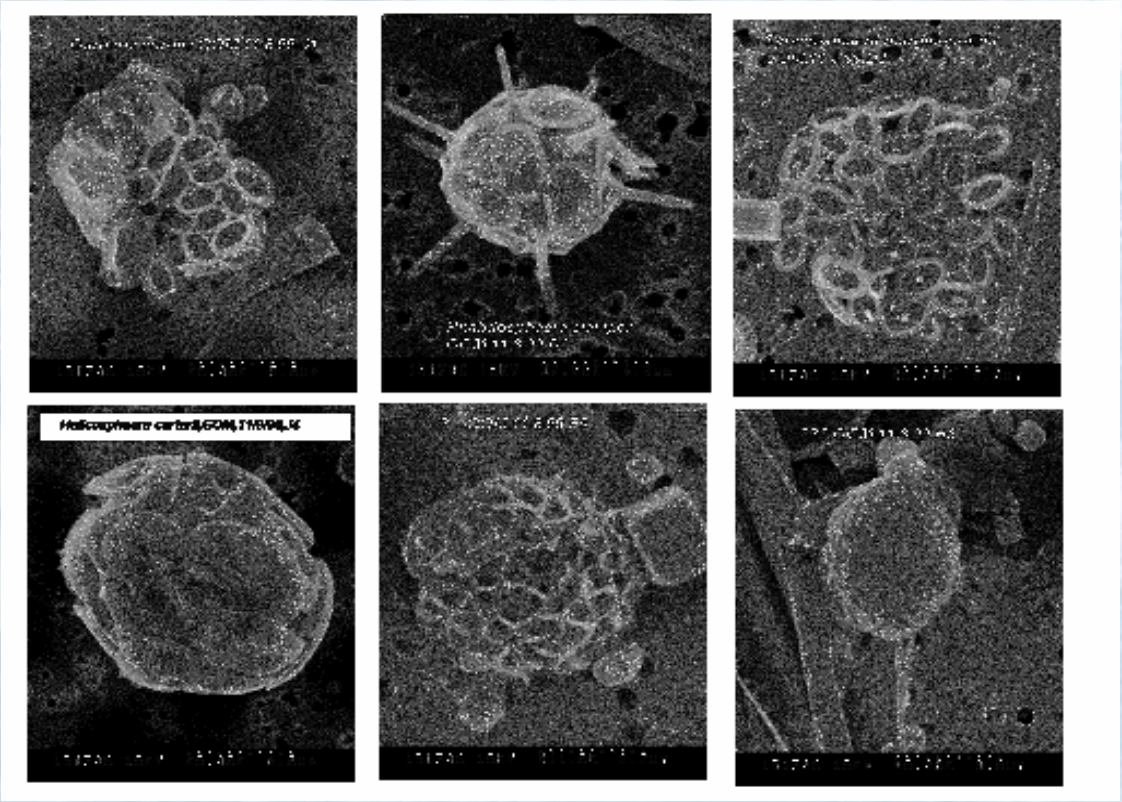
- Increasing fossil fuel CO_2 is lowering pH in the surface ocean
- Pre-industrial CO_2 = 280ppm, pH_{surf} = 8.15
- "2X" scenario (560 ppm) → pH_{surf} of 7.91
- "3X" scenario (840ppm) → pH_{surf} of 7.76
- CO_2 + sea water produces carbonic acid, which dissolves $CaCO_3$
- This will probably happen first at the poles

One of the most important biocalcifiers in the ocean: coccolithophores (Class Prymnesiophycea, family Haptophyta)



SEM's courtesy of Dr. Delors Blasco, Institute de Ciencias del Mar, Barcelona, Spain; Markus Geisen, Alfred Wegener Inst for Polar and Marine Res

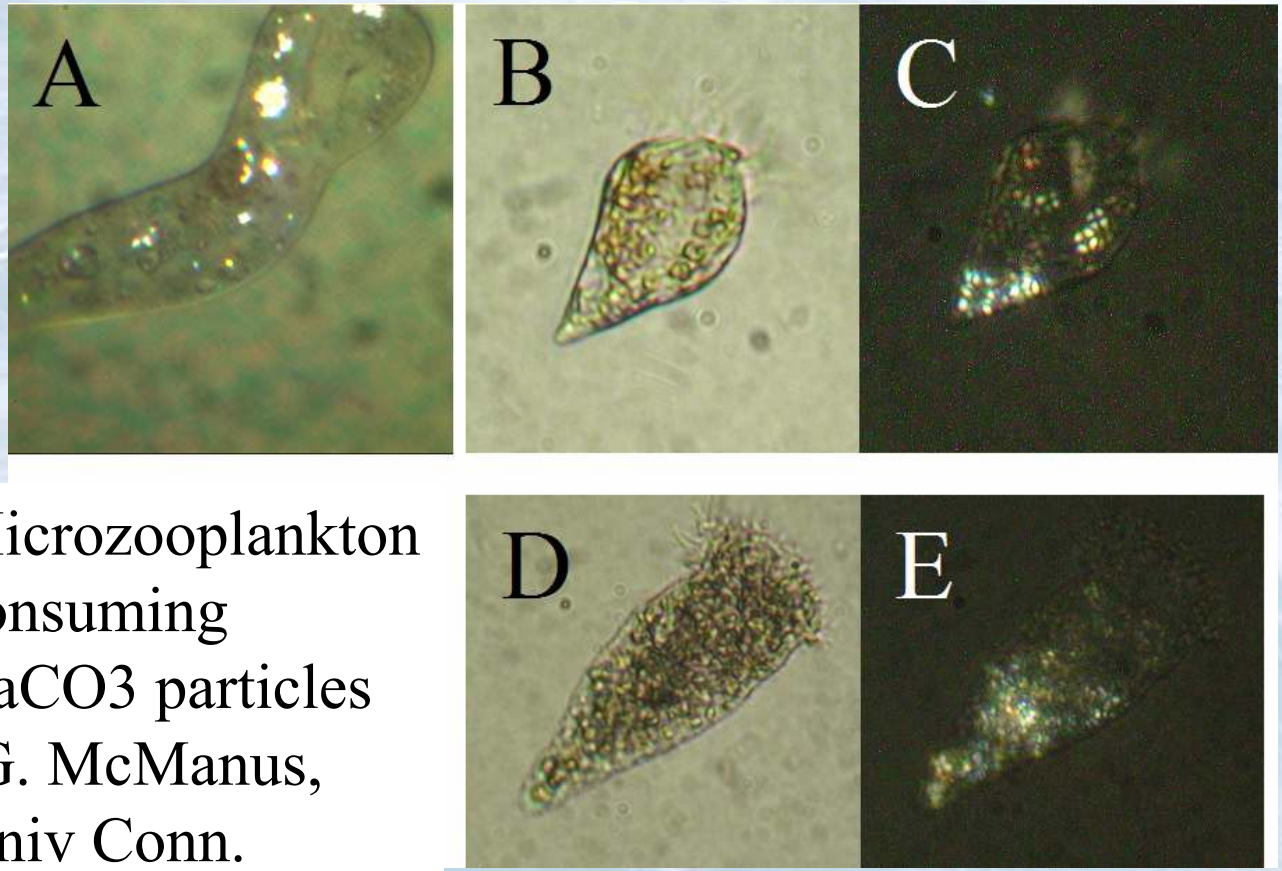
They come in a wide assortment of shapes and sizes with exquisite architecture…



SEM's courtesy of Dr. Delors Blasco, Institute de Ciencias del Mar, Barcelona, Spain

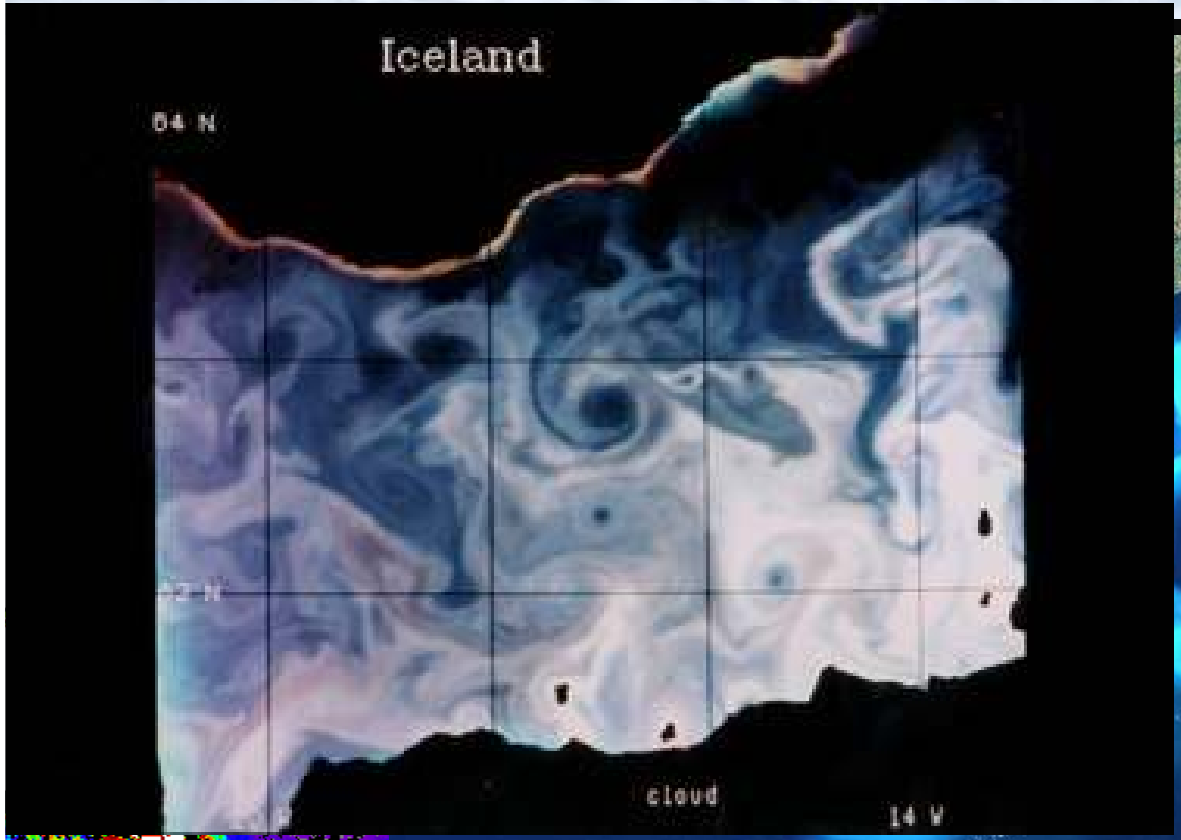
They drop their coccoliths constantly, producing an oceanic "dandruff", which can discolor the water

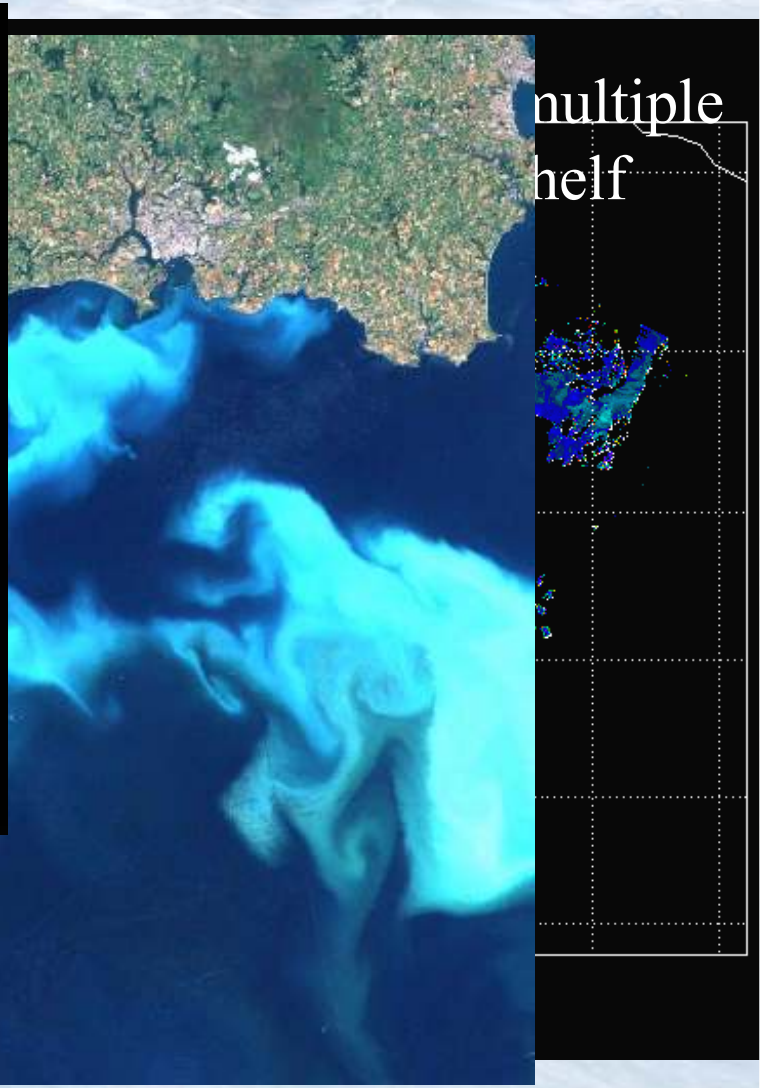
Coccoliths are consumed in the marine food web, like billions of mini “Tums” antacid tablets



