

Ocean Carbon & Biogeochemistry

*Studying marine biogeochemical cycles
and associated ecosystems
in the face of environmental change*

OCB OCEAN ACIDIFICATION SHORT COURSE

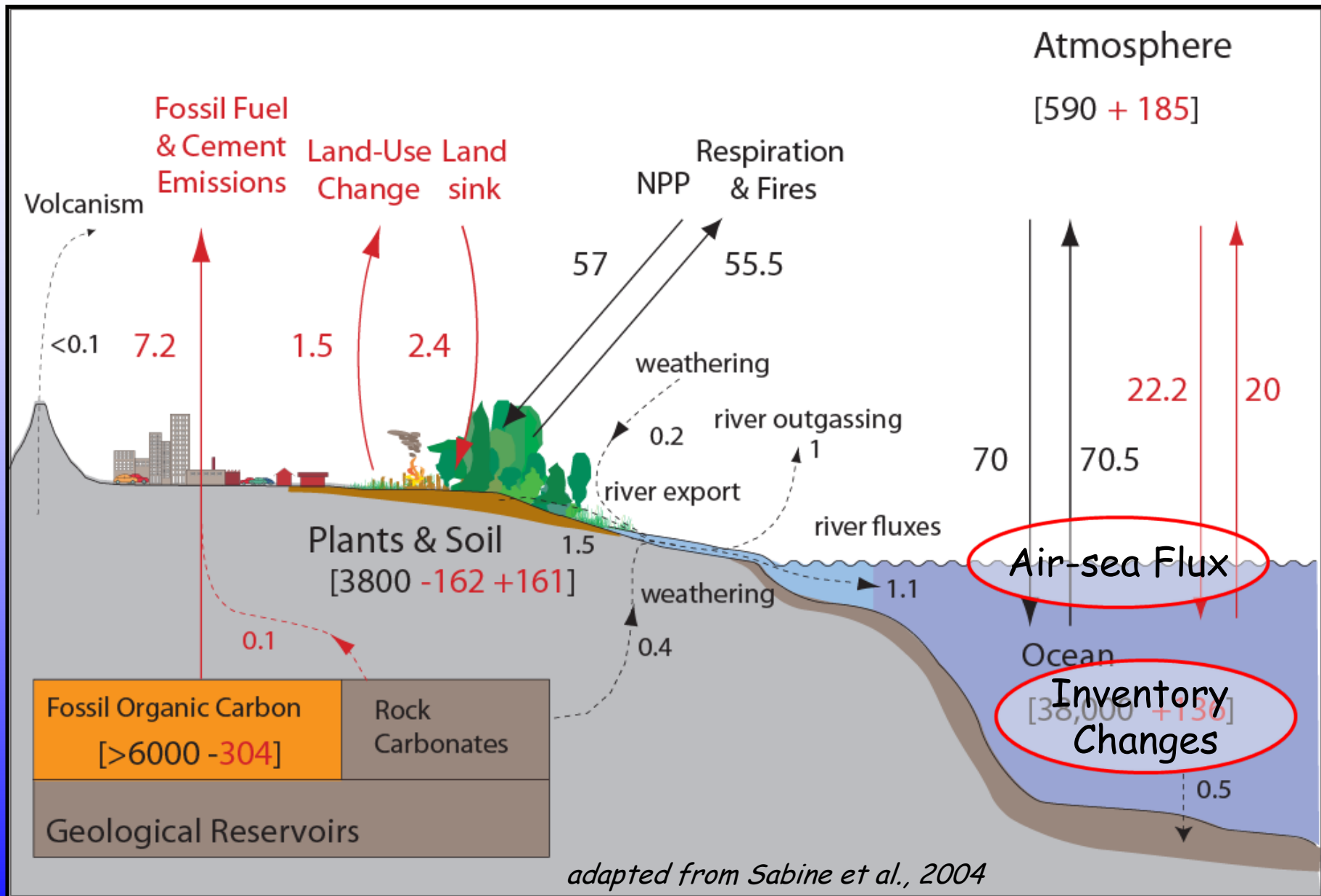
NOVEMBER 2-13, 2009

Overview of Marine Carbon System

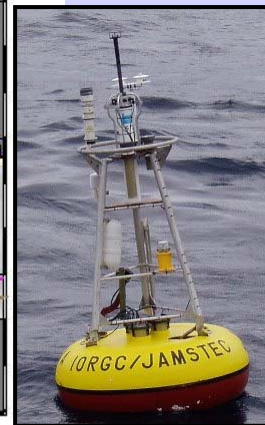
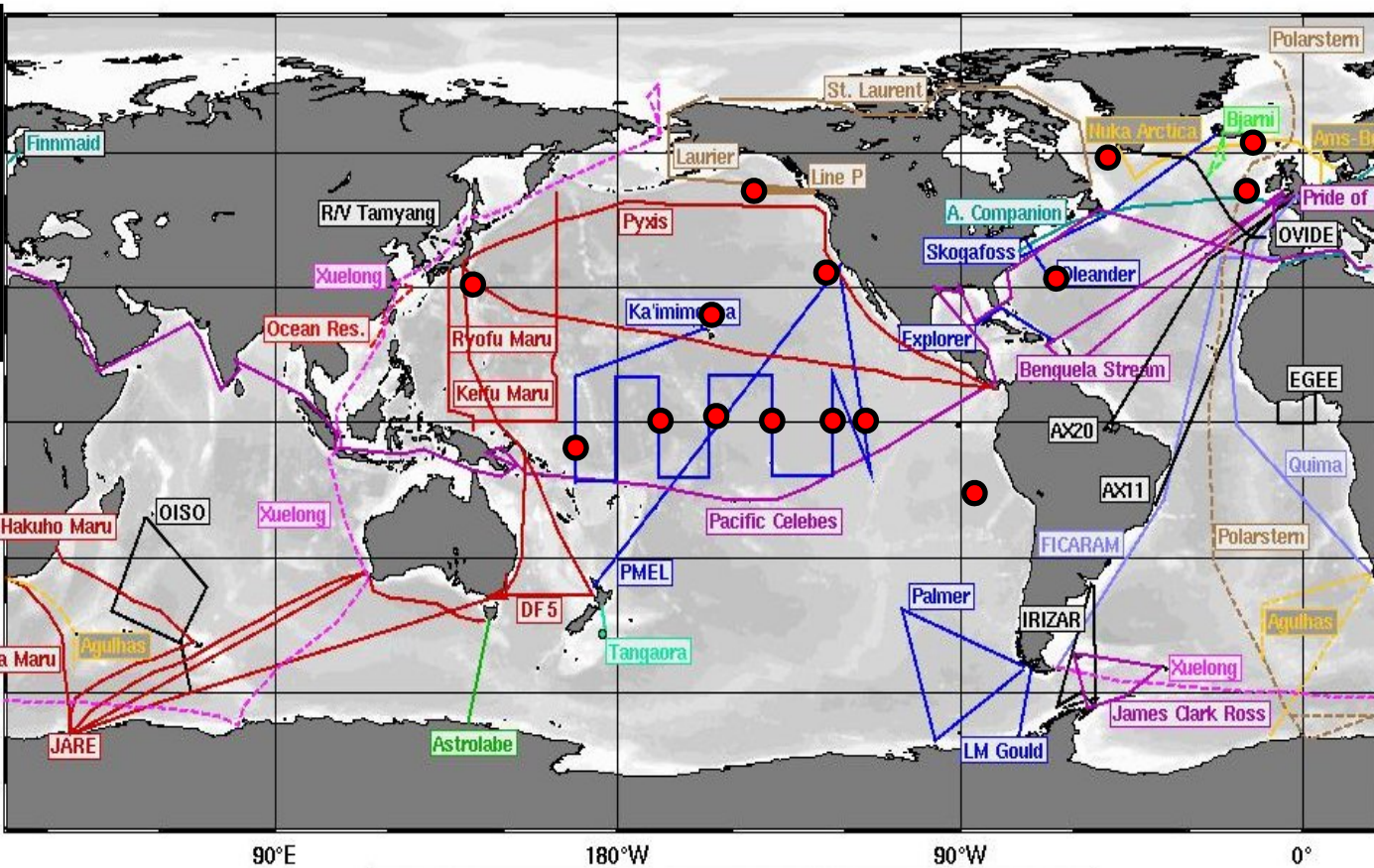
Christopher L. Sabine (NOAA/PMEL)



Global Carbon Budget for 2000-2005



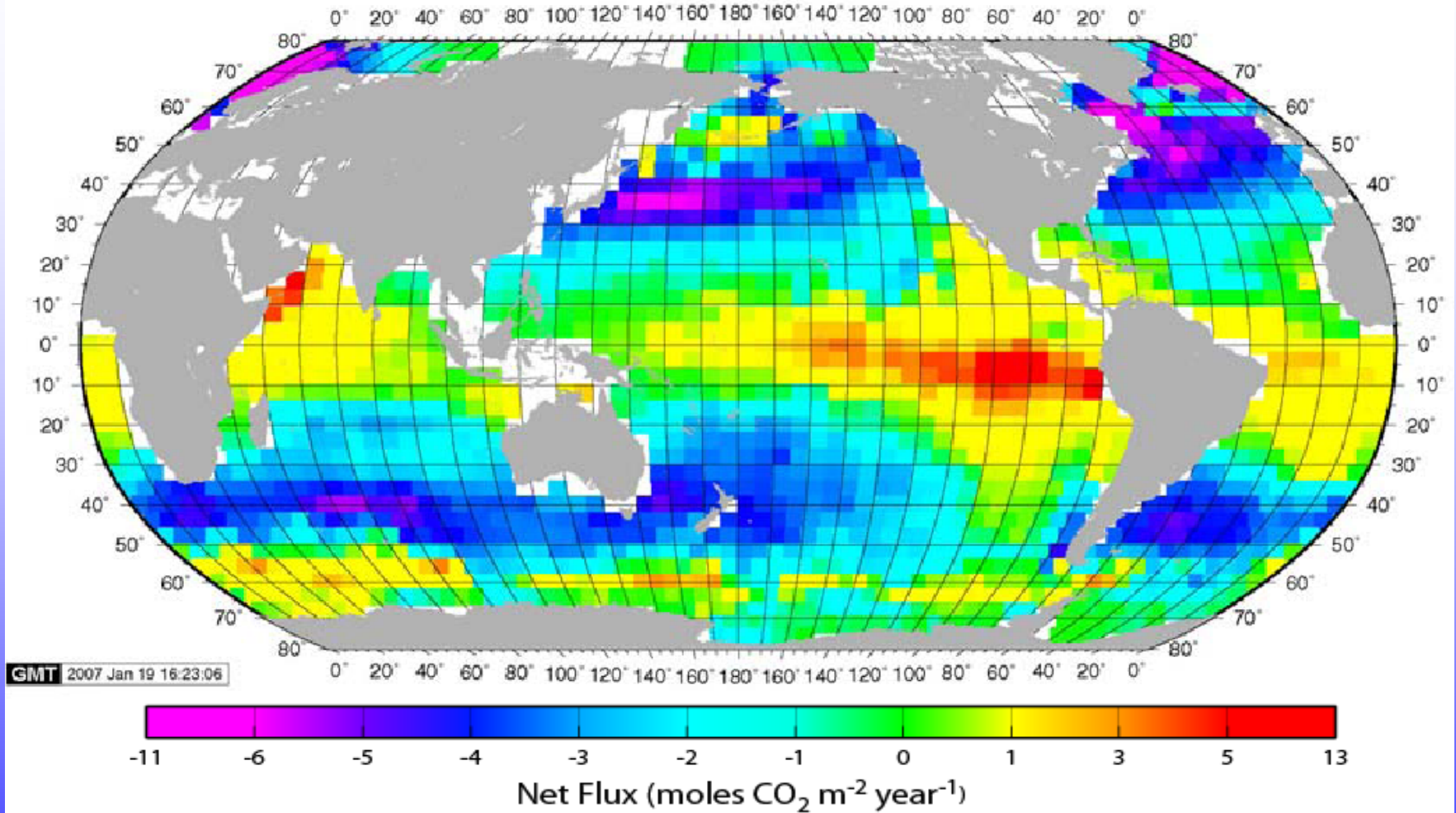
Surface CO₂ observation network



— US	— France	— Canada	— New Zealand
— Japan	— Germany	— Spain	— China
— UK	— Australia	— Norway	— Taiwan
— Iceland	— Netherlands	— Korea	— South Africa