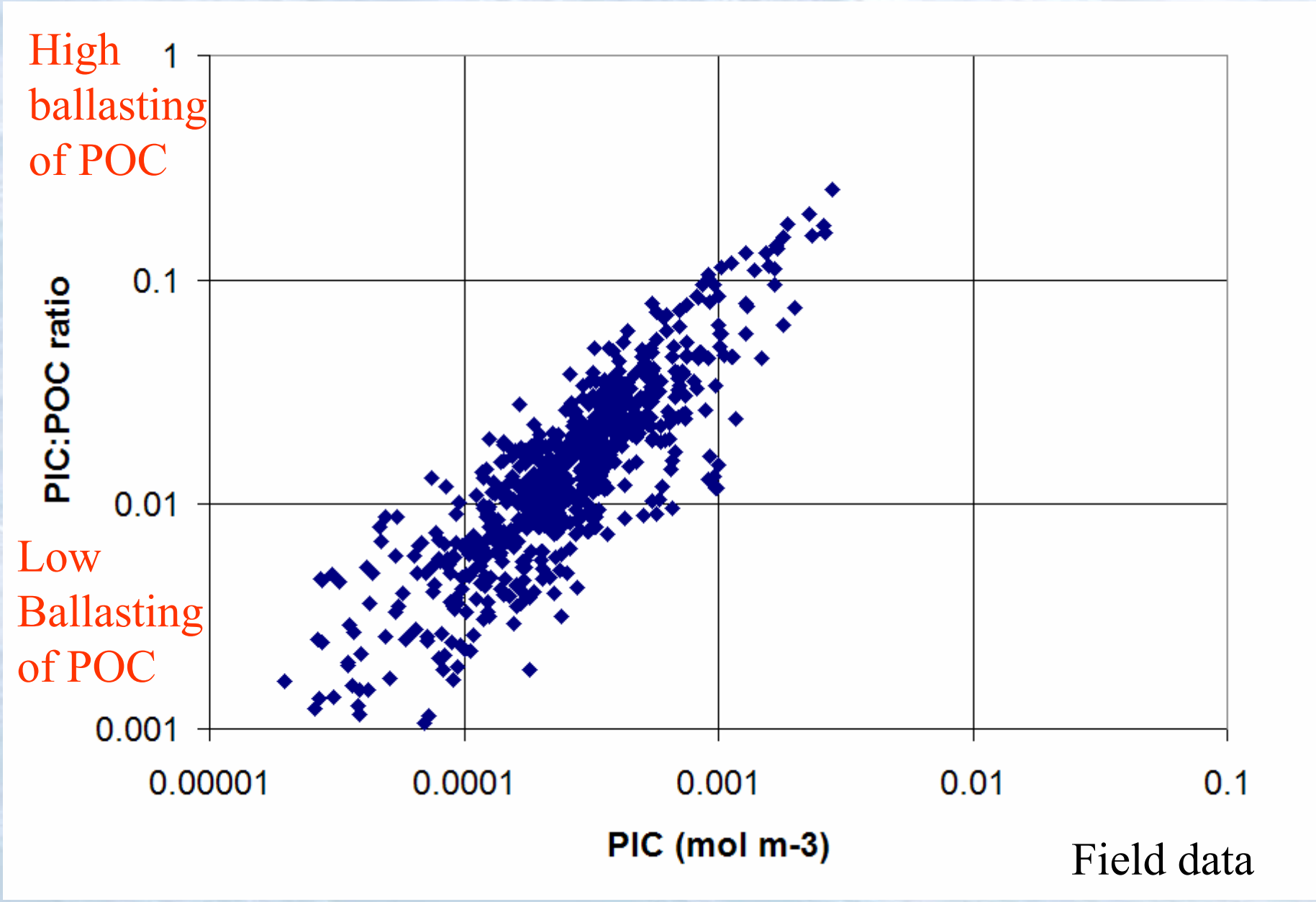
Microzooplankton consuming $CaCO_3$ particles (G. McManus, Univ Conn.

They produce massive ocean blooms





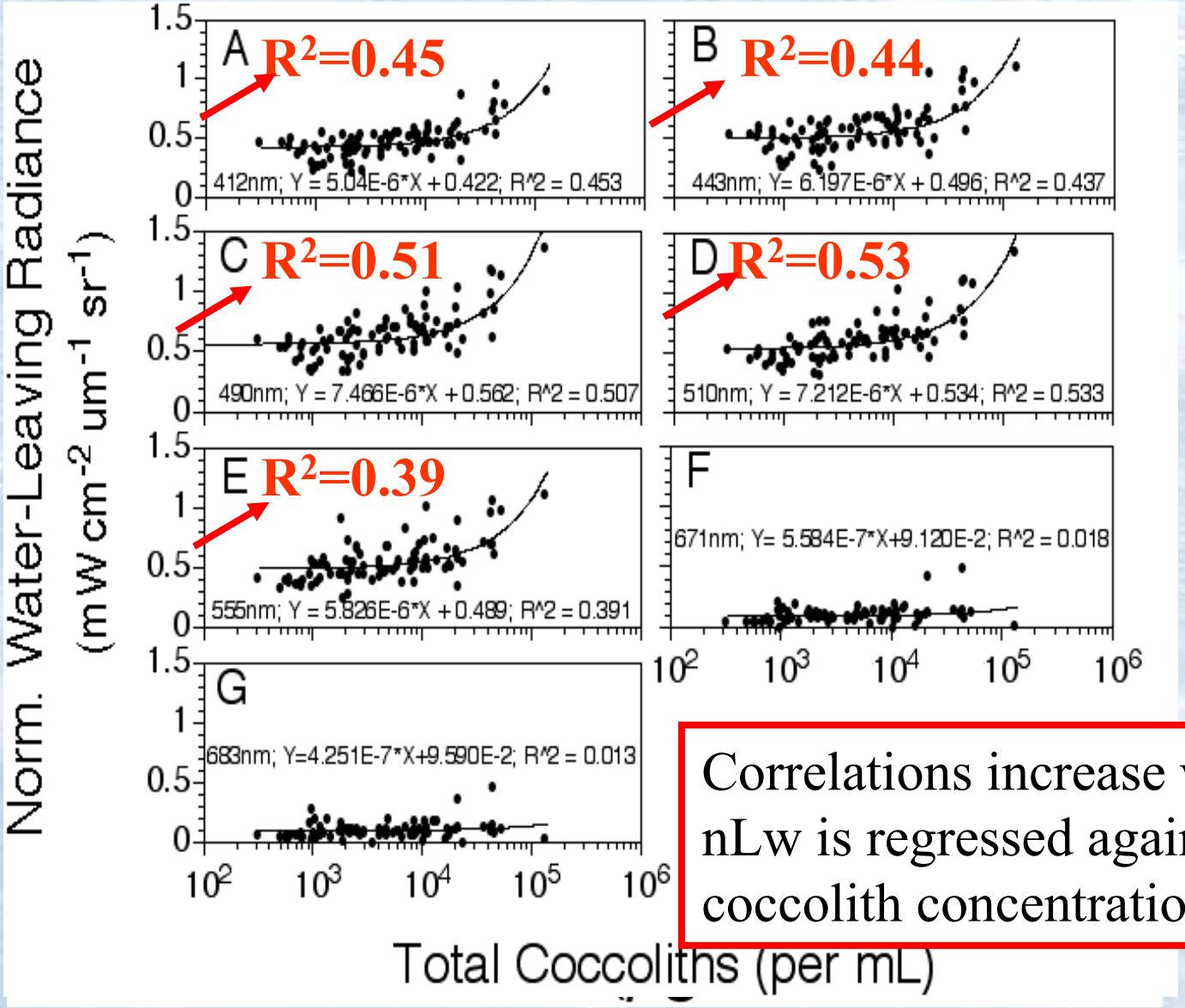
PIC and ballasting of organic matter



Optical properties of PIC

- PIC relative refractive index = 1.19 (POC relative refractive index = 1.05), thus PIC is highly scattering.
- Dense ocean suspensions of coccoliths can have a high albedo (0.35)
- PIC is birefringent, rotates the plane of linearly polarized light by 90^{o}
- Low absorbance
- Mass and shape of coccoliths varies by species, hence the scattering cross section is variable but a good average value is 1.1-1.6 m^2 $mole^{-1}$
- Coccoliths can be a primary determinant of nLw…

PIC can be a 1º determinant of nLw



Correlations increase when nLw is regressed against coccolith concentration!

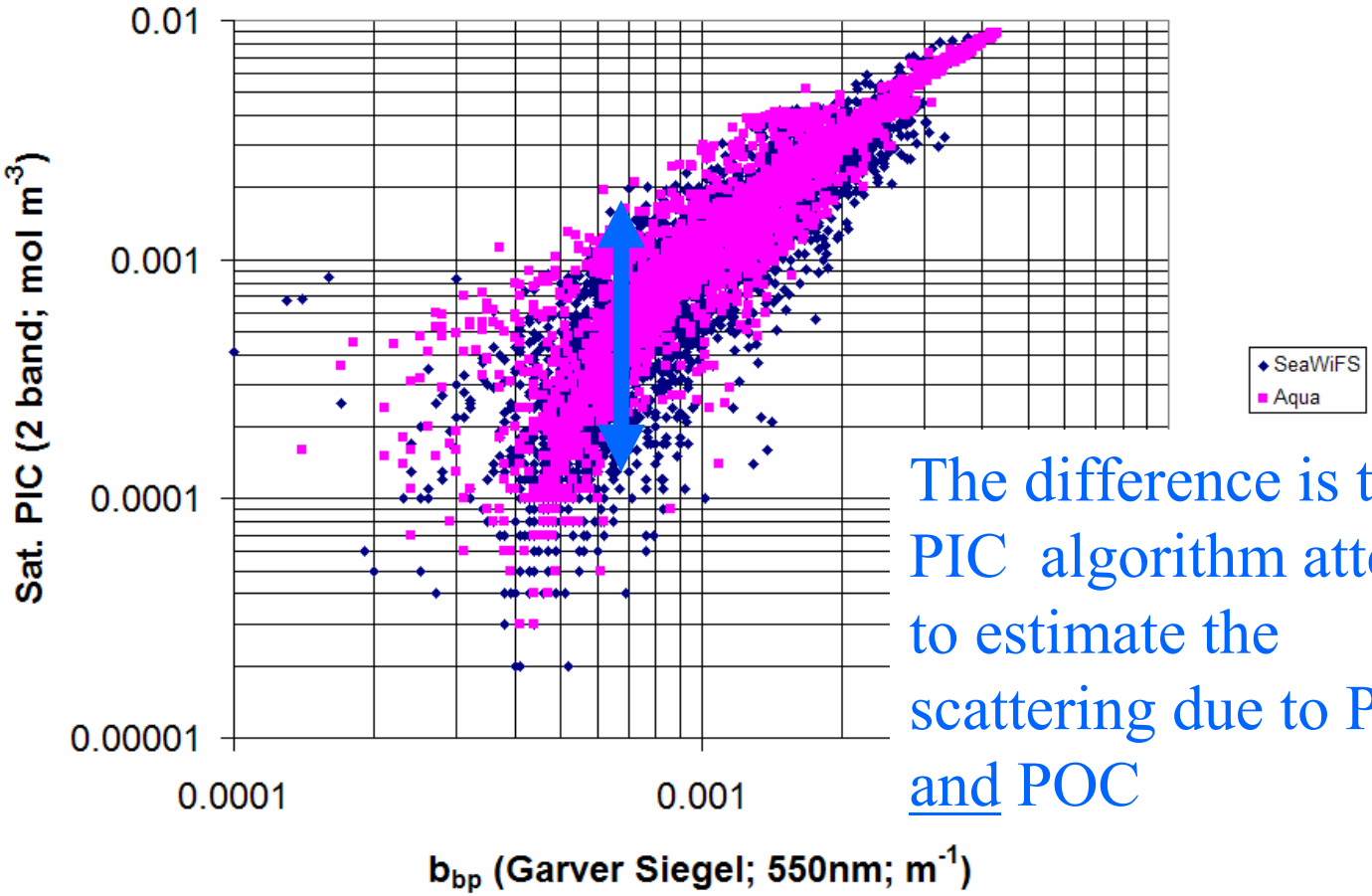
Gulf of Maine

Two PIC algorithms exist

- Two band algorithm (based on nLw440 and nLw550); Balch et al. (2005 Calcium Carbonate Measurements in the Surface Global Ocean based on MODIS Data. *JGR-Oceans* ***110****, C07001 doi:10.1029/2004JC002560*)

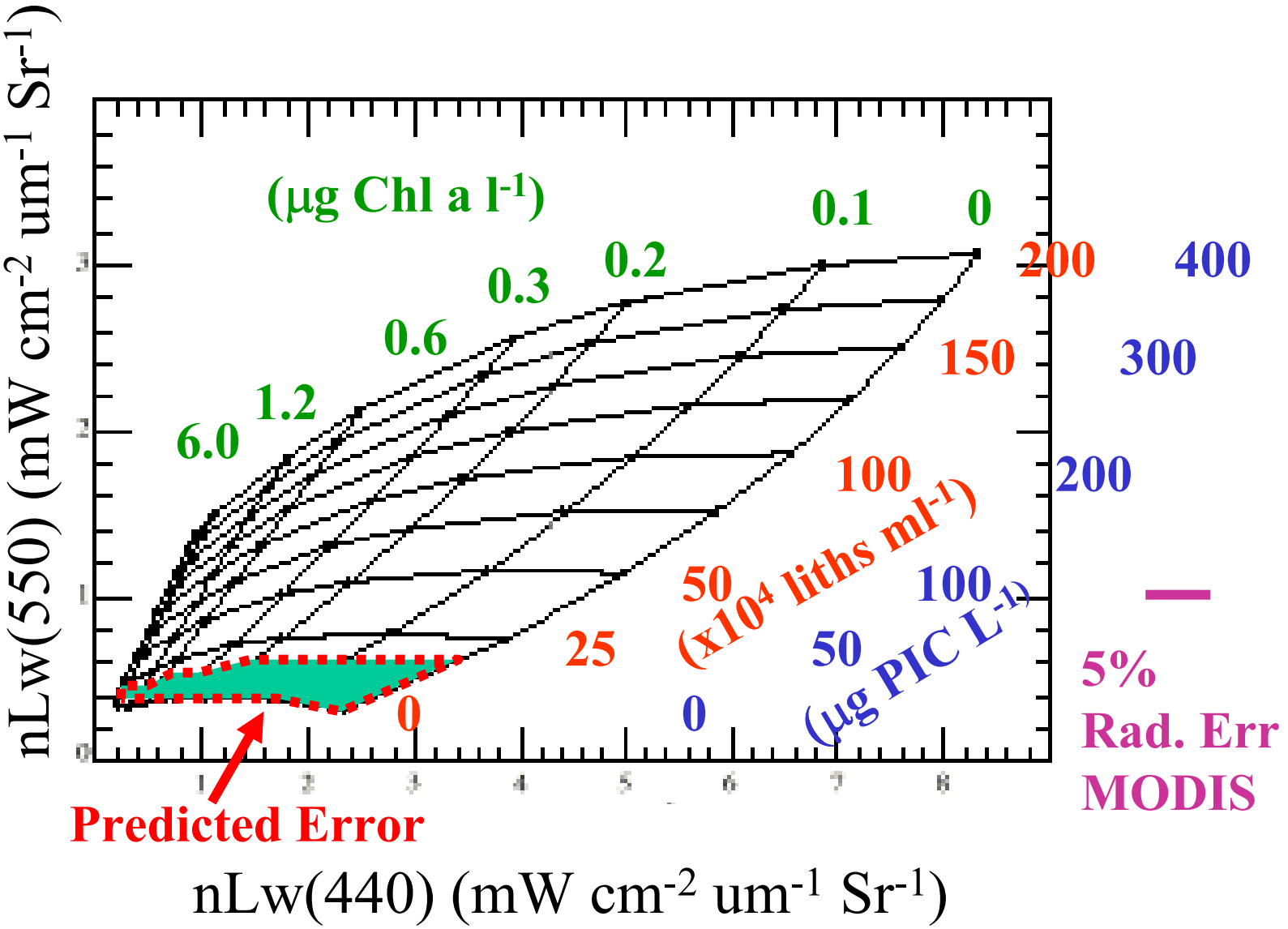
- Three-band algorithm (based on 670, 765, and 865nm bands; Gordon et al. (2001. Retrieval of coccolithophore calcite concentration from SeaWiFS imagery, *Geochemical Research Letters*, *28* (8), 1587-1590.)

The algorithms are fundamentally backscattering algorithms…



The difference is the the PIC algorithm attempts to estimate the scattering due to PIC and POC

The 2-band PIC algorithm is based on a look-up table



3-Band Algorithm

- At 670nm, 765, and 865nm, we assume absorption is mainly due to water (a_w):

$$R=\sim b_b/[3(b_b+a_w)]$$

Measure $R(\lambda)$, use published $a_w(\lambda)$, estimate $b_b(\lambda)$.

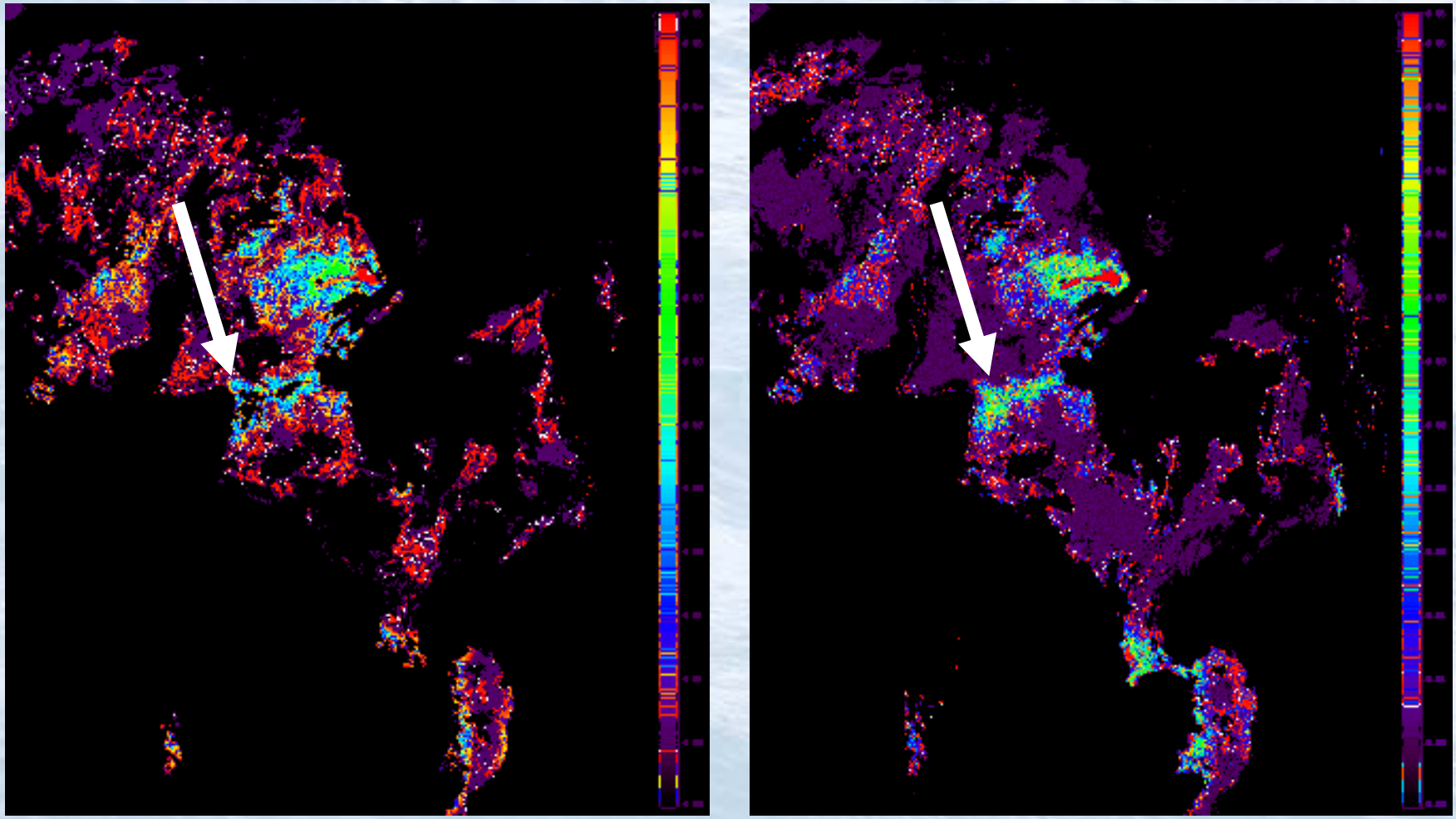
- Also assume that: $b_b(\lambda)=b_b(550)*(550/\lambda)^n$

where n~1.35 based on empirical results

- These assumptions allow estimation of b_b at other wavelengths
- Works best in turbid waters

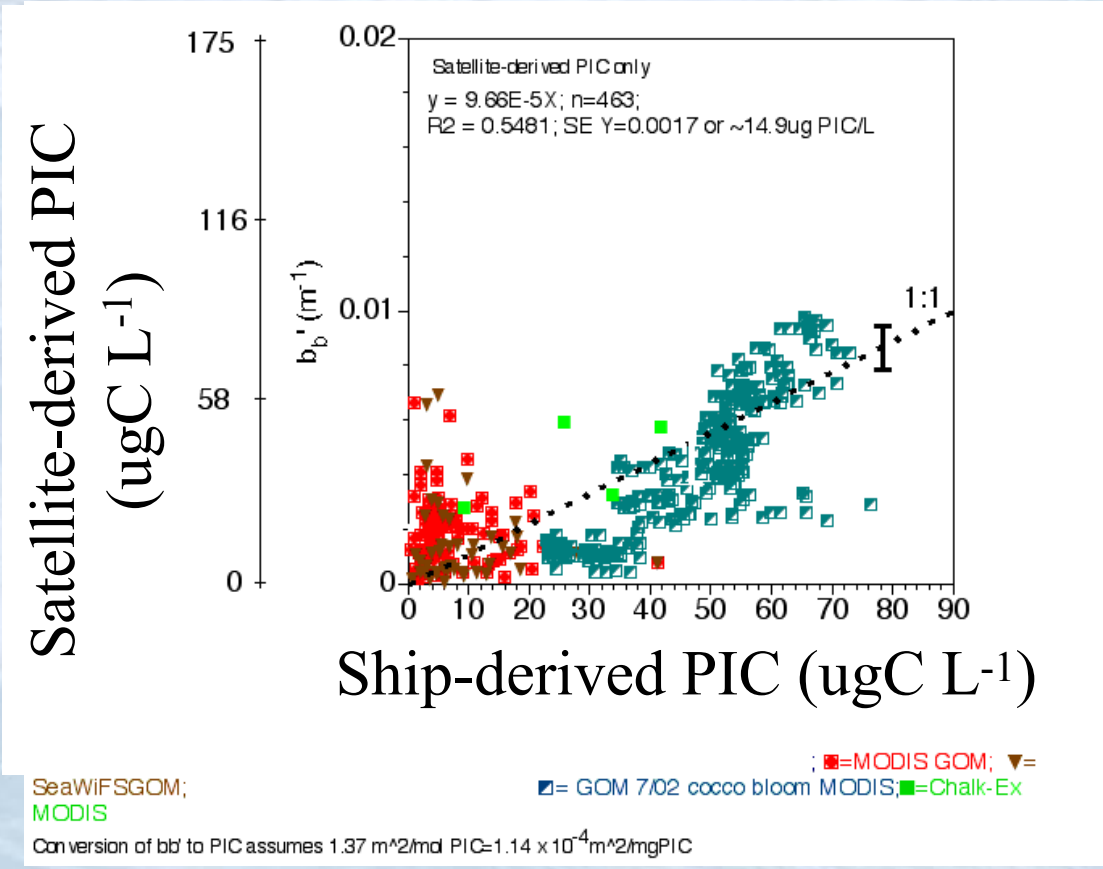
2 Band

3 Band



SeaWiFS scene S2003147125430 of a coccolithophore bloom in the North Sea on May 27 2003. Comparison between 2-band PIC algorithm and 3-band PIC algorithm. Color scales range from 0-0.05 moles PIC m-3. Images by Sean Bailey and Brian Franz.