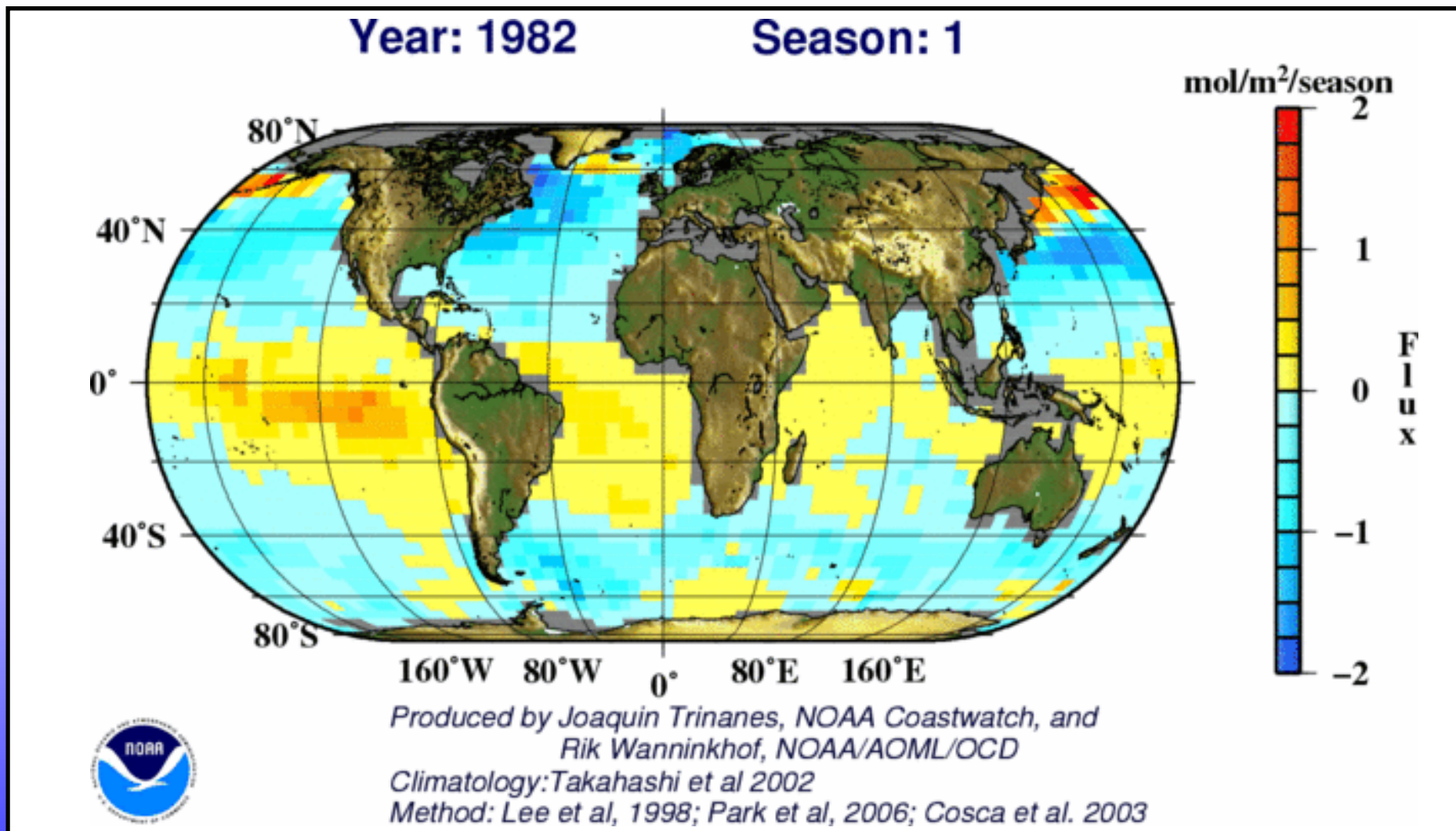


Takahashi climatological annual mean air-sea CO_2 flux for reference year 2000



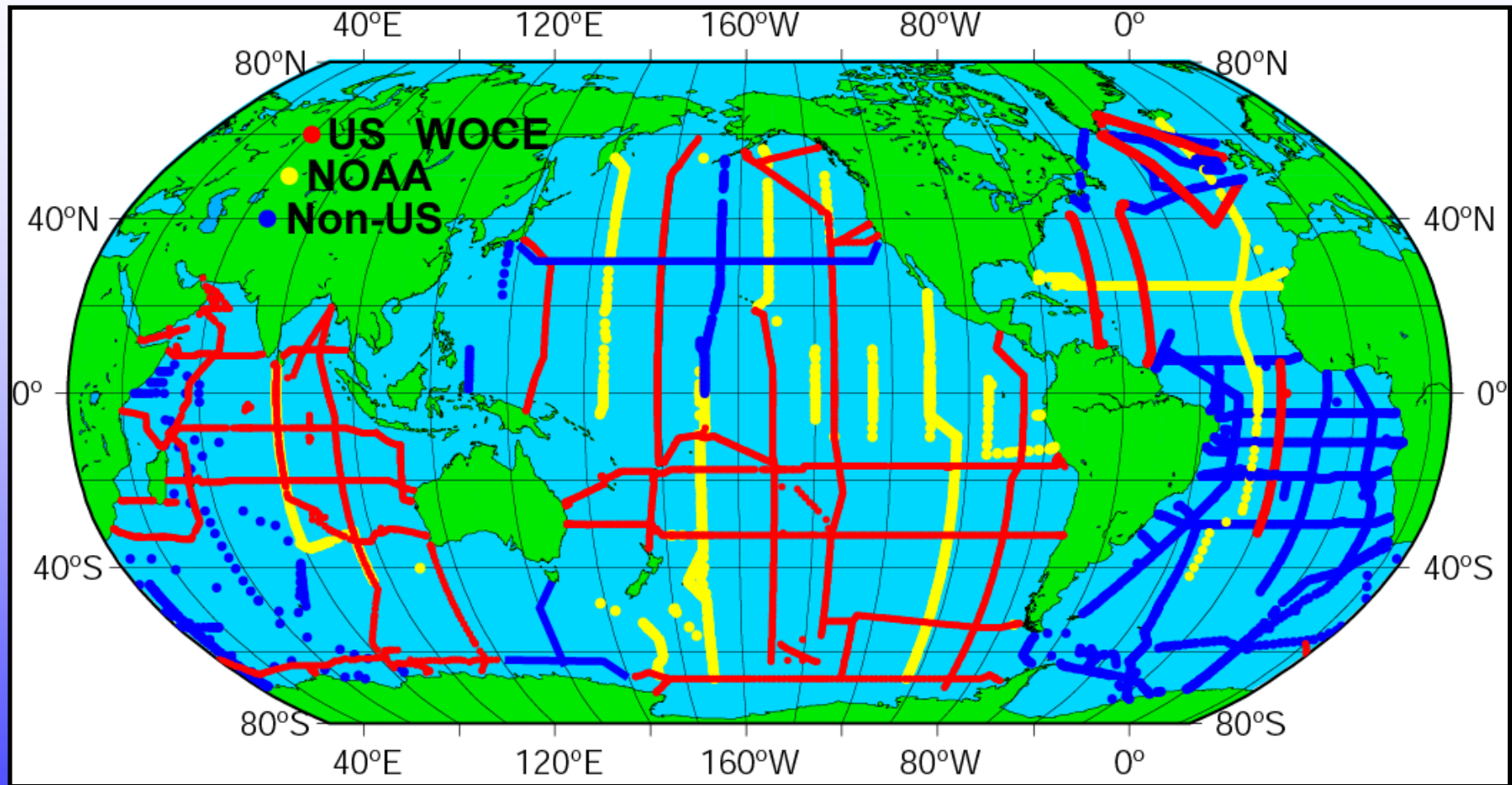
Based on ~3 million measurements since 1970 and
NCEP/DOE/AMIP II reanalysis.
Global flux is $1.4 \pm 0.7 \text{ Pg C/yr}$

Global Flux Map suggests an interannual variability of 0.23 Pg C



Surface observations have large variability over a wide range of time and space scales making it very difficult to properly isolate the anthropogenic increases. Uptake of 2 Pg C yr⁻¹ only requires a $\Delta p\text{CO}_2$ of 8ppm.

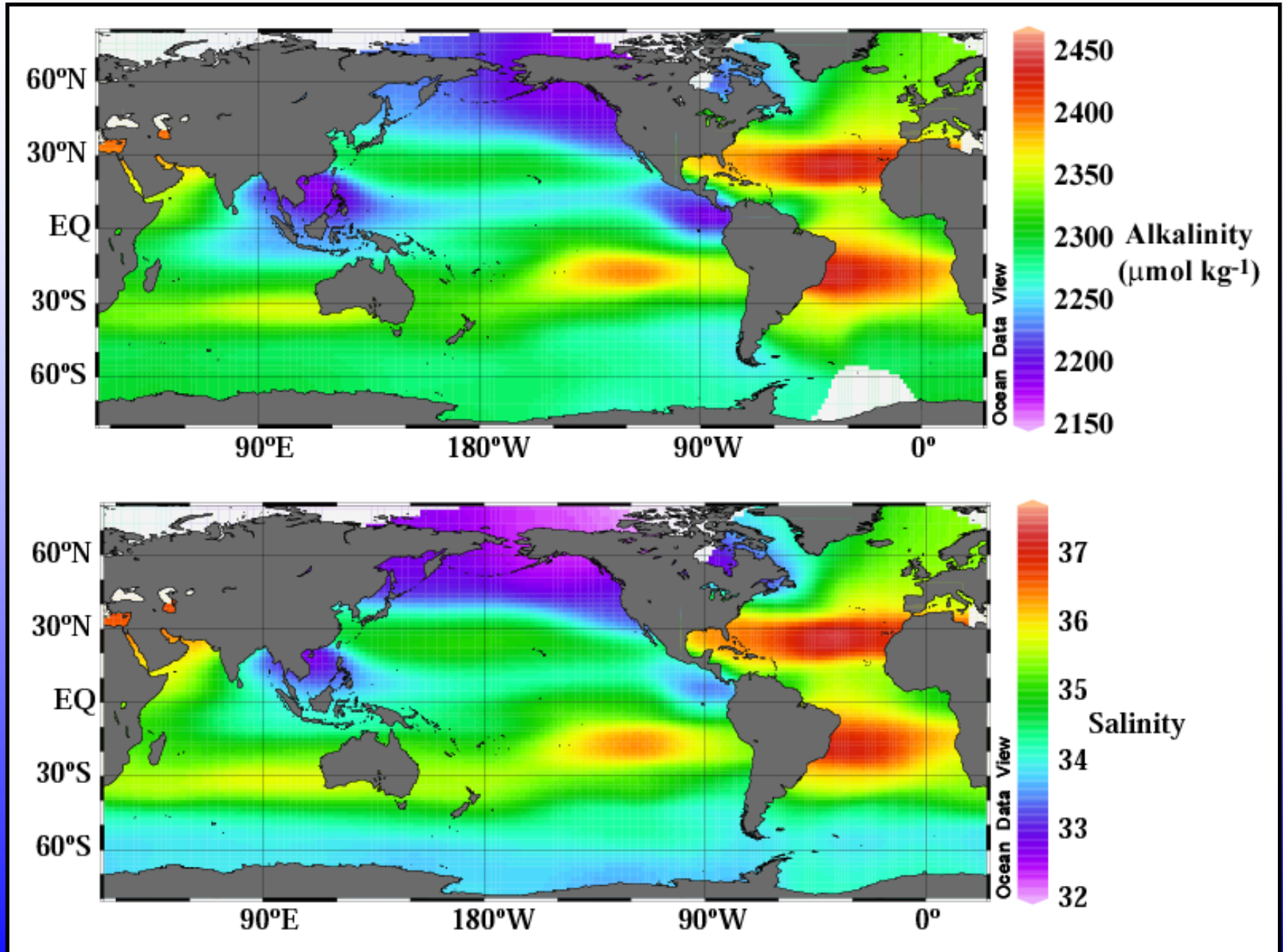
In the early 1990s the World Ocean Circulation Experiment (WOCE), the Joint Global Ocean Flux Study (JGOFS), and the NOAA/OACES program joined forces to conduct a global survey of CO_2 in the oceans.



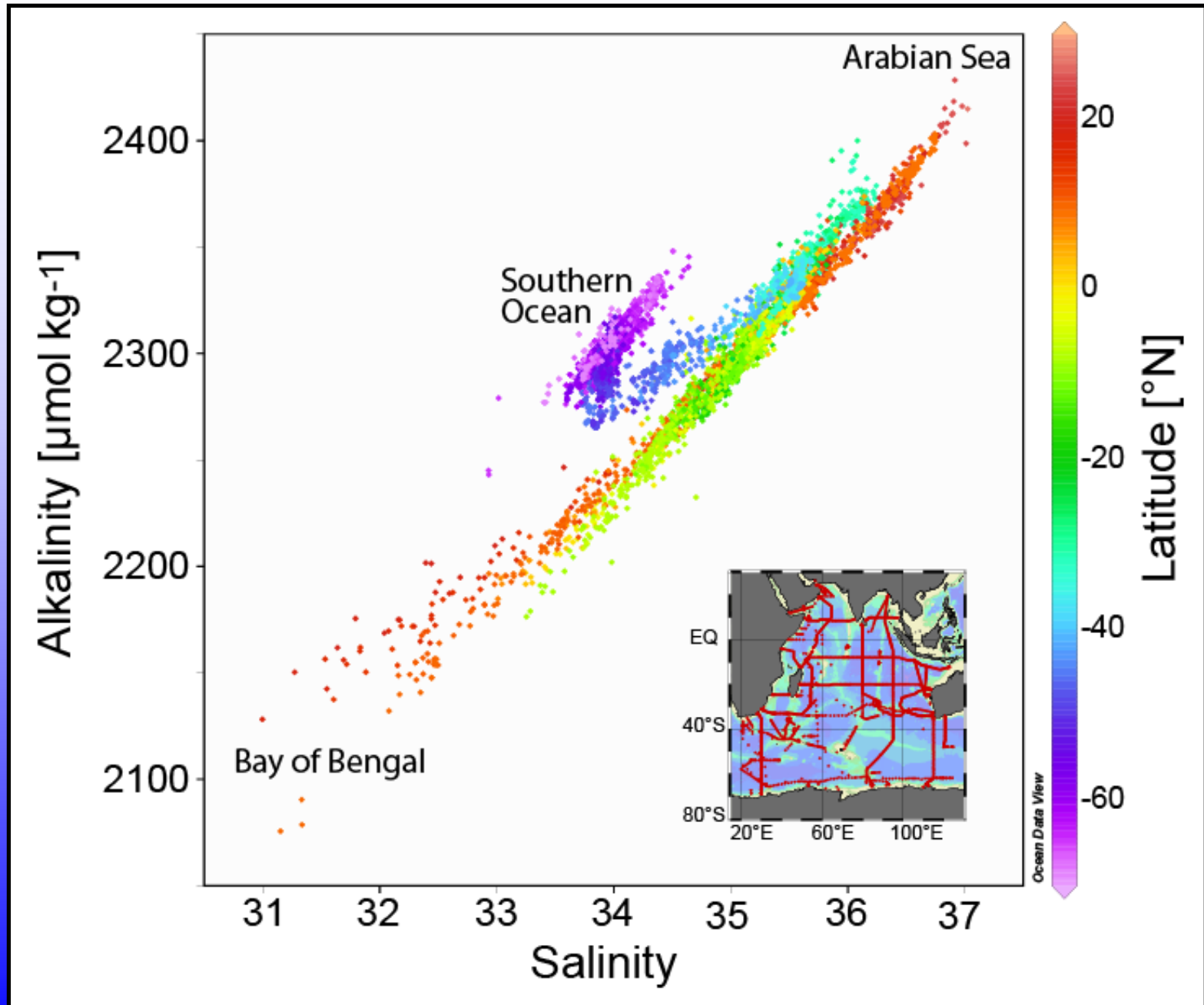
>70,000 sample locations; $\text{DIC} \pm 2 \mu\text{mol kg}^{-1}$; $\text{TA} \pm 4 \mu\text{mol kg}^{-1}$