The real world is never simple…ship-satellite comparisons with 2-band algorithm



There is natural variability in PIC-specific scattering

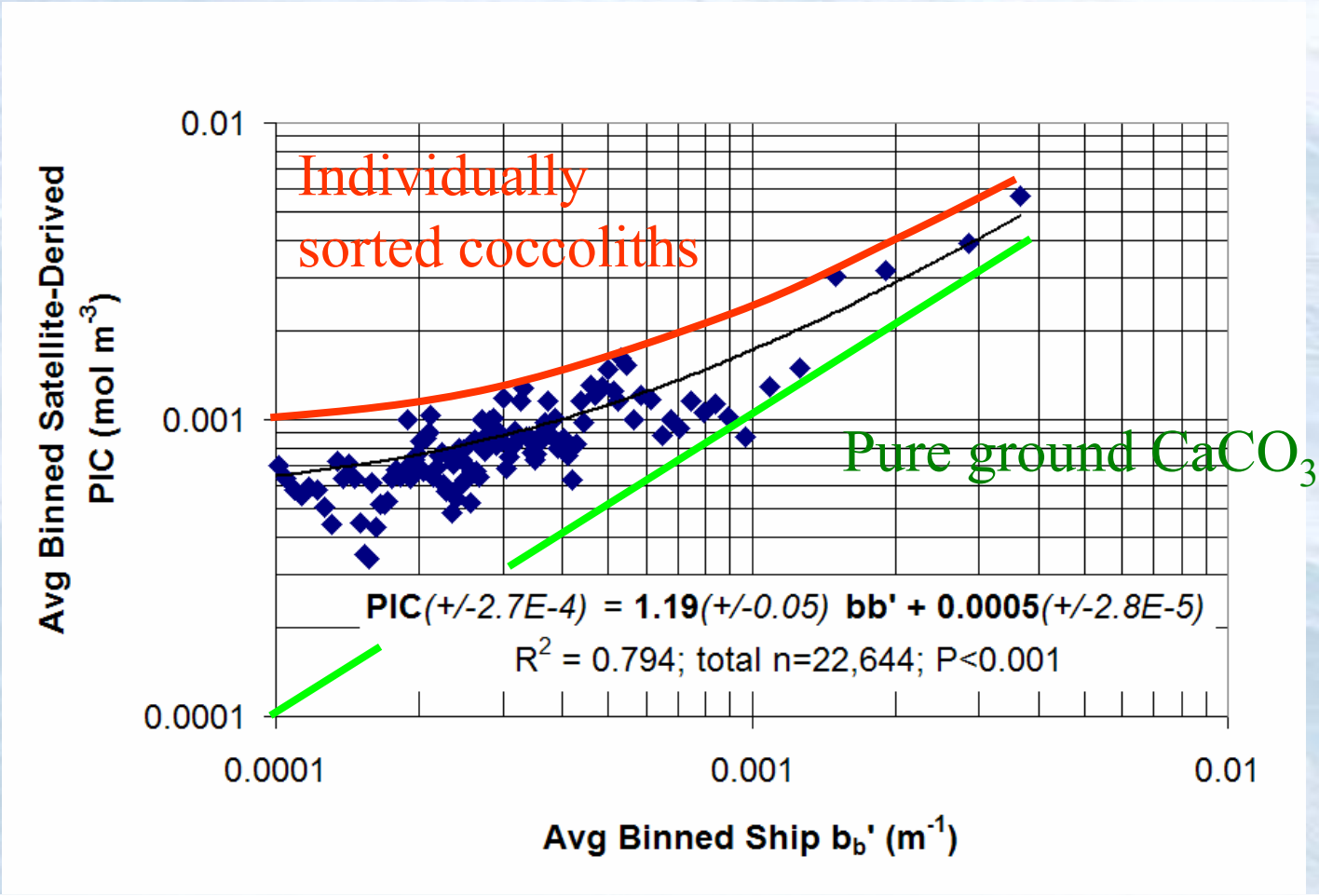
Global views: Important caveats

- The 2-band or 3-band PIC algorithm can be "fooled" by other scattering materials (e.g. error from scattering by suspended sediments or diatom frustules).
- Expected standard error for mean satellite-derived b_b is ~14.9 ug PIC $L^{-1}/(n^{1/2})$ based on 1km daily data.

SE of time/space binned PIC averages (ug C L^{-1})

Spatial res (km)	1	4.63	36	111.2
Time bins (d)				
1	14.900	3.218	0.414	0.134
7	5.632	1.216	0.156	0.051
30	2.720	0.588	0.076	0.024
365	0.780	0.168	0.022	0.007

Using our data base of ship measurements, it is straight forward to show how binning at 36km can make a huge difference. SE of the PIC estimate is ~ +/- 3ugPIC/l.

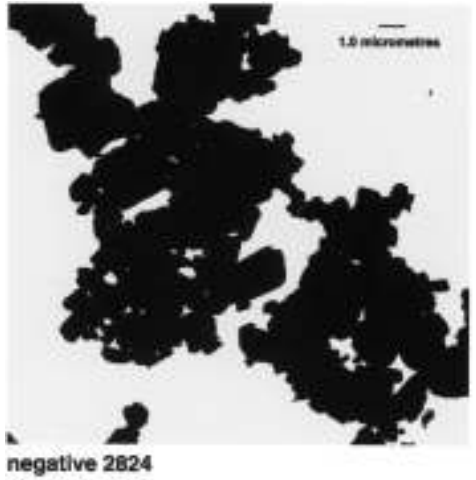


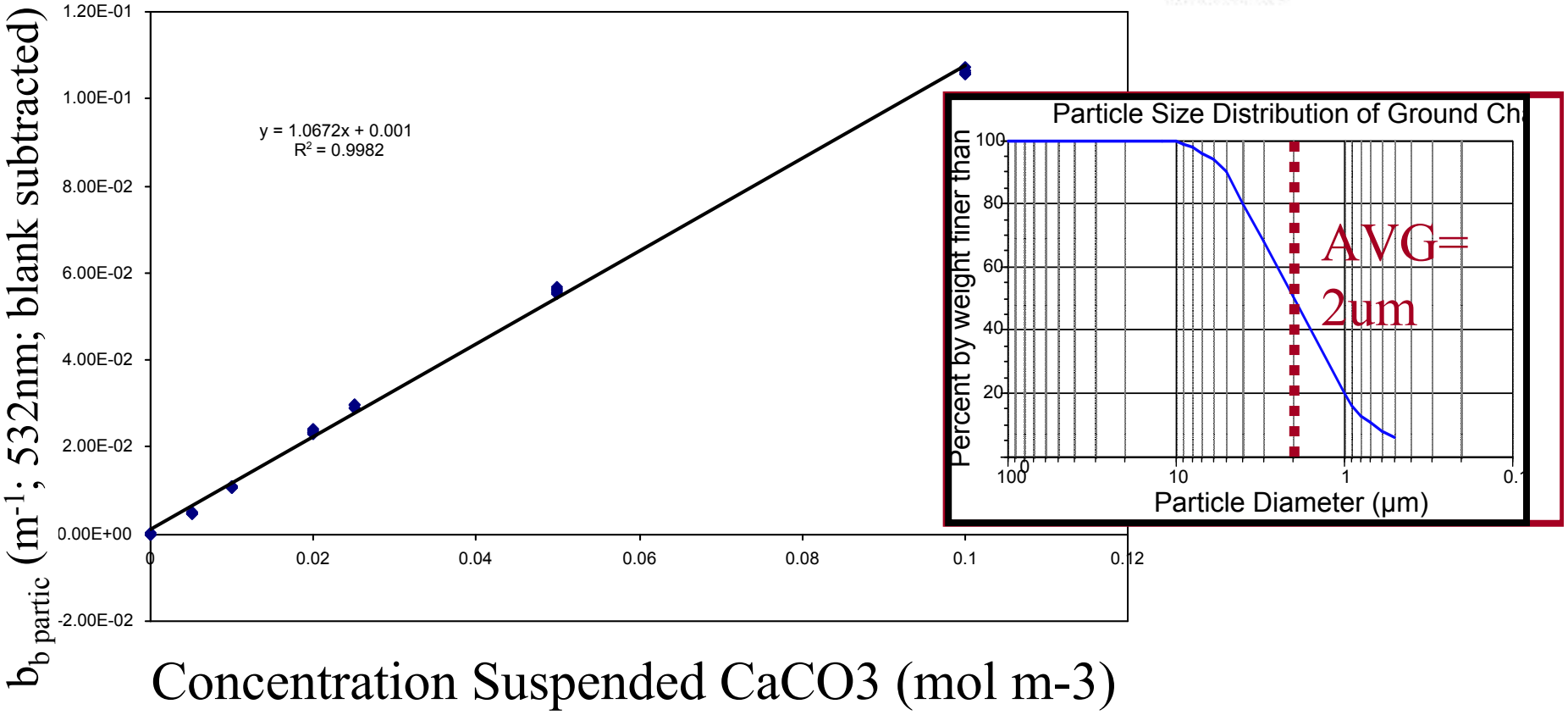
Still need some higher PIC concentrations: Chalk-ex

- Blooms are relatively rare events
- "Do it yourself coccolithophore bloom"
- It doesn't take much coccolith chalk to make a patch visible from space (13T)
- Could time deployments to clear-sky days…also gets over the problem of scheduling ships around rare bloom events!
- Essential for the EPA and Coast Guard environmental impact process that ¼ of all marine sediments on earth are chalk… we did deployments in regions of known cocco blooms as well as chalk-dominated sediments