http://cdiac.esd.ornl.gov/oceans/glodap/Glodap_home.htm

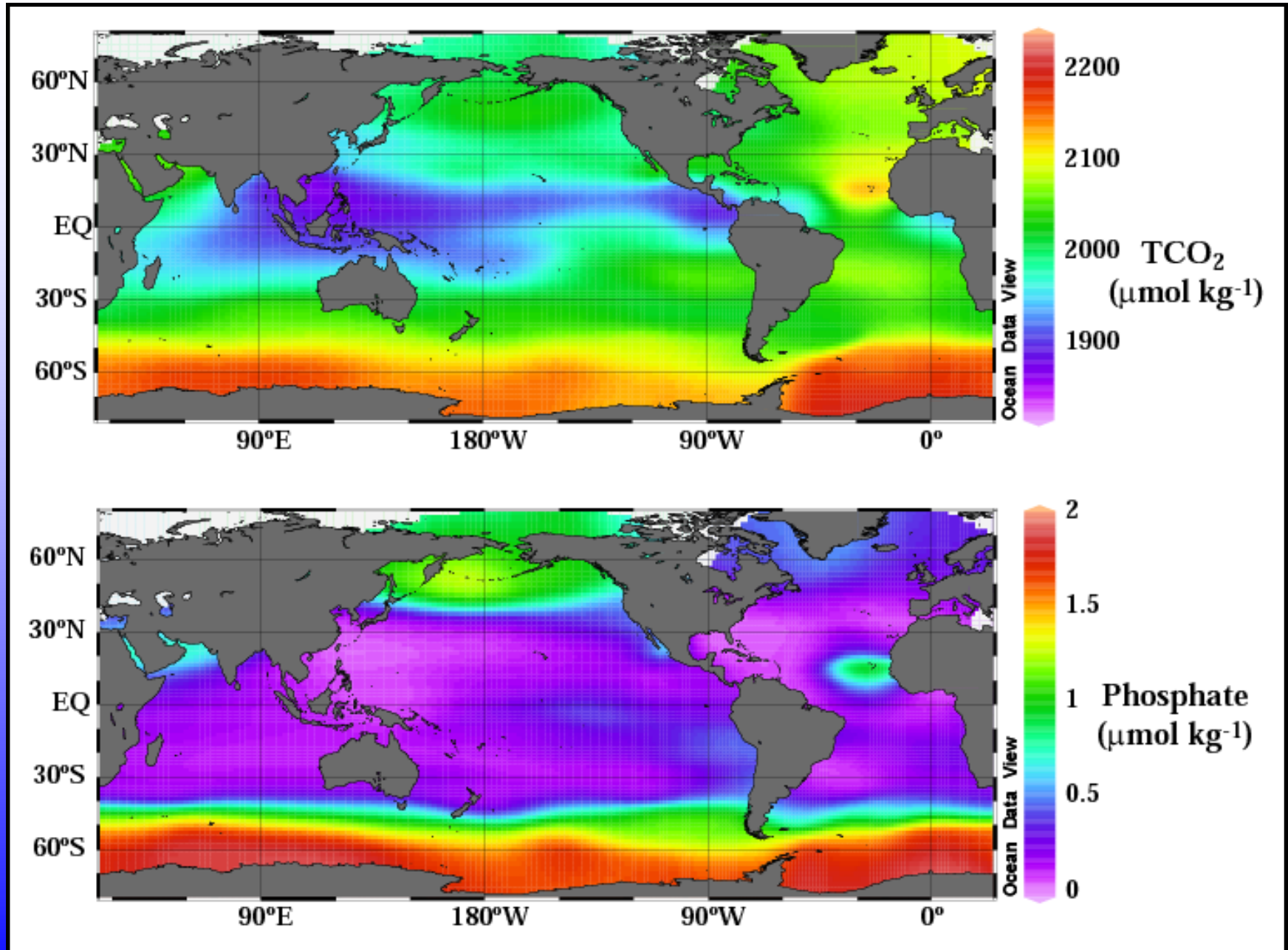
Surface TA/Talk/Alk/ A_T Distribution is Very Similar to Salinity



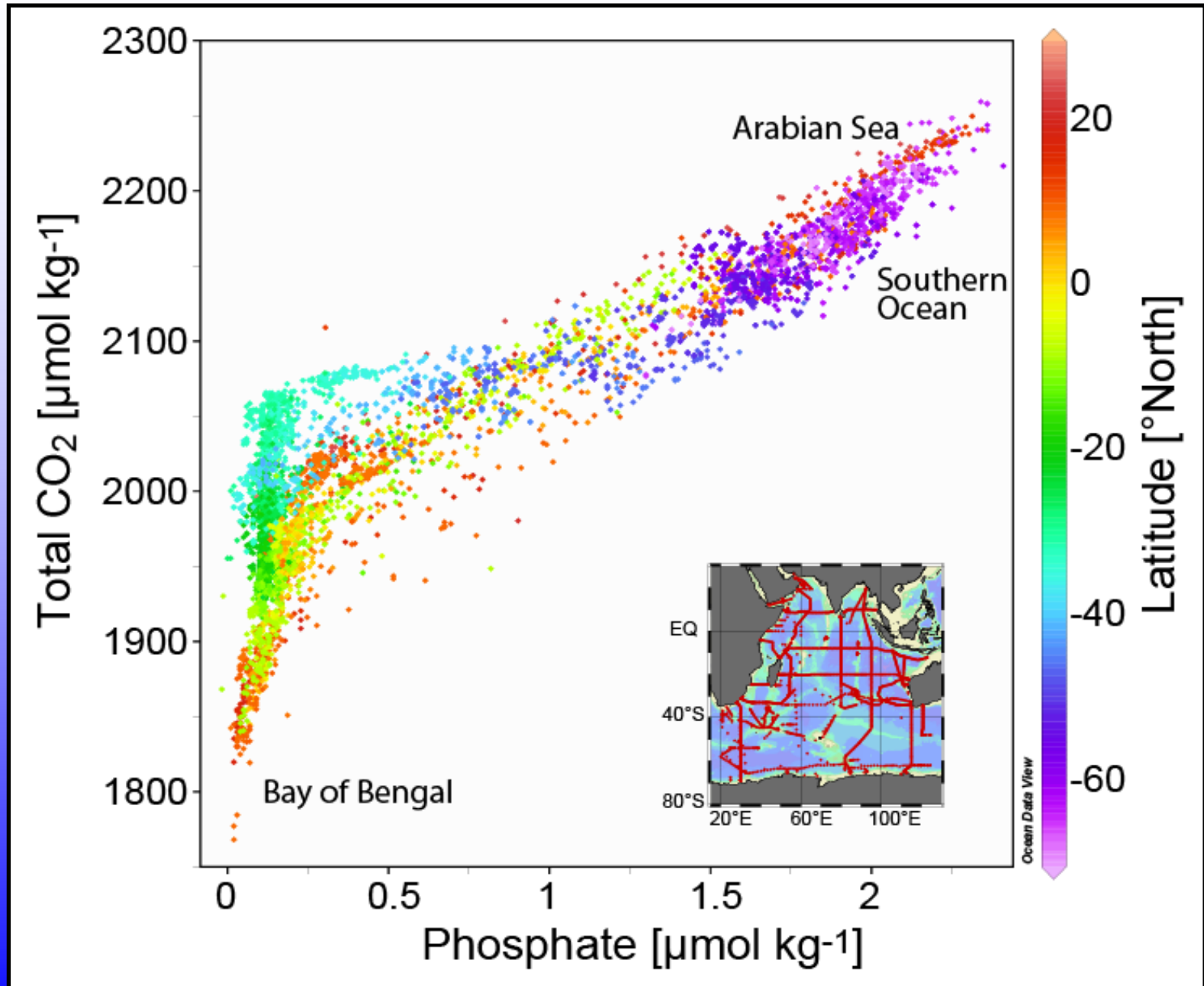
Shallow Indian Ocean Data (depth < 100 m)



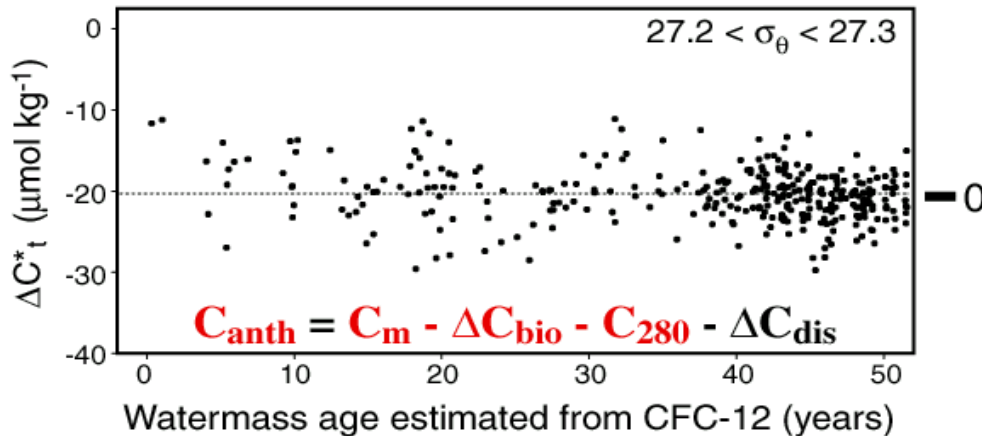
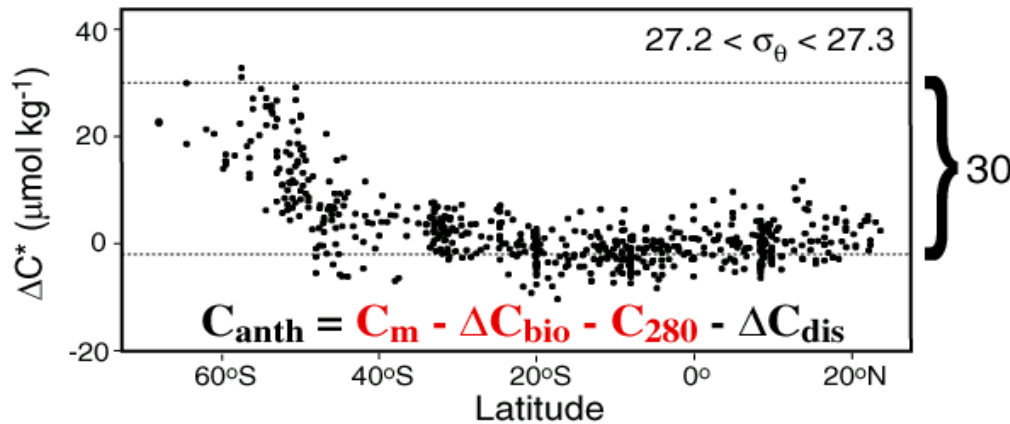
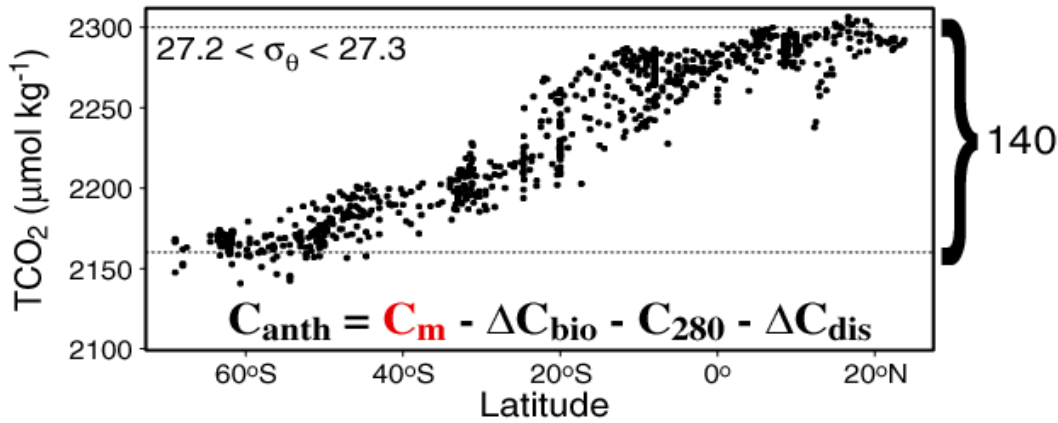
$\text{TCO}_2/\text{DIC}/C_T$: Surface Distribution is Similar to Nutrient Distributions