Chalk concentration is highly correlated to its backscattering

Cretaceous chalk suspended in Filtered Sea Water





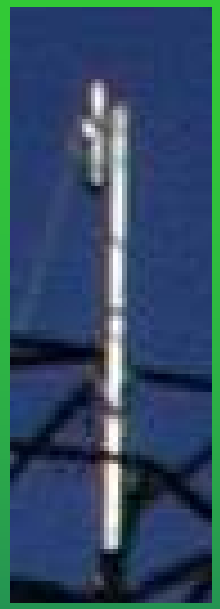
Loading Chalk In Portland, ME

Chalk spreading; steaming in an expanding ellipse, 1.5 x 0.5 km over 4h

Completed patch

Aerial balloon images from patch#2

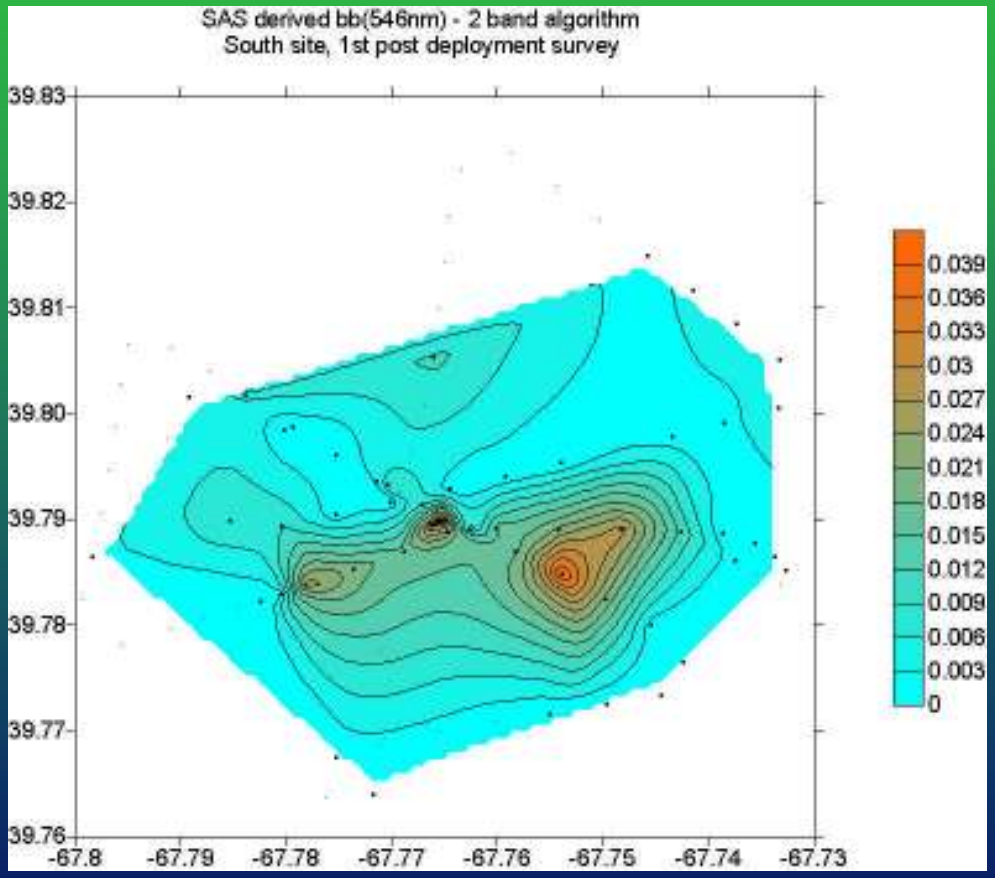
Satlantic radiometers on *R/V Endeavor*



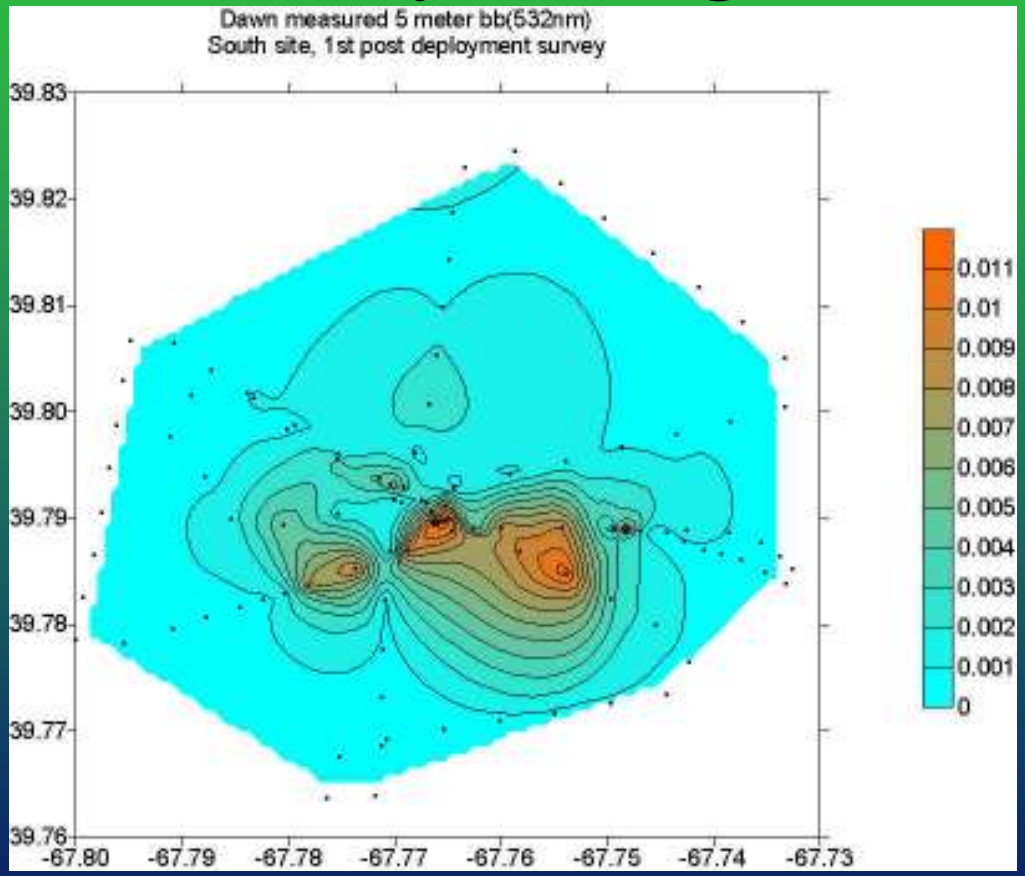
Ed (λ) sensor

Lu(λ) and Lsky (λ) sensors

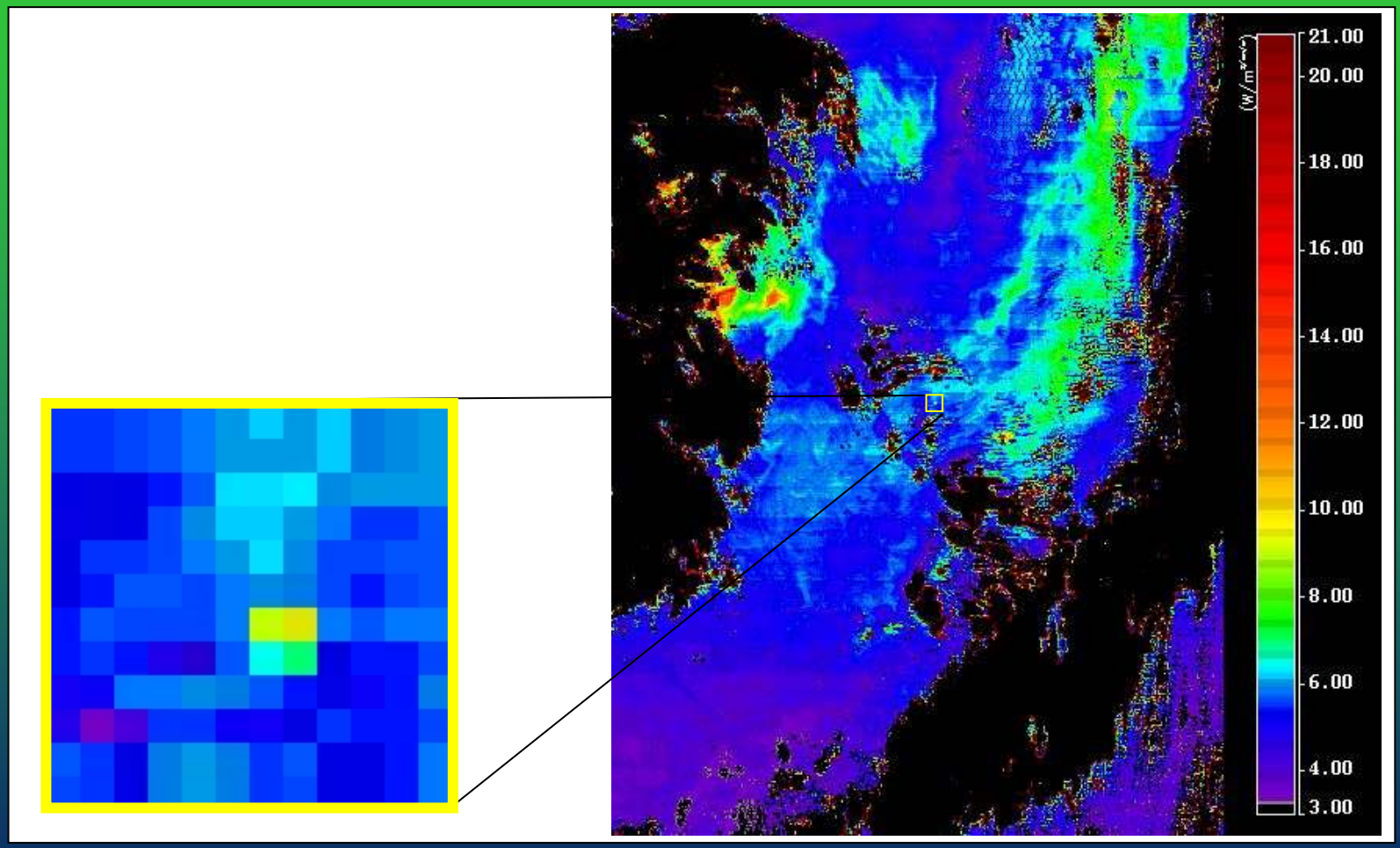
Post-Chalk Survey 1; Estimates of backscattering made from above-water radiance measurements ($b_{b546\ SAS}$)



Post-Chalk Survey 1; Shipboard measurements ($b_{b532\ Wyatt}$) made continuously using 5m water

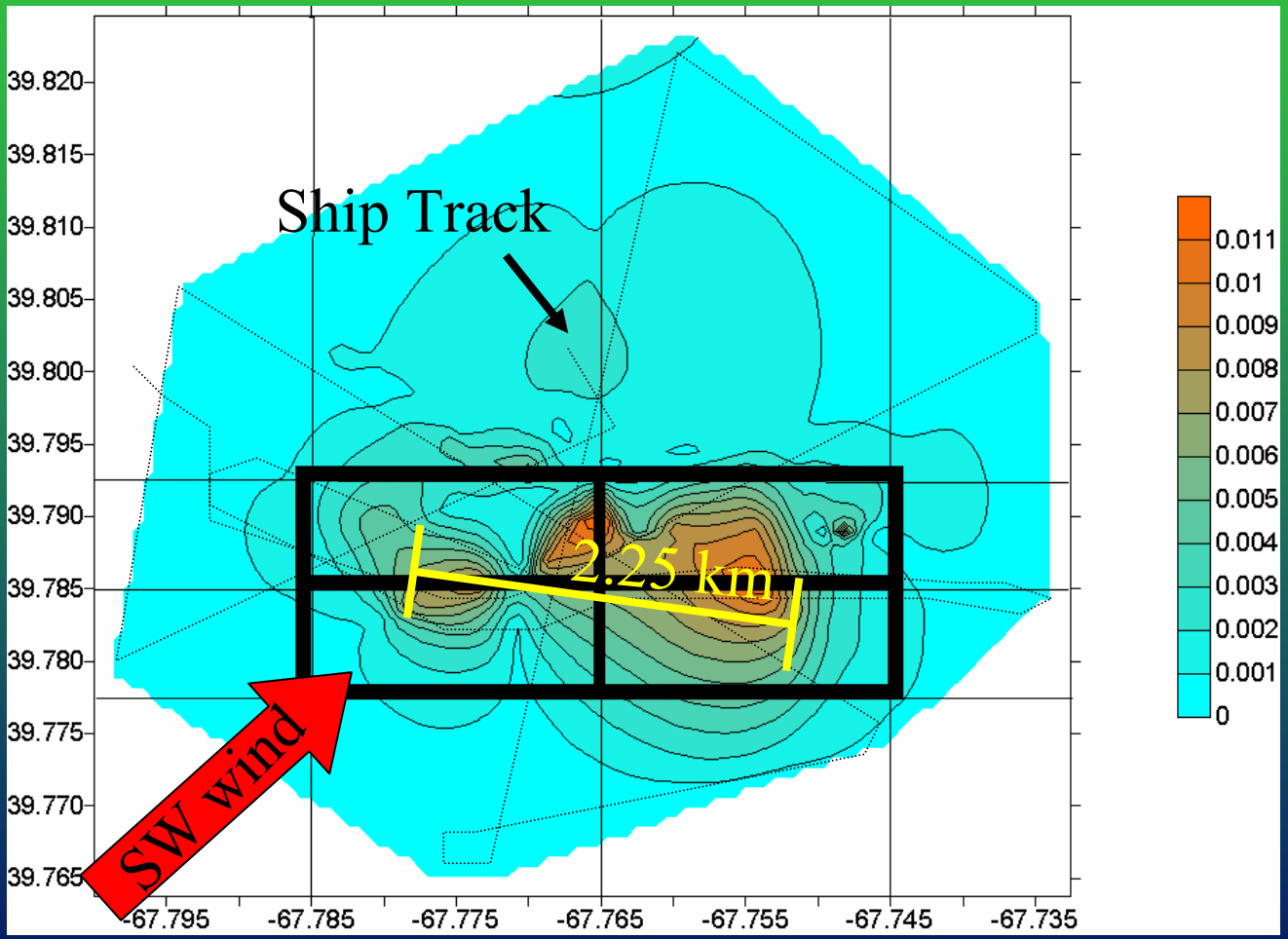


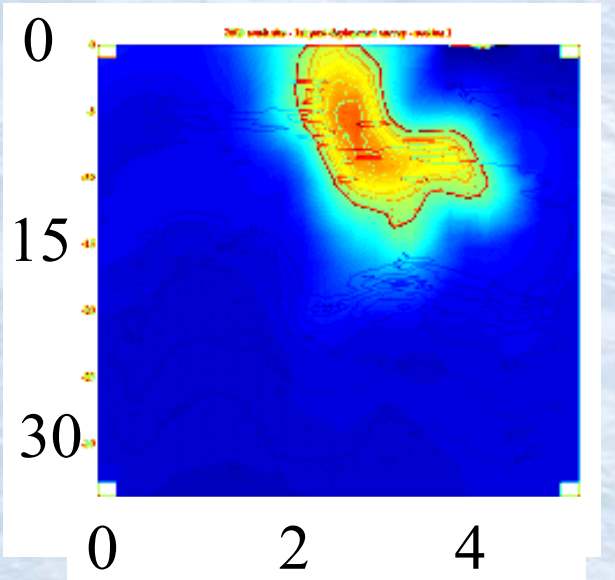
MODIS view of Chalk-Ex Patch #2: 551nm, 1Km data, 15 November 2001

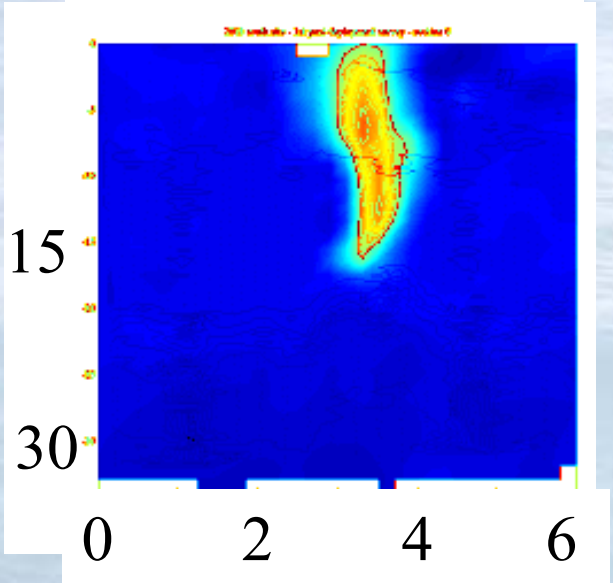


Two highest nLw pixels: 39.81°N x 67.78°W (9.04 W m^{-2} um^{-1} sr^{-1})
39.80°N x 67.76°W (9.47 W m^{-2} um^{-1} sr^{-1})