Shallow Indian Ocean Data (depth < 100 m)



Gruber, N., J. L. Sarmiento and T. F. Stocker, An improved method for detecting anthropogenic CO_2 in the oceans, *Global Biogeochem. Cycles*, 10, 809-837, 1996.



$$C_{\text{anth}} = C_m - \Delta C_{\text{bio}} - C_{280} - \Delta C_{\text{dis}}$$

Where:

C_{anth} = Anthropogenic C concentration

C_m = Measured total C concentration

ΔC_{bio} = Change in TCO₂ as a result of biological activity

C_{280} = TCO₂ of waters in equilibrium with a preindustrial atmospheric CO₂ concentration of 280 μatm

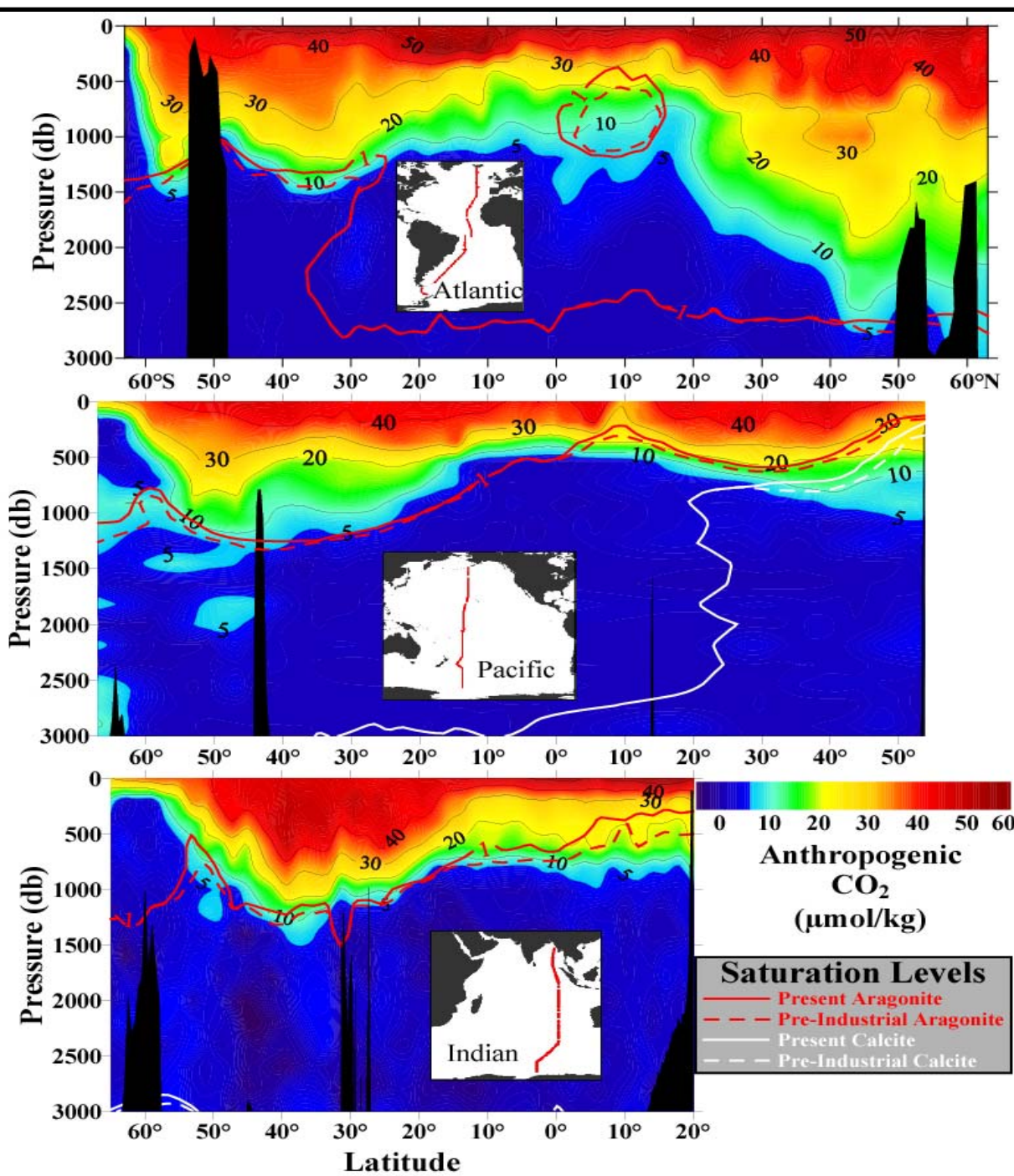
ΔC_{dis} = Air-sea difference in CO₂ concentration in $\mu\text{mol kg}^{-1}$ of TCO₂

$$\Delta C^* = C_m - \Delta C_{\text{bio}} - C_{280} = C_{\text{anth}} + \Delta C_{\text{dis}}$$

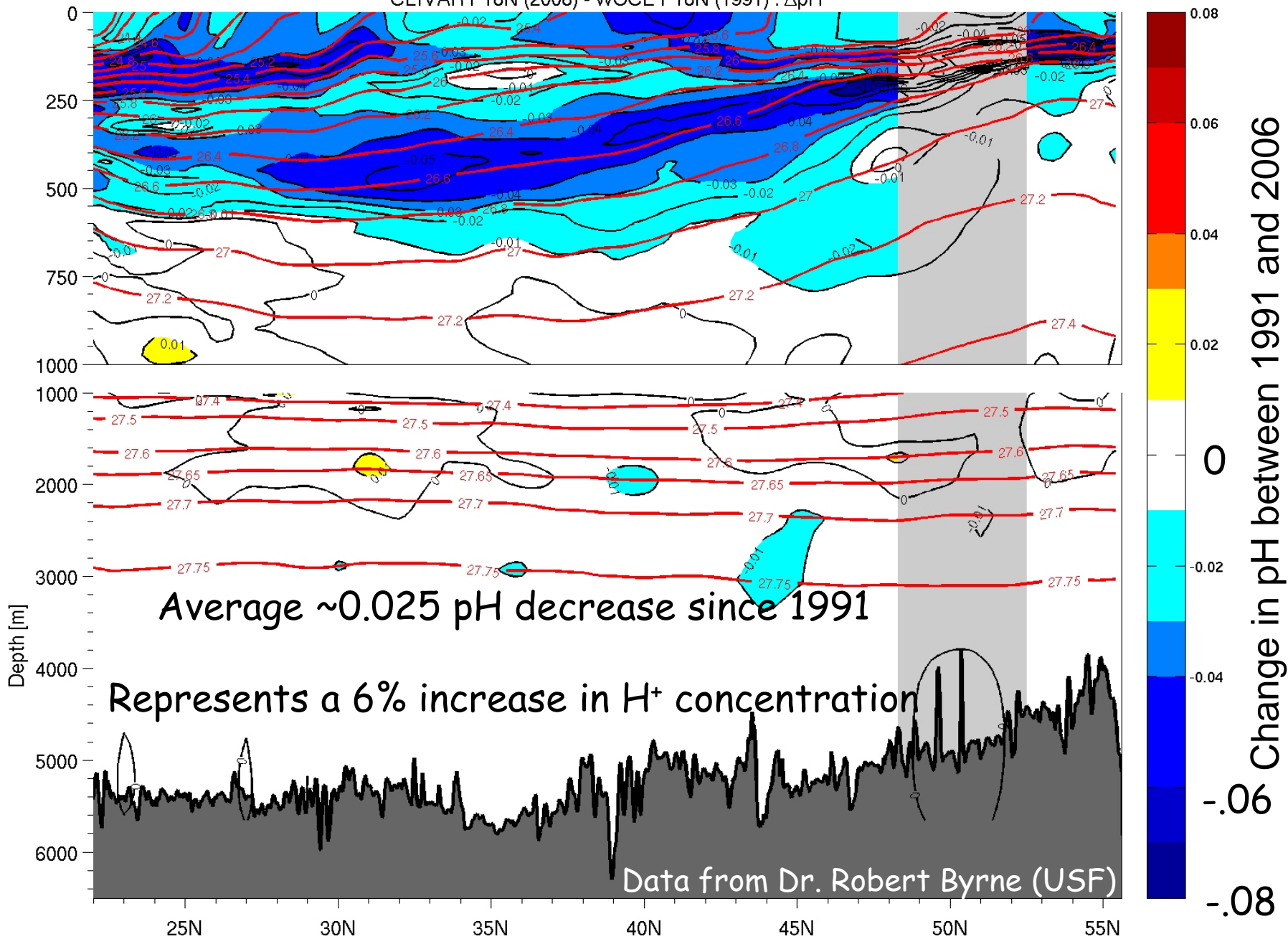
Anthropogenic CO_2 is predominantly found in the upper ocean.

50% of the anthropogenic CO_2 is found shallower than 400m

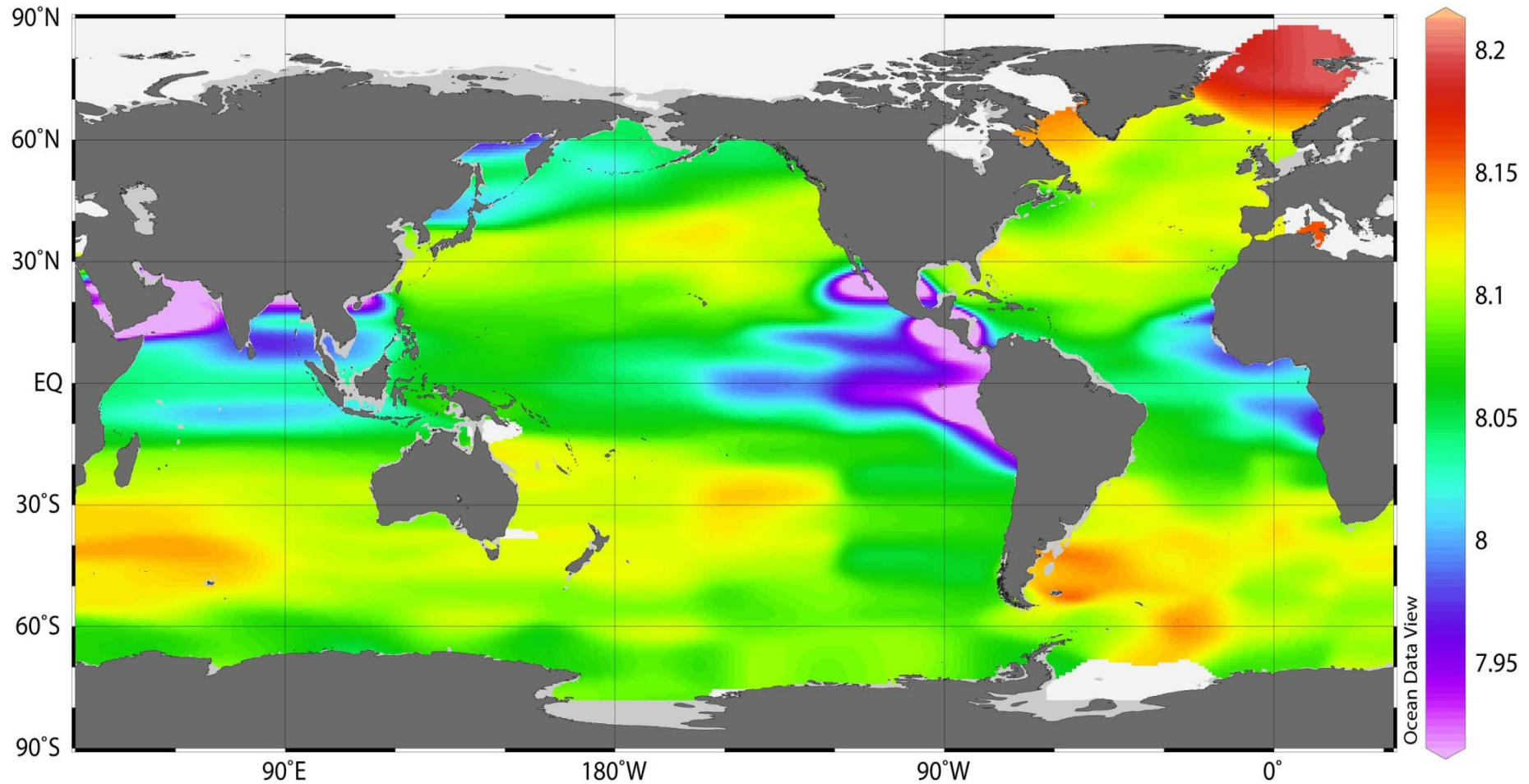
The anthropogenic CO_2 is causing the saturation horizons to shoal



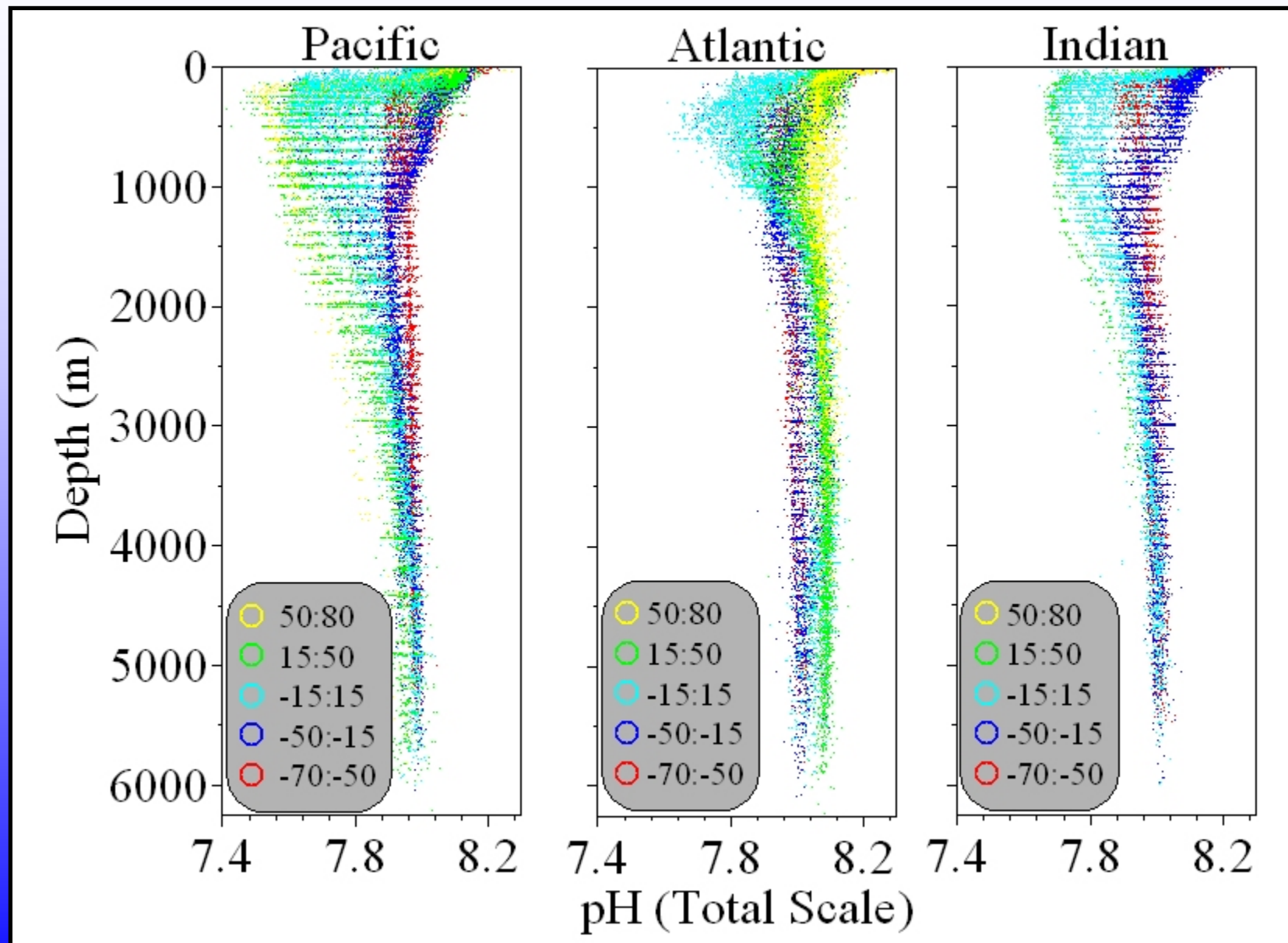
CLIVAR P16N (2006) - WOCE P16N (1991) : Δ pH



Surface pH distribution reflects combined patterns of alkalinity and TCO_2



pH Minimum Associated With O₂ Minimum



Take home message:
Each of the 4 measurable
carbon parameters can
tell us something
different about the basic
processes operating in
the Ocean

Gas
Exchange

$p\text{CO}_2$

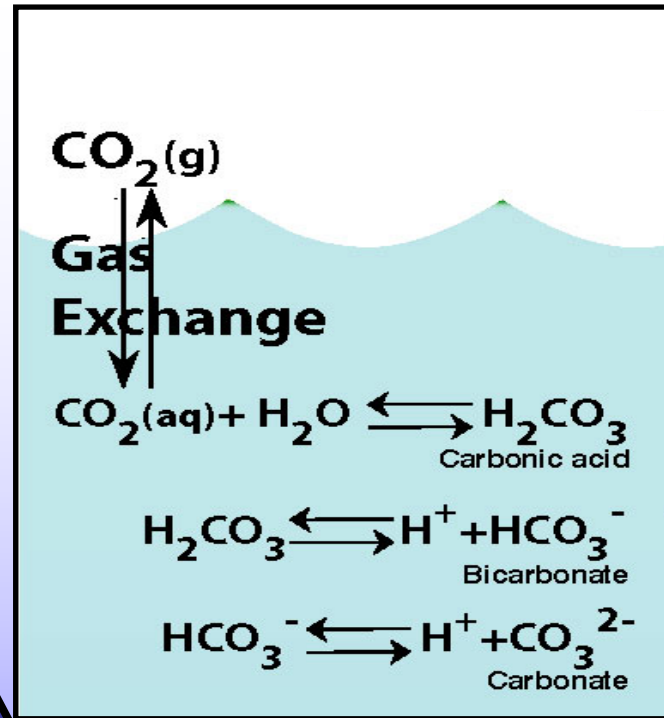
pH

TCO_2

Ocean
Physics

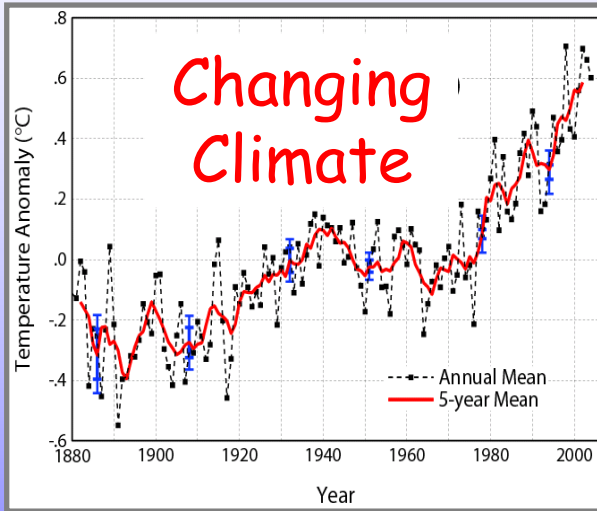
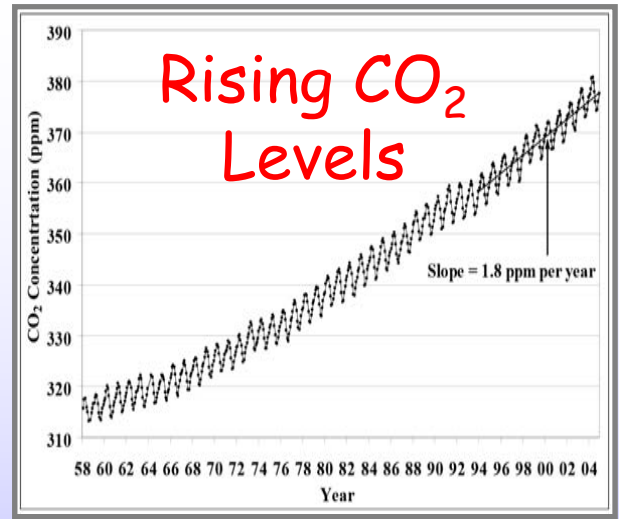
TALK

Biology

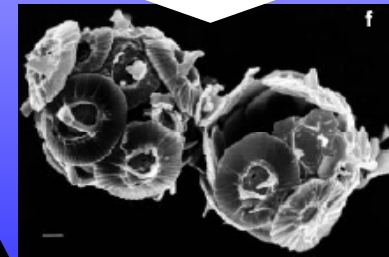


Question:
How will ocean carbon system respond to changes in ocean processes?

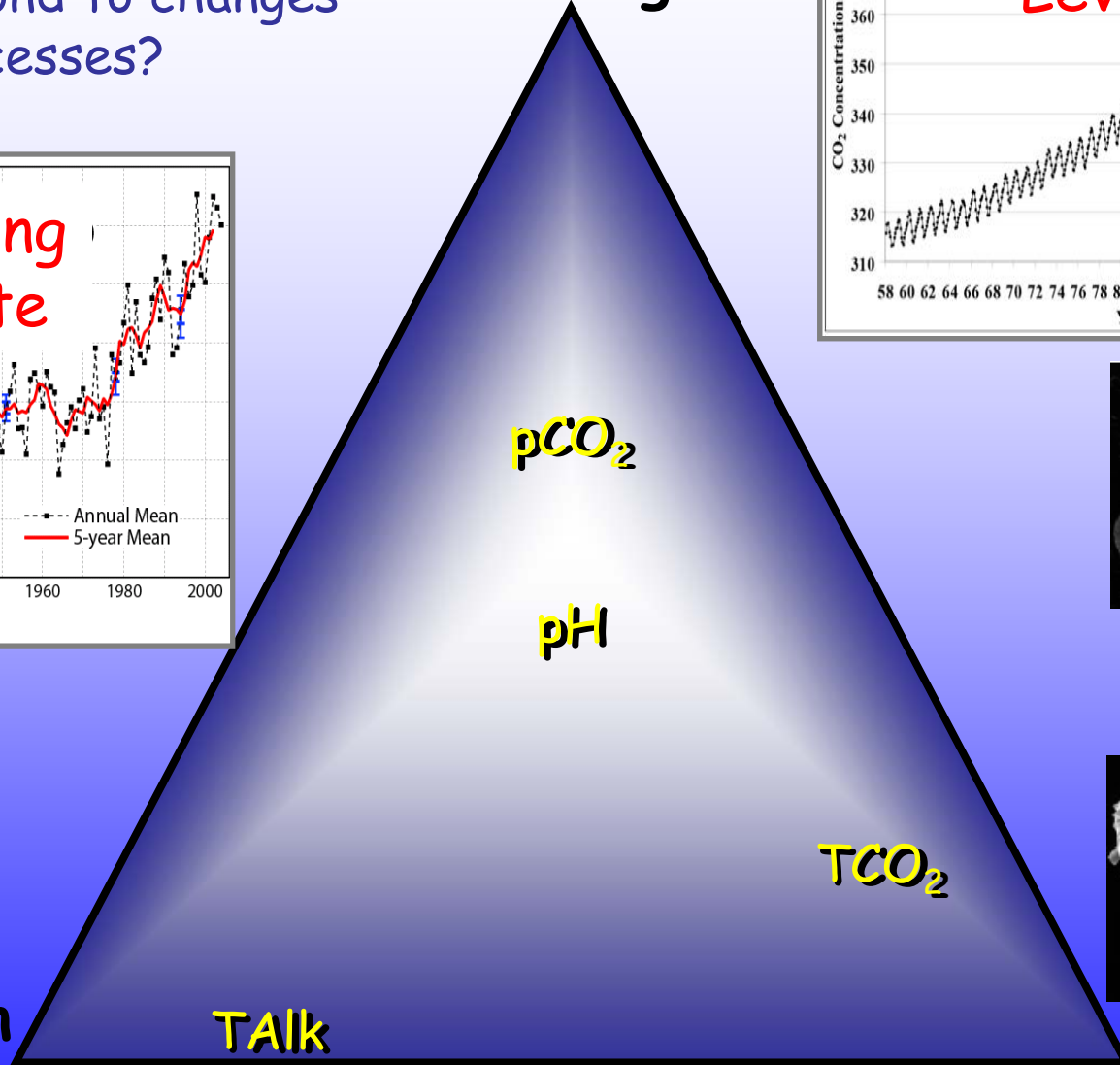
Gas Exchange ←



Changing Biology?