Ship-measured/contoured surface b_b showing four most intense MODIS pixels

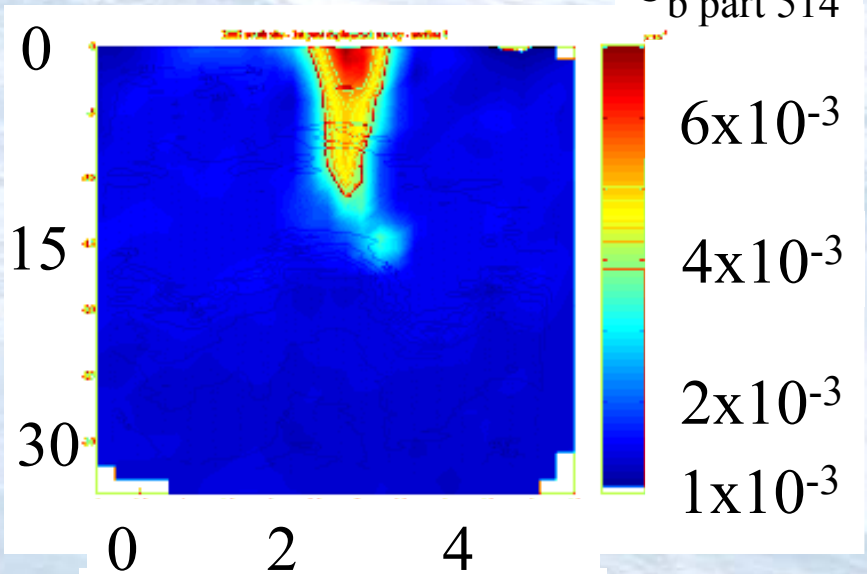






Depth (m)

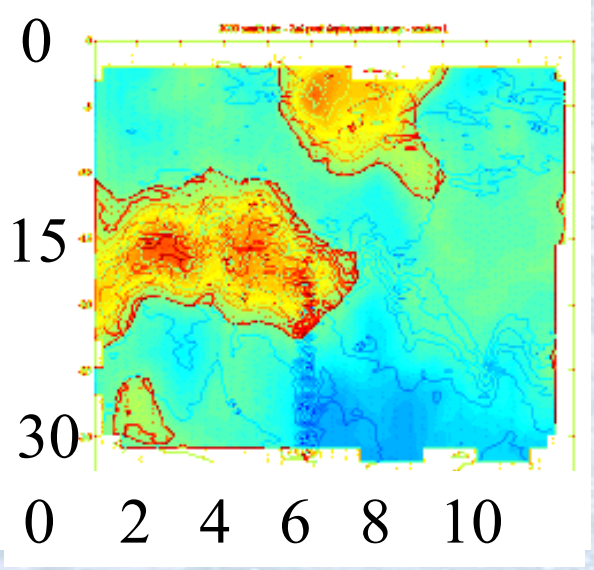
Distance (km)

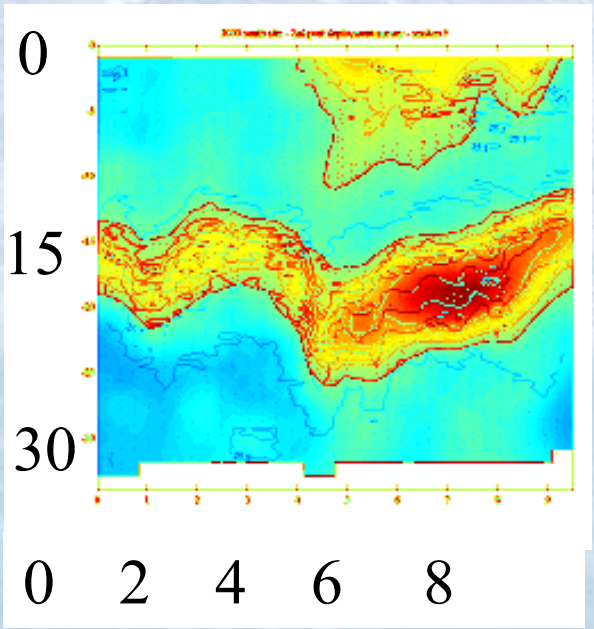


Distance (km)

South Patch 2003; Survey 1 Sections

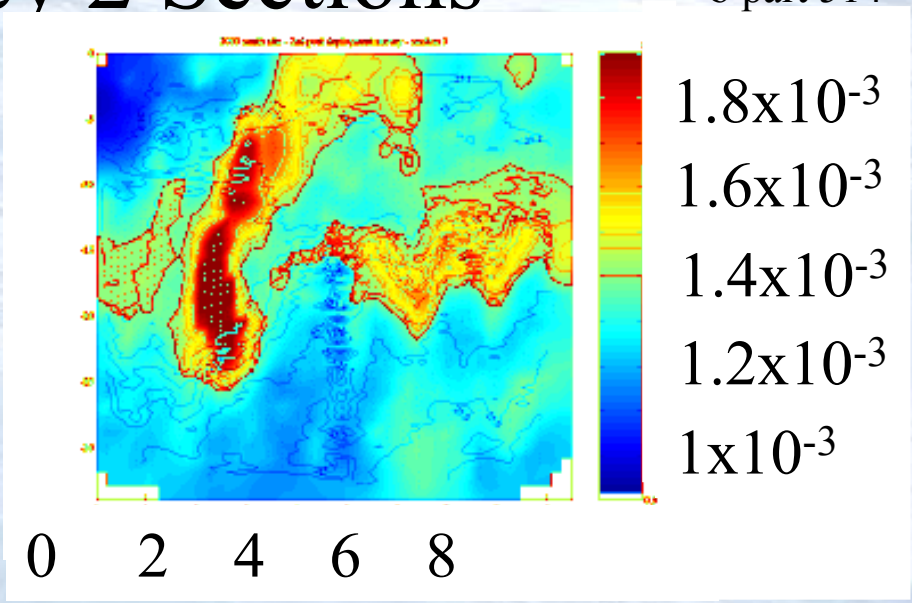
South Patch 2003: Survey 2 Sections





Depth (m)

Distance (km)



We succeeded in producing "thin-layers" using inanimate chalk particles!

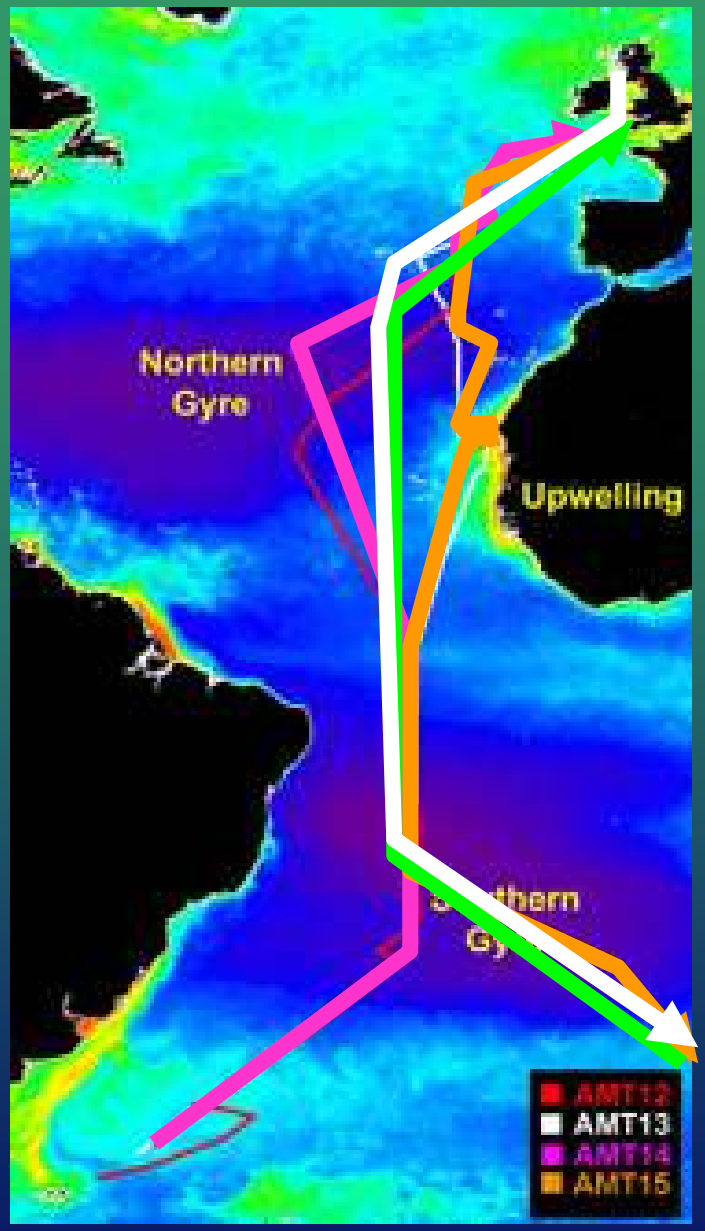
For more representative data from the central ocean, we participated in several 45 day cruises over the last two years. The U.K. Atlantic Meridional Transect Cruises :

AMT-14(May-June '04)

AMT 15 (Sept-Oct '04

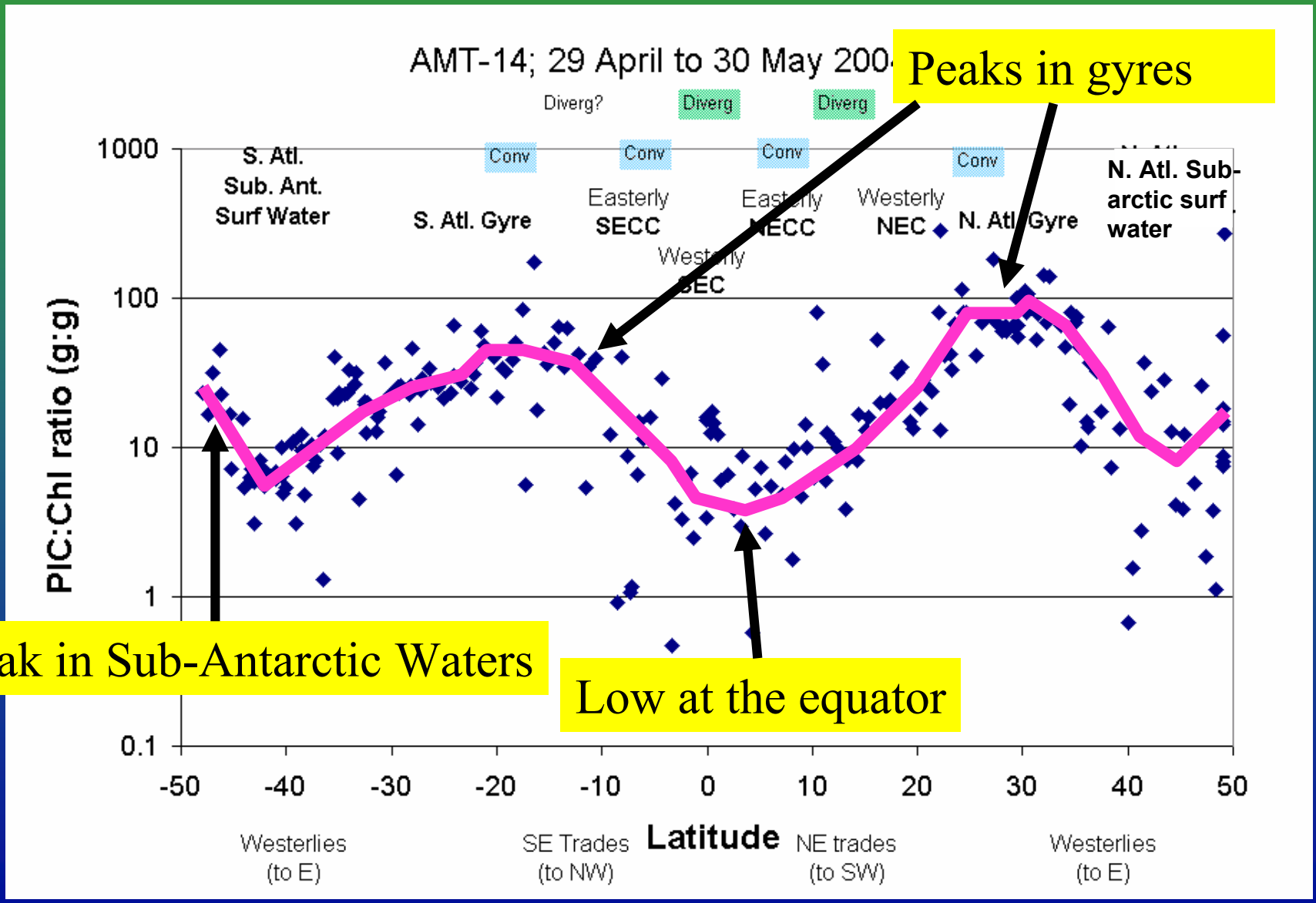
AMT16 (May-June '05)

AMT 17 (Oct-Nov. 05)

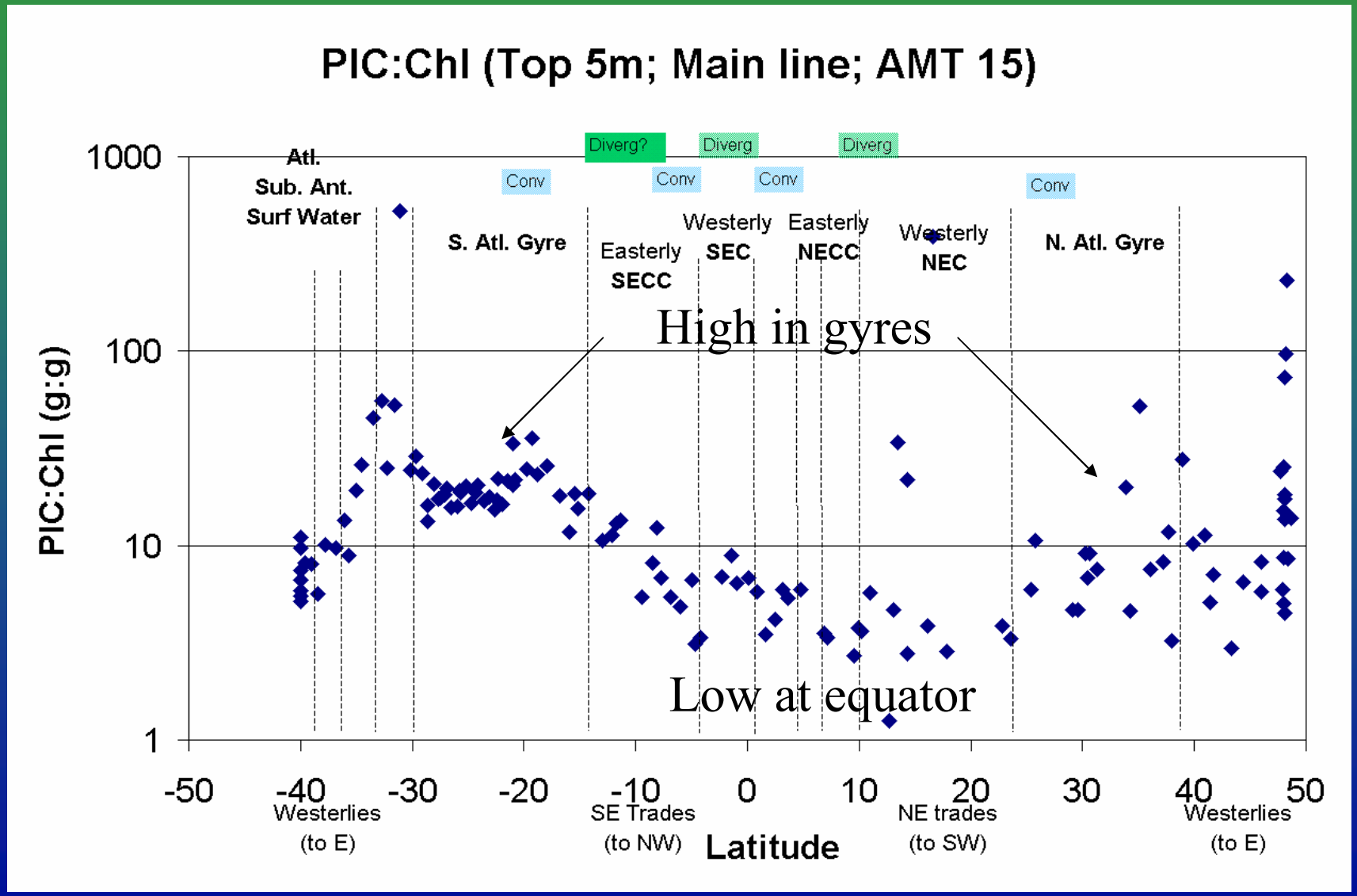


Many thanks to our British colleagues who allowed our participation…Dr. PM Holligan, Dr. Carol Robinson

Note the ratio of the two optically-active molecules, chlorophyll and PIC, here plotted on a log scale…

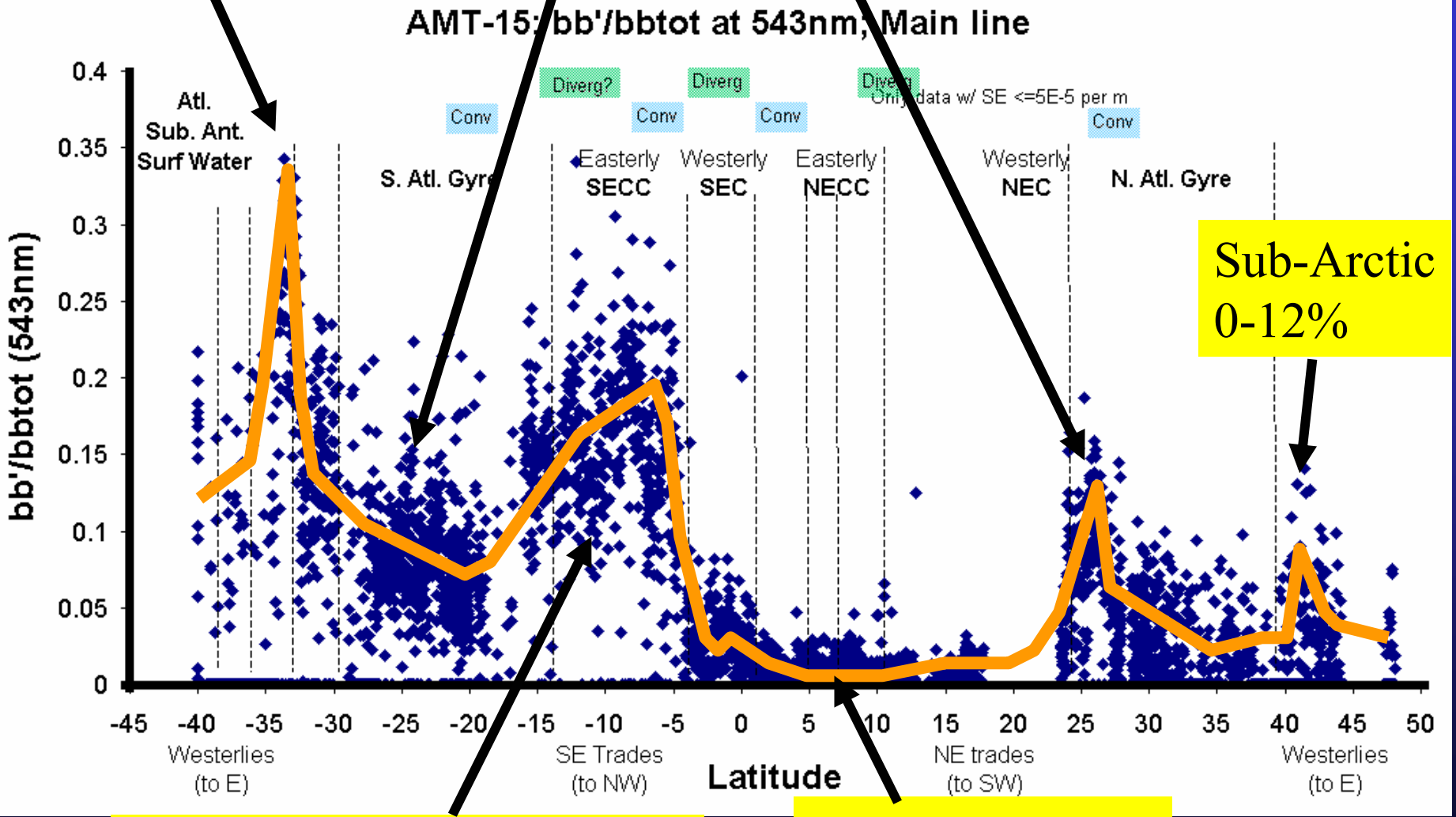


AMT 15: Again notice the high values in the gyres!