Biology ↻



Ocean Physics

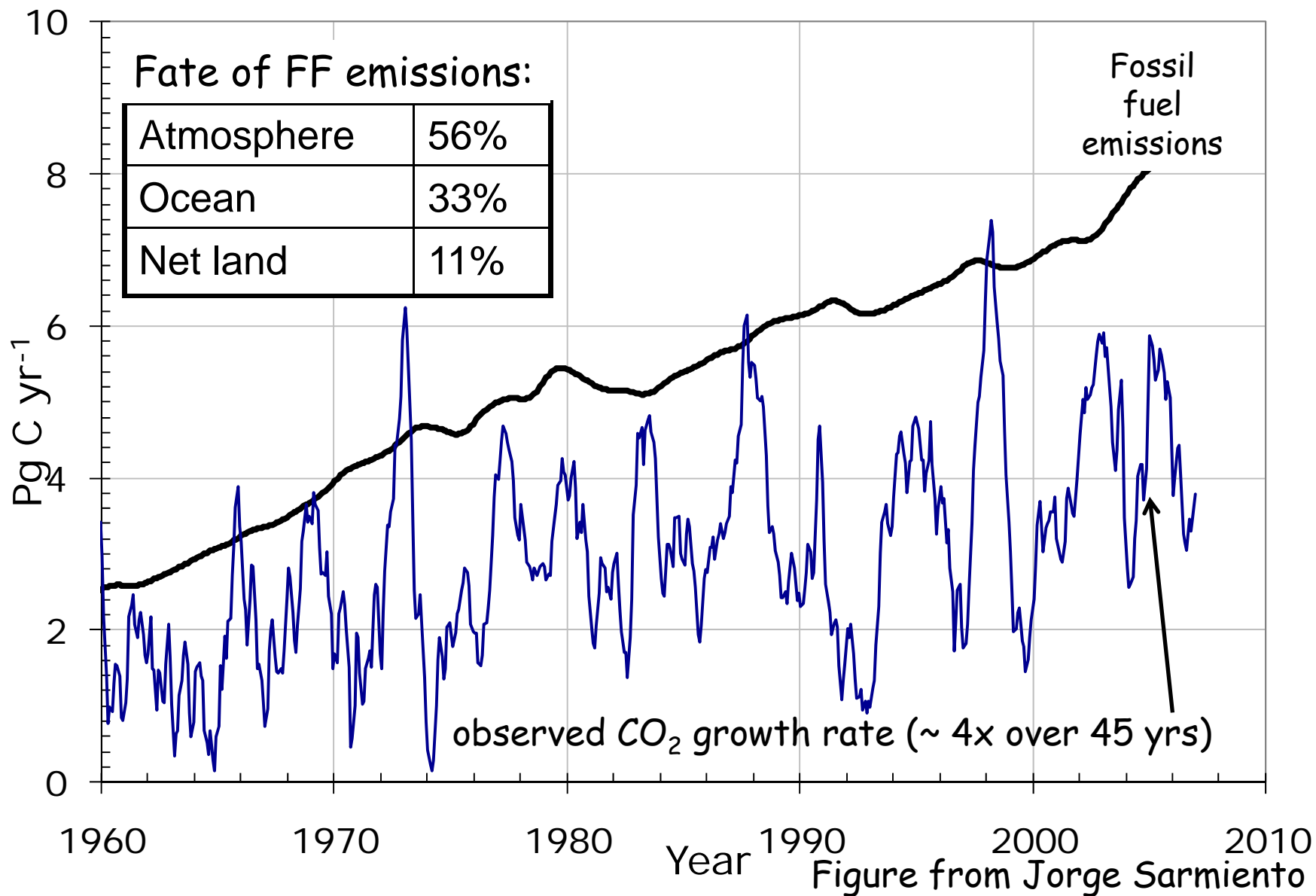
TALK

TCO₂

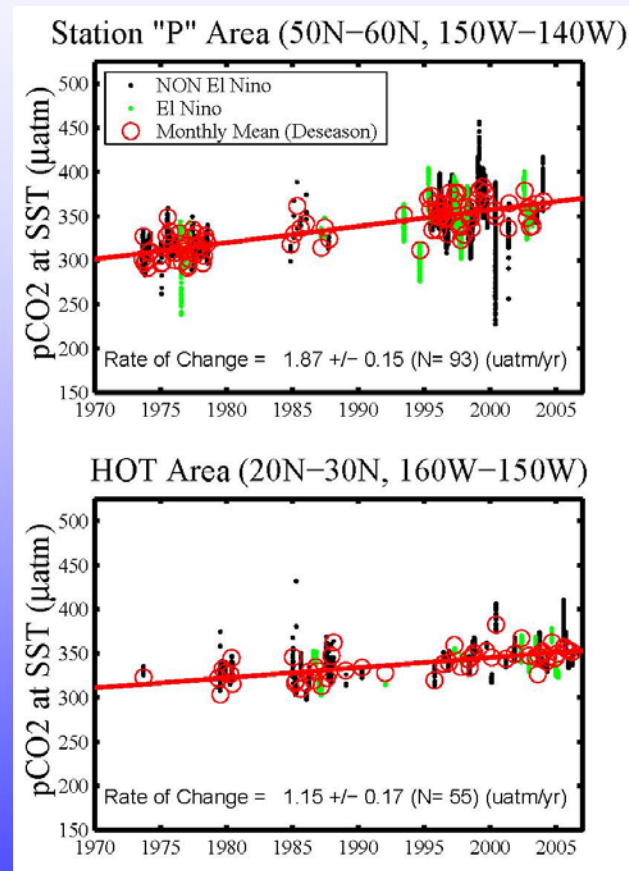
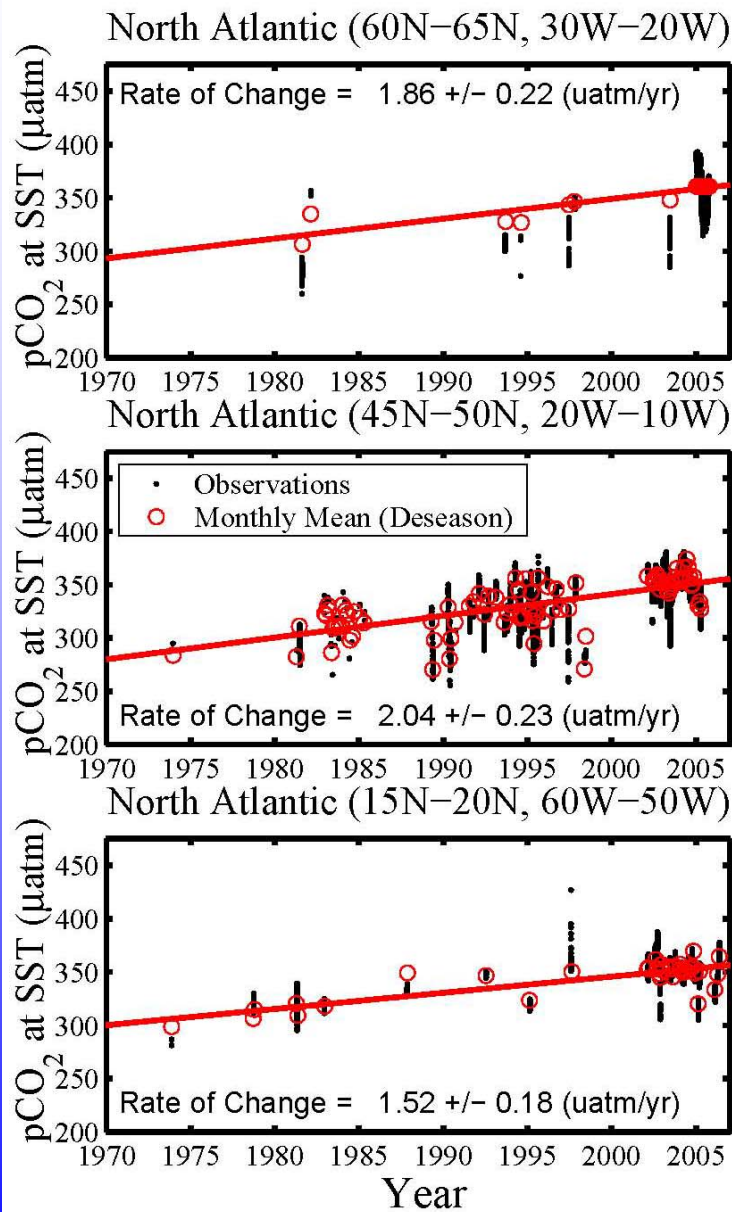
pCO₂

pH

The atmospheric CO_2 growth rate is highly variable and increases with time

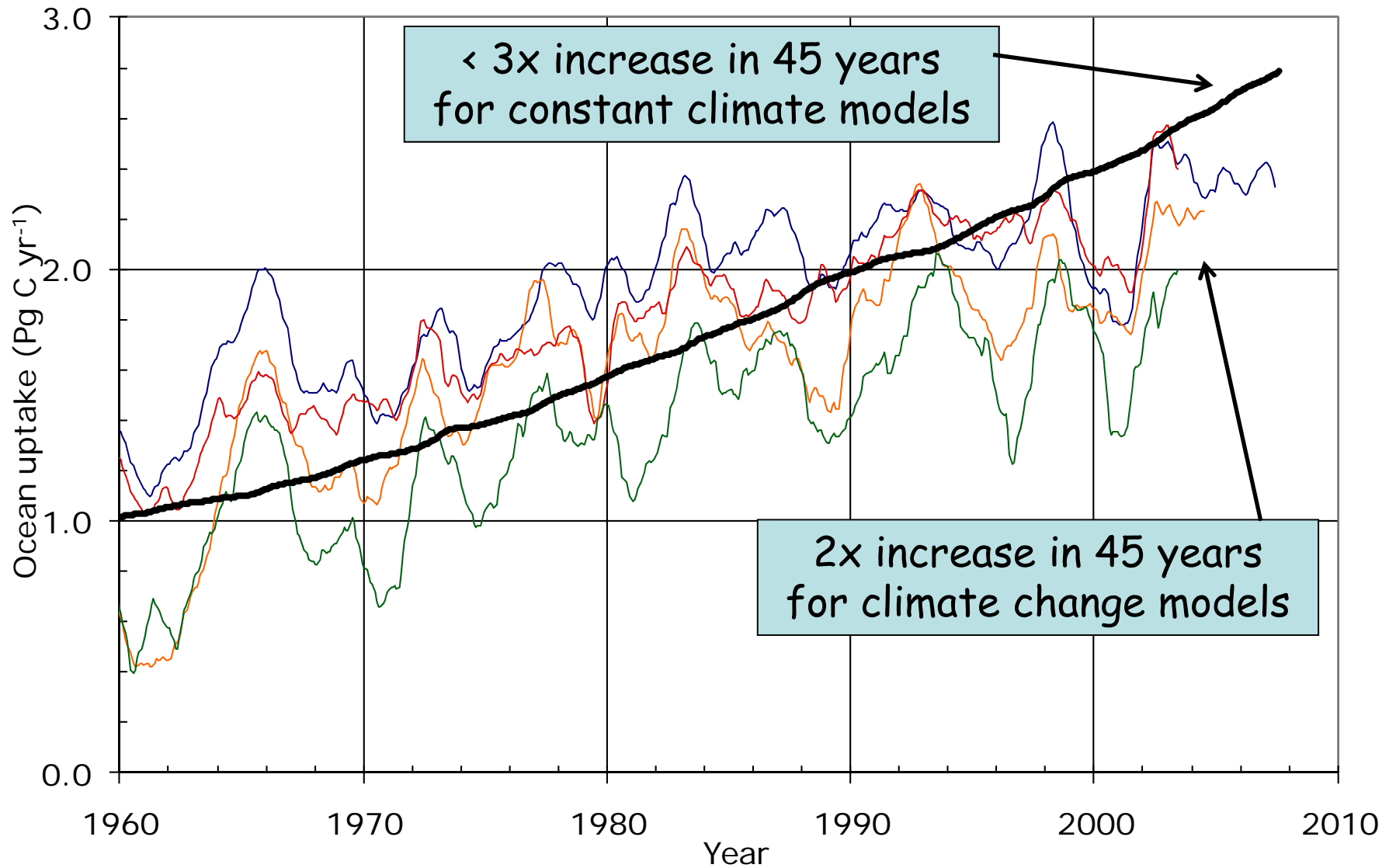


Generally surface ocean CO_2 values track the atmospheric increase



From Takahashi et al 2009

Models suggest that uptake efficiency will decrease in future



— Le Quere et al. (2007)

— Lovenduski et al. (subm.)

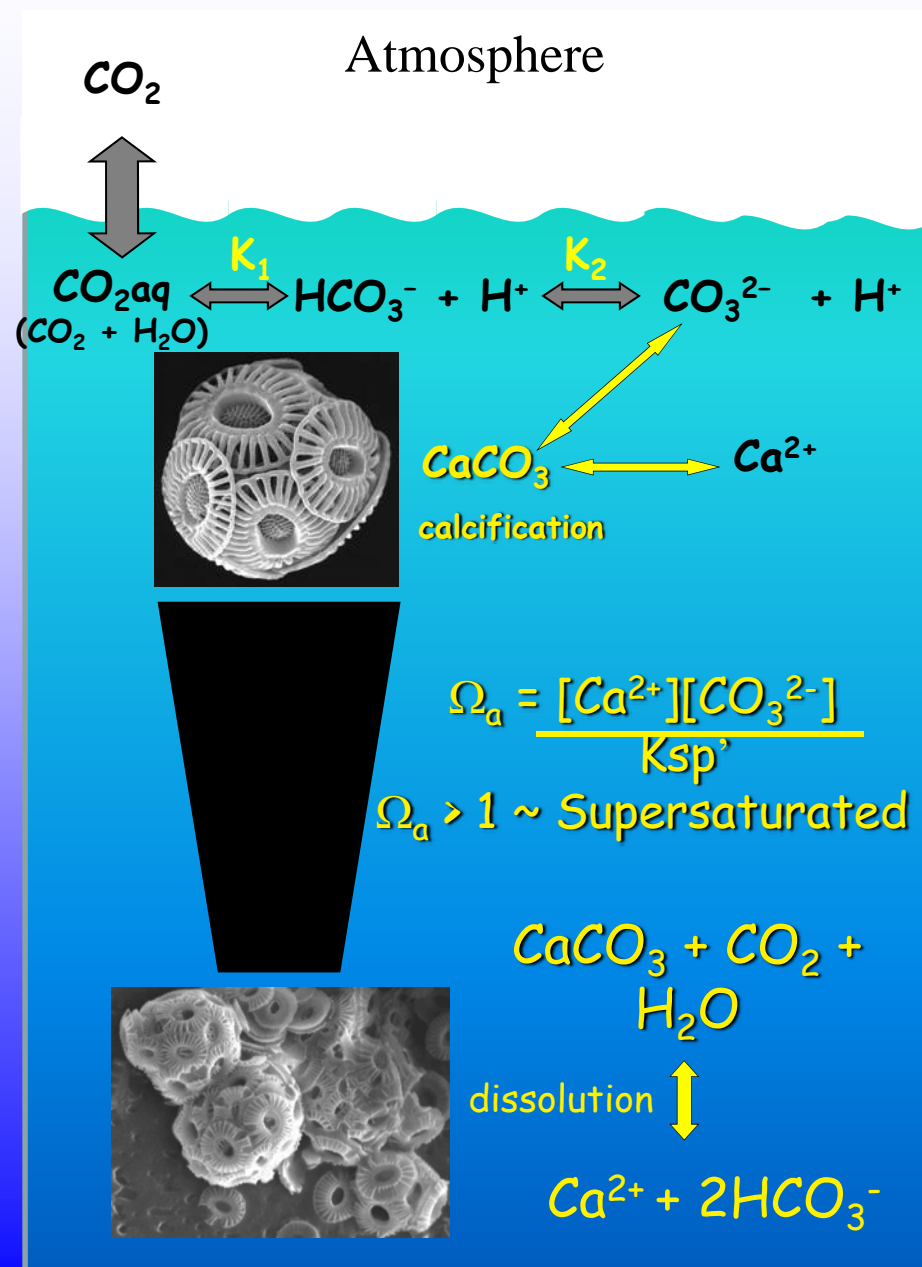
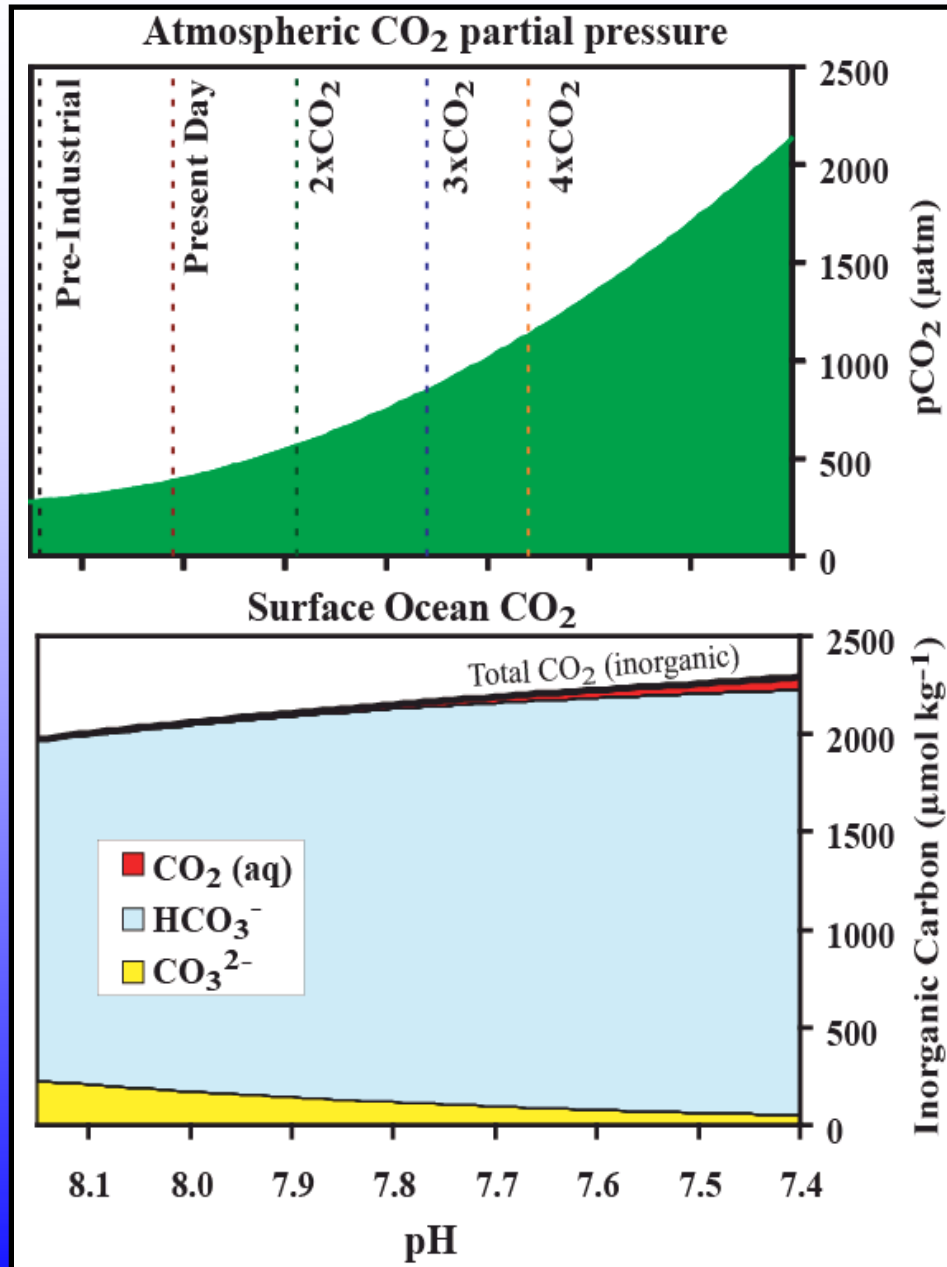
— Rodgers et al. (in press)

— Wetzel et al. (2005)

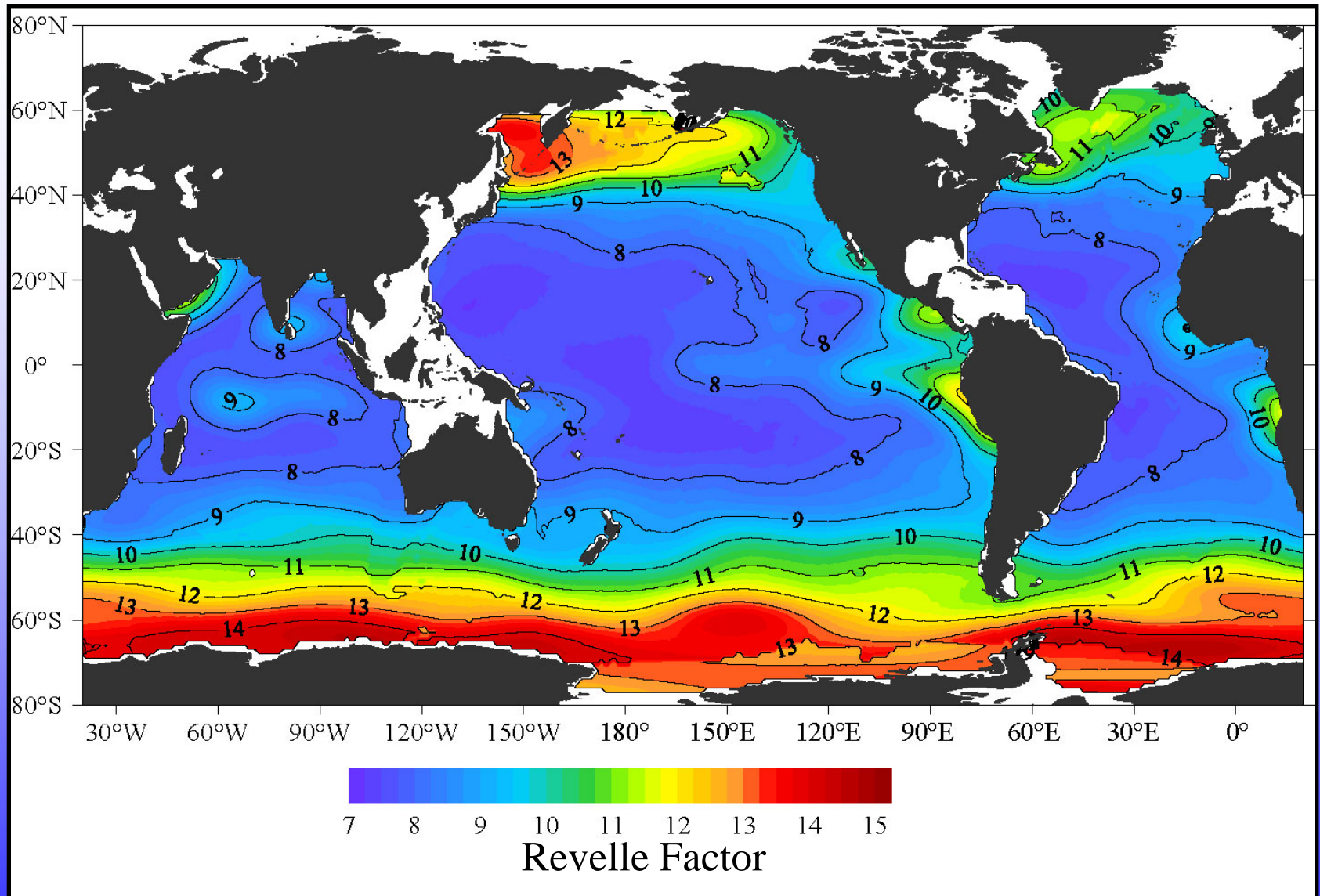
— Mikaloff-Fletcher et al. (2007)

Data from Jorge Sarmiento

Chemical Reactions of Carbonate Species in Seawater



Global Distribution of Surface Revelle Factor



R. Revelle, H.E. Suess, *Tellus* 9, 18 (1957)

$$\frac{(\Delta fCO_2 / \Delta DIC)}{(fCO_2 / DIC)}$$

$$(fCO_2 / DIC)$$

Here we define six new buffer factors,
each of which can be explicitly calculated:

$$\gamma_{\text{DIC}} = \left(\frac{\partial \ln[\text{CO}_2]}{\partial \text{DIC}} \right)^{-1} = \text{DIC} - \frac{\text{Alk}_C^2}{S} \quad \text{equivalent to traditional Revelle Factor that can be used to determine the efficiency of the ocean sink as } \text{CO}_2 \text{ rises}$$

$$\gamma_{\text{Alk}} = \left(\frac{\partial \ln[\text{CO}_2]}{\partial \text{Alk}} \right)^{-1} = \frac{\text{Alk}_C^2 - \text{DIC} \times S}{\text{Alk}_C} \quad \text{similar to Revelle Factor but looks at the impact of changing alkalinity on } \text{CO}_2$$

$$\beta_{\text{Alk}} = \left(\frac{\partial \ln[\text{H}^+]}{\partial \text{Alk}} \right)^{-1} = \frac{\text{Alk}_C^2}{\text{DIC}} - S \quad \text{general buffer capacity - resistance of pH to addition of acid/base}$$

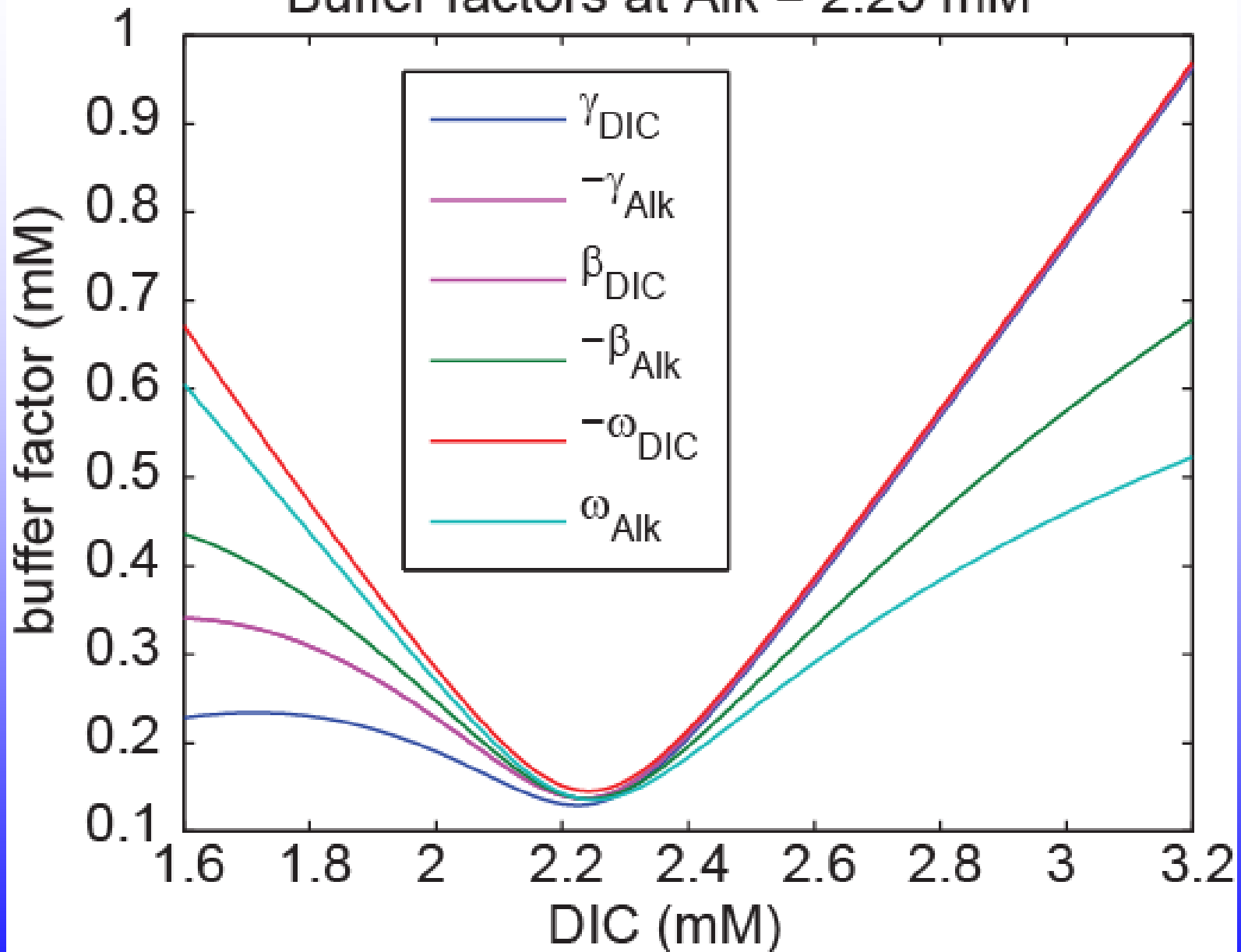
$$\beta_{\text{DIC}} = \left(\frac{\partial \ln[\text{H}^+]}{\partial \text{DIC}} \right)^{-1} = \frac{\text{DIC} \times S - \text{Alk}_C^2}{\text{Alk}_C} \quad \text{in practice this is equivalent to } -\gamma_{\text{Alk}}$$

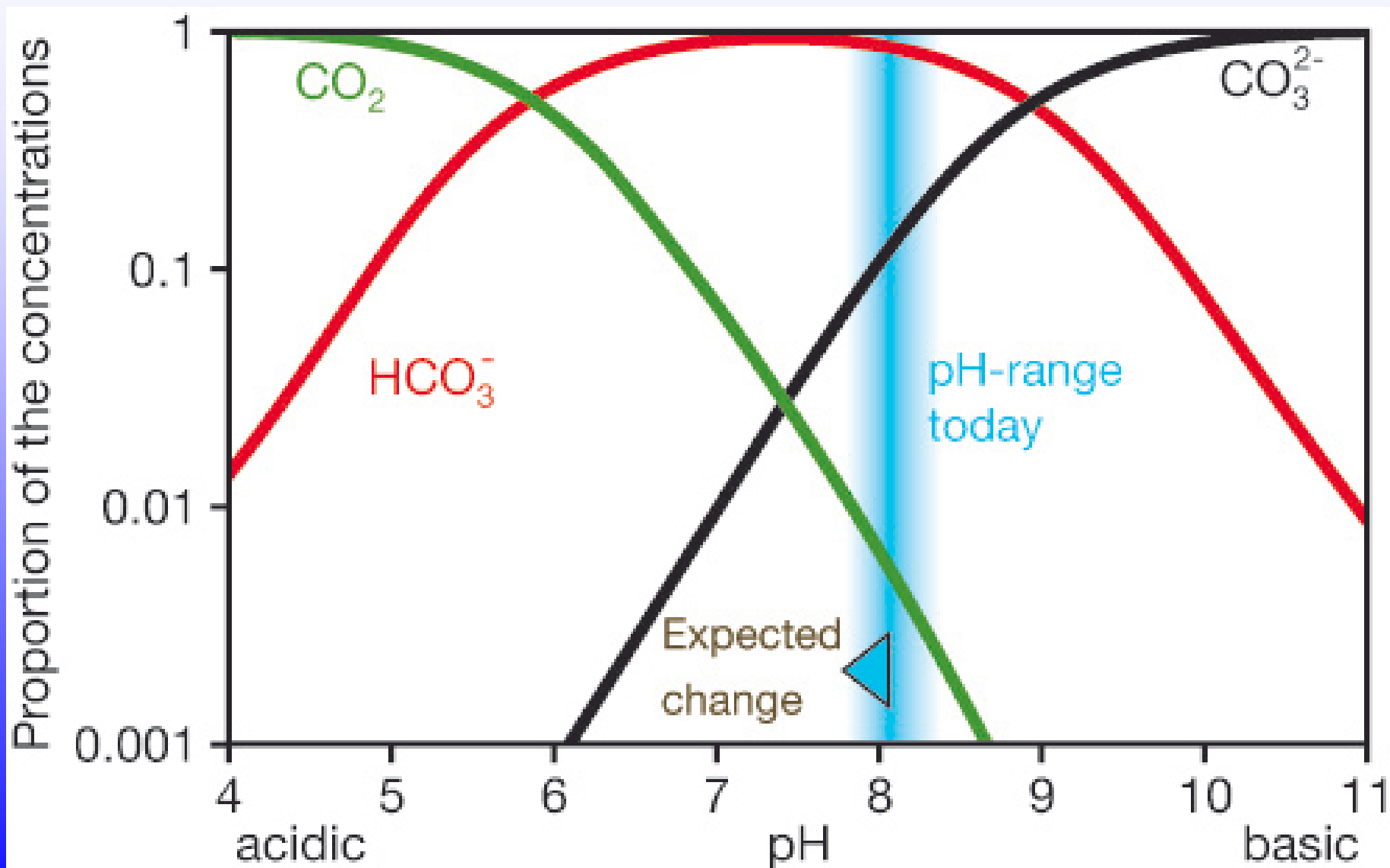
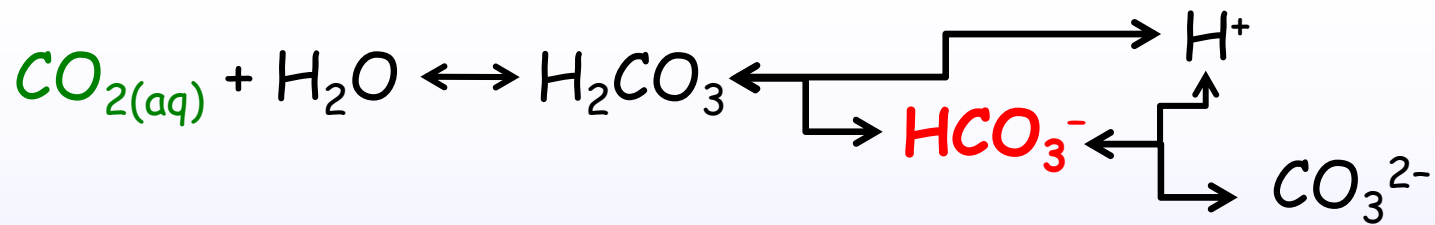
$$\omega_{\text{DIC}} = \left(\frac{\partial \ln \Omega}{\partial \text{DIC}} \right)^{-1} = \text{DIC} - \frac{\text{Alk}_C \times P}{[\text{HCO}_3^-]} \quad \text{a measure of the impact of DIC changes on saturation state}$$

$$\omega_{\text{Alk}} = \left(\frac{\partial \ln \Omega}{\partial \text{Alk}} \right)^{-1} = \text{Alk}_C - \frac{\text{DIC}[\text{HCO}_3^-]}{P} \quad \text{a measure of the impact of alkalinity changes on saturation state}$$

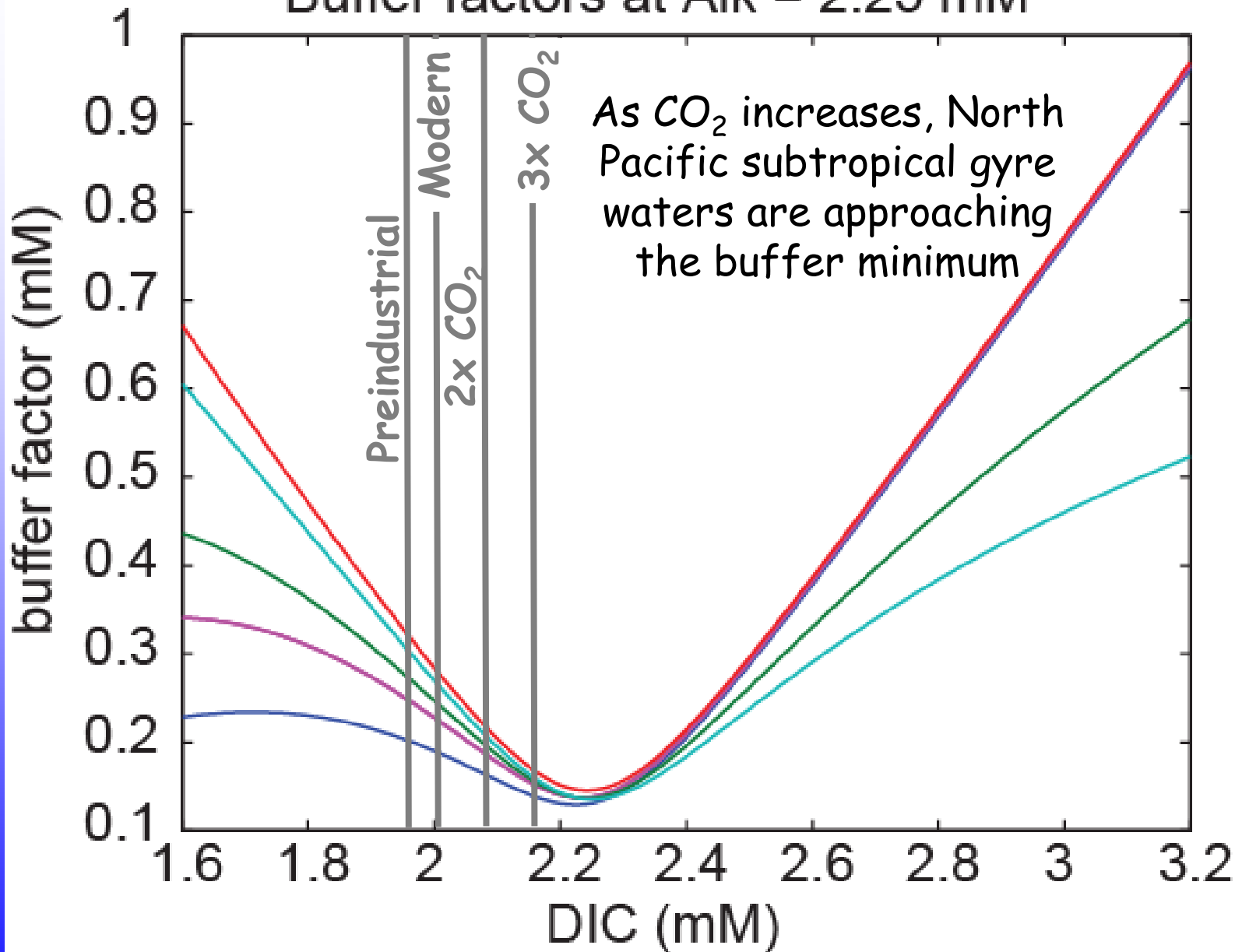
$$S = [\text{HCO}_3^-] + 4[\text{CO}_3^{2-}] + \frac{[\text{H}^+][\text{B}(\text{OH})_4^-]}{K_{hb} + [\text{H}^+]} + [\text{H}^+] - [\text{OH}^-] \quad P = 2[\text{CO}_2] + [\text{HCO}_3^-]$$

All Buffer Factors show a minimum where DIC=Alk
Buffer factors at Alk = 2.25 mM

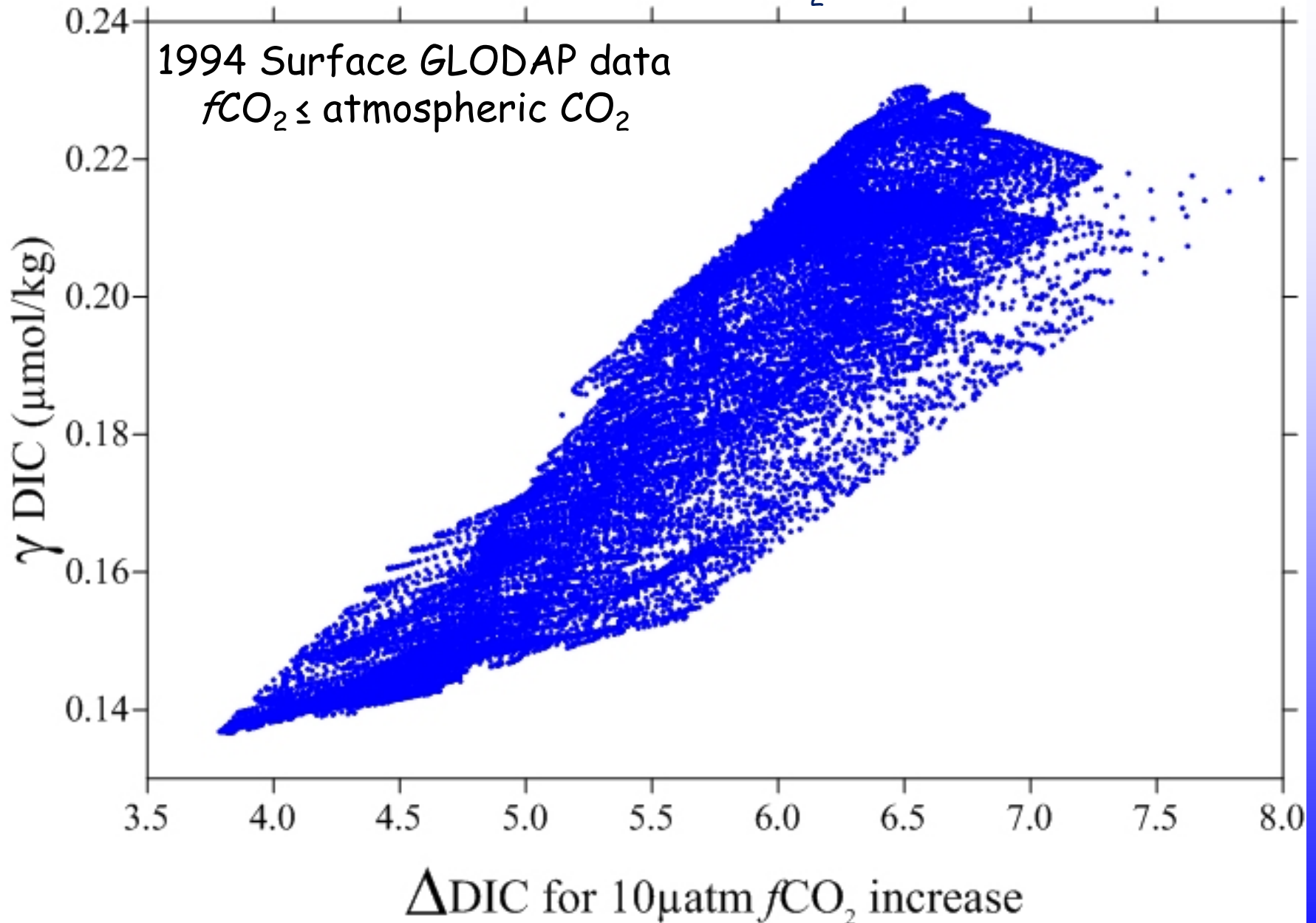