b_b' is up to 5-35% of b_{btot}

S. and N. Atl Gyre 0-20%

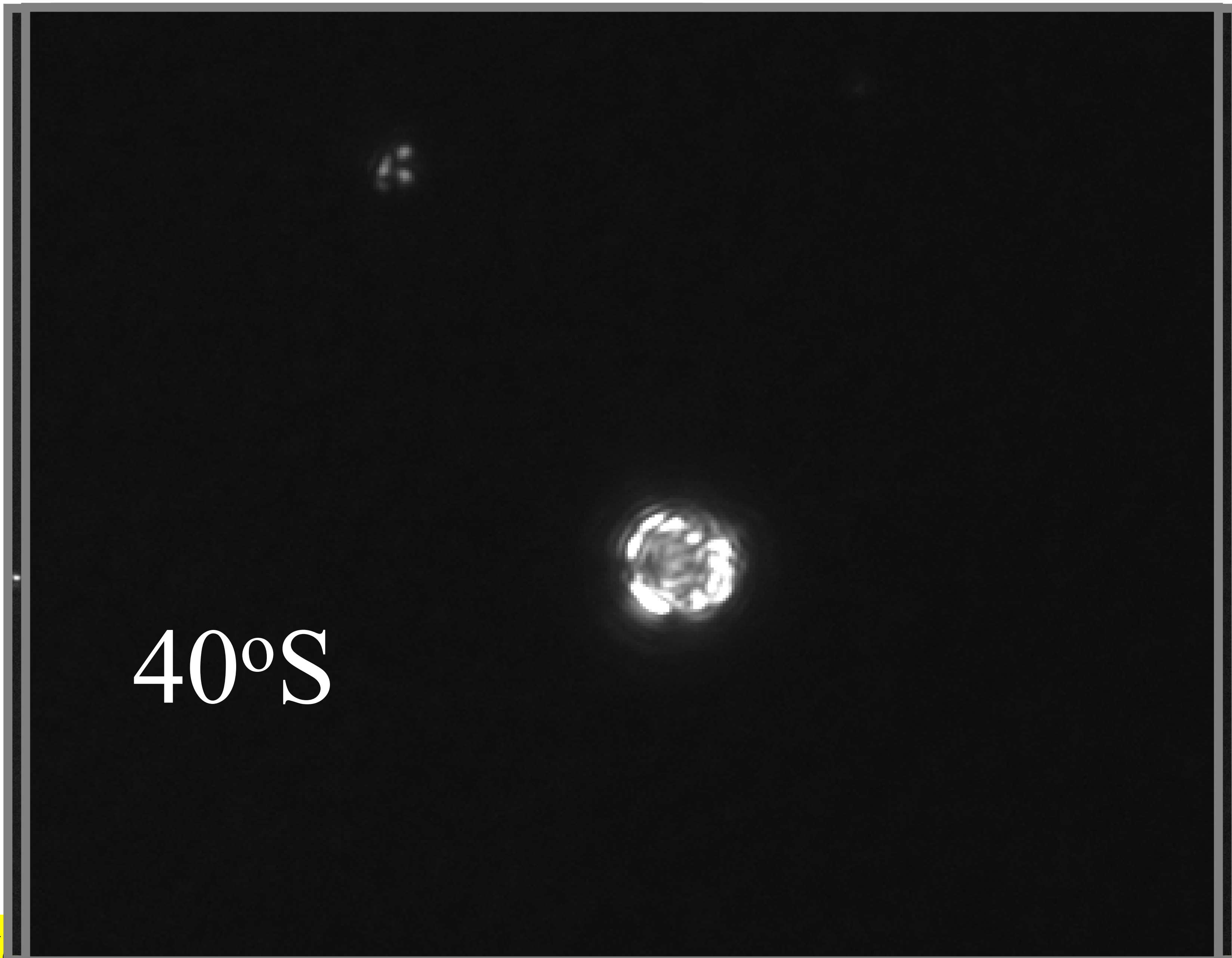


Sub-Arctic 0-12%

In SECC values of 10- 30%

5°S to 18°N <5%

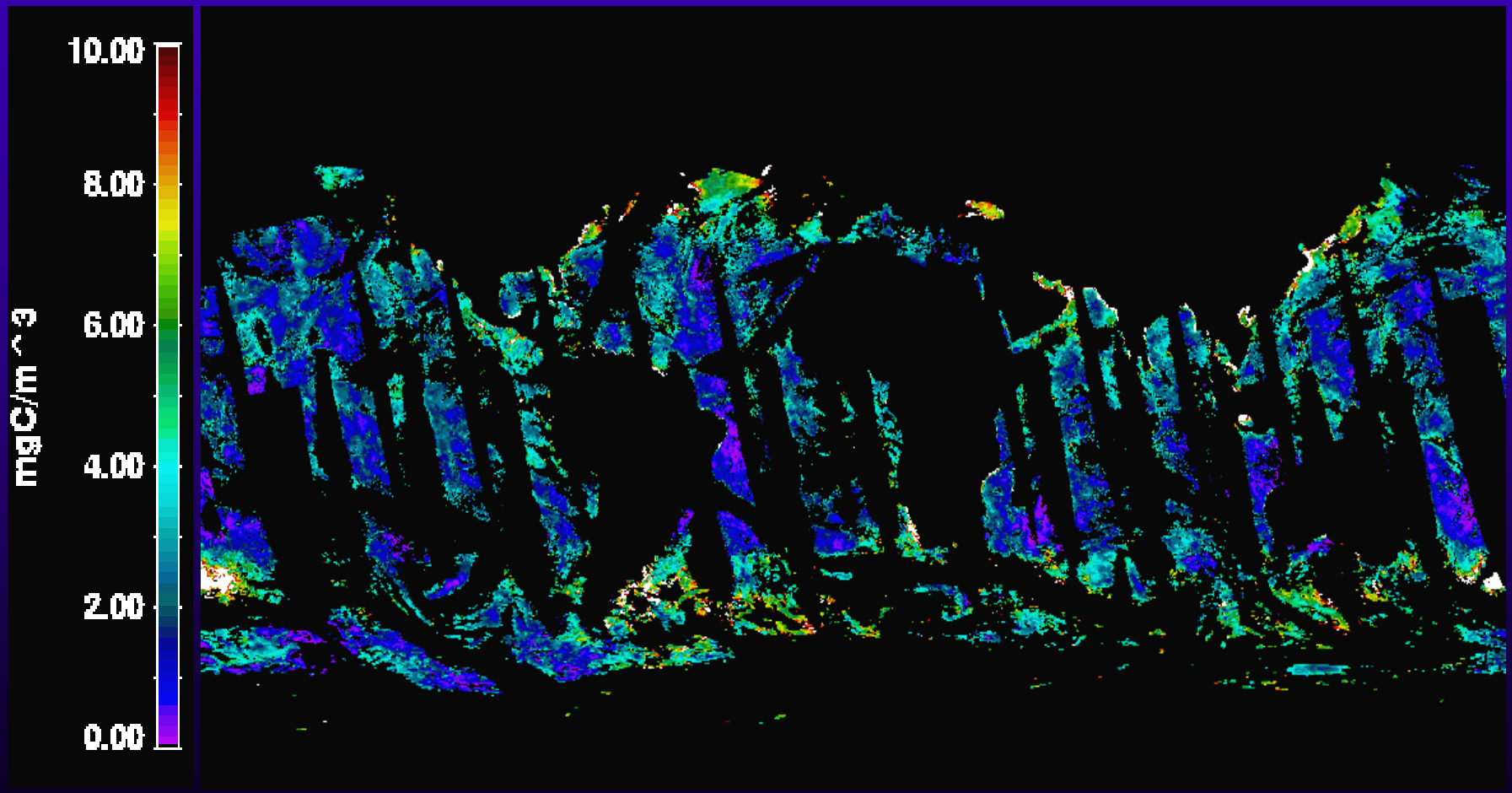
Log (Particles+0.1; per mL)



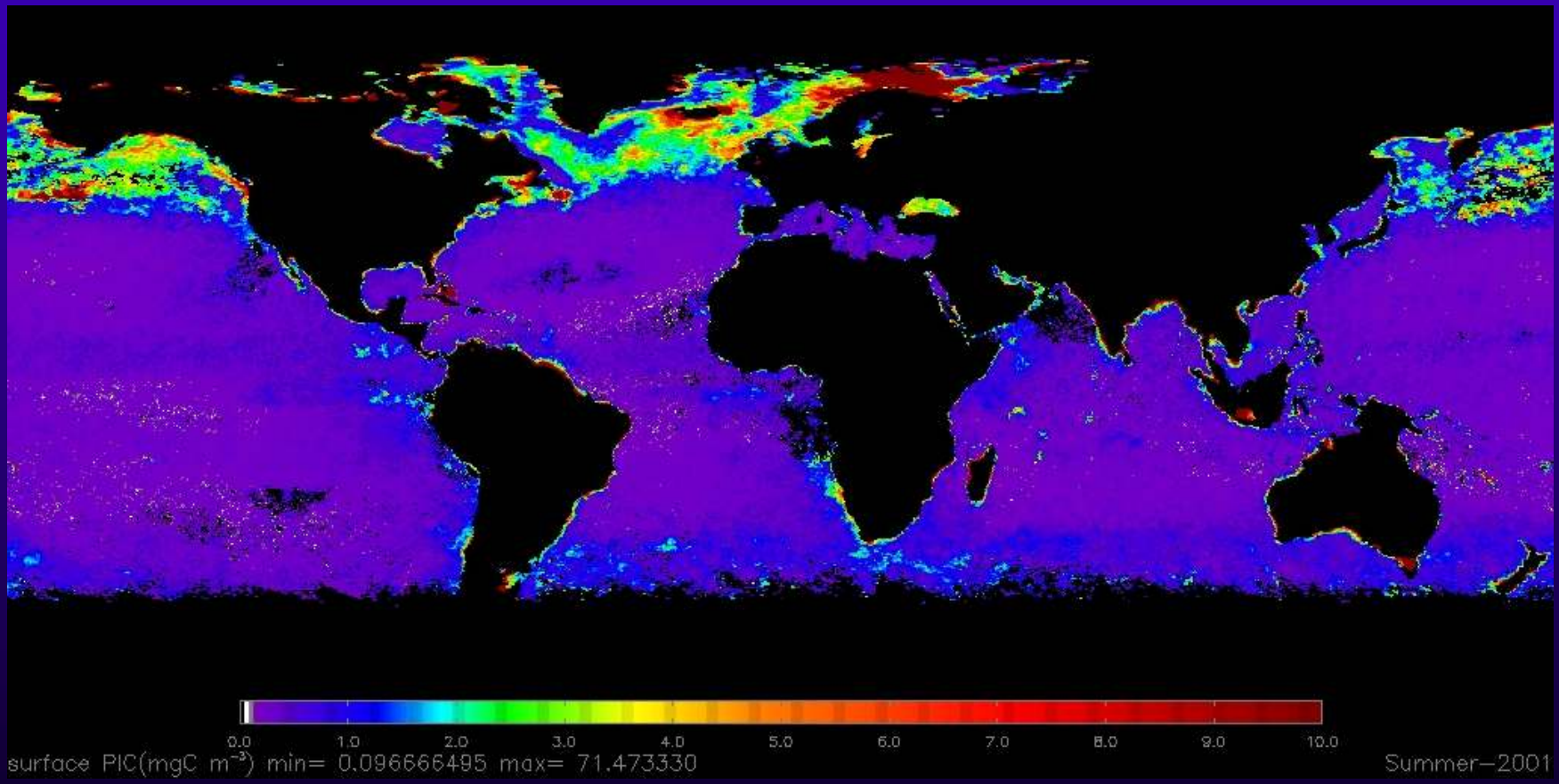
"True

n Limit
count"

An even larger perspective…Global calcite-Example Aqua; 8 November 2004

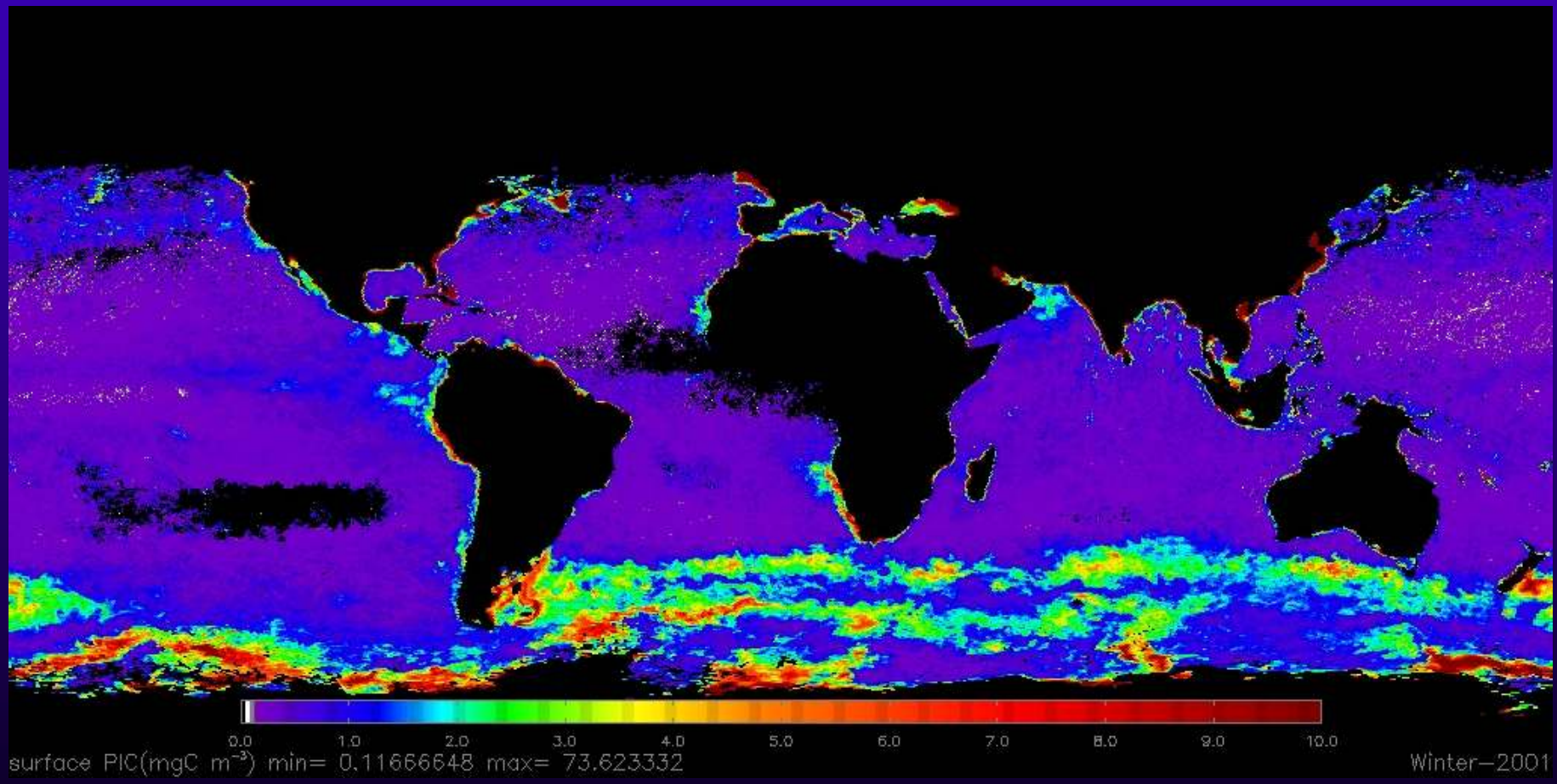


Global calcite- July-Sept



Balch; Bigelow Lab

Southern hemisphere summer- Jan-Mar



Balch; Bigelow Lab

A quantitative summary of global PIC imagery

Integrated PIC over Euph. Zone

Biome	***Jan-Mar***	**Tot PIC Mt**	**% Total**	**Avg Int.PIC (mg/m2)**	**PIC:POC**
Polar		2.41	12.3	91.3	0.040
Westerlies		7.70	39.4	67.0	0.033
Trades		6.41	32.8	51.0	0.026
Coastal		2.99	15.3	134.3	0.062
Total		19.55	100.0	88.4	0.048
	July-Sept				
Polar		2.14	11.4	172.5	0.067
Westerlies		6.58	35.2	106.0	0.057
Trades		6.57	35.1	51.8	0.025
Coastal		3.38	18.1	116.9	0.052
Total		18.70	100.0	99.5	0.051

…or "x10^{12}g PIC"

Plug:

Global PIC budgets can be found in our paper in *Journal Geopysical Research*

JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 110, C07001, doi:10.1029/2004JC002560, 2005

Calcium carbonate measurements in the surface global ocean based on Moderate-Resolution Imaging Spectroradiometer data

W. M. Balch
Bigelow Laboratory for Ocean Sciences, West Boothbay Harbor, Maine, USA

Howard R. Gordon
Physics Department, University of Miami, Coral Gables, Florida, USA

B. C. Bowler, D. T. Drapeau, and E. S. Booth
Bigelow Laboratory for Ocean Sciences, West Boothbay Harbor, Maine, USA

Worlds shortest feature movie (5s)

“Revenge of the coccolith”

Summary

- Ocean calcite from coccolithophores has important biogeochemical ramifications to the biological pump and is a major part of the global carbon cycle
- Ocean calcite is an important source of light scattering in the sea, regularly contributing 20-30% of particulate backscattering
- It is feasible to quantify PIC from space provided space-time binning is used
- Global ocean acidification is rapidly becoming a major environmental issue with respect to the calcifying plants
- No need to have “POC envy”!

Acknowledgements

- Many discussions about coccolithophores, their optics and biogeochemistry with Dr. Patrick Holligan, Dr. Howard Gordon, Dr. Ken Voss, Dr. John Milliman, Dr. Bob Evans
- Expert technical support-Bruce Bowler, Dave Drapeau, Emily Booth, Laura Windecker.
- Algorithm implementation: Sean Bailey, Brian Franz, Kay Kilpatrick, Jim Brown, Gene Feldman
- Captains and crews of the many vessels that we have sailed on, *M/S Scotia Prince, R/V Cape Hatteras, R/V Endeavor, R/V Thomas Thompson, R/V Revelle, RRS Discovery*
- Funding generously provided by NASA, NSF and ONR


Thank you!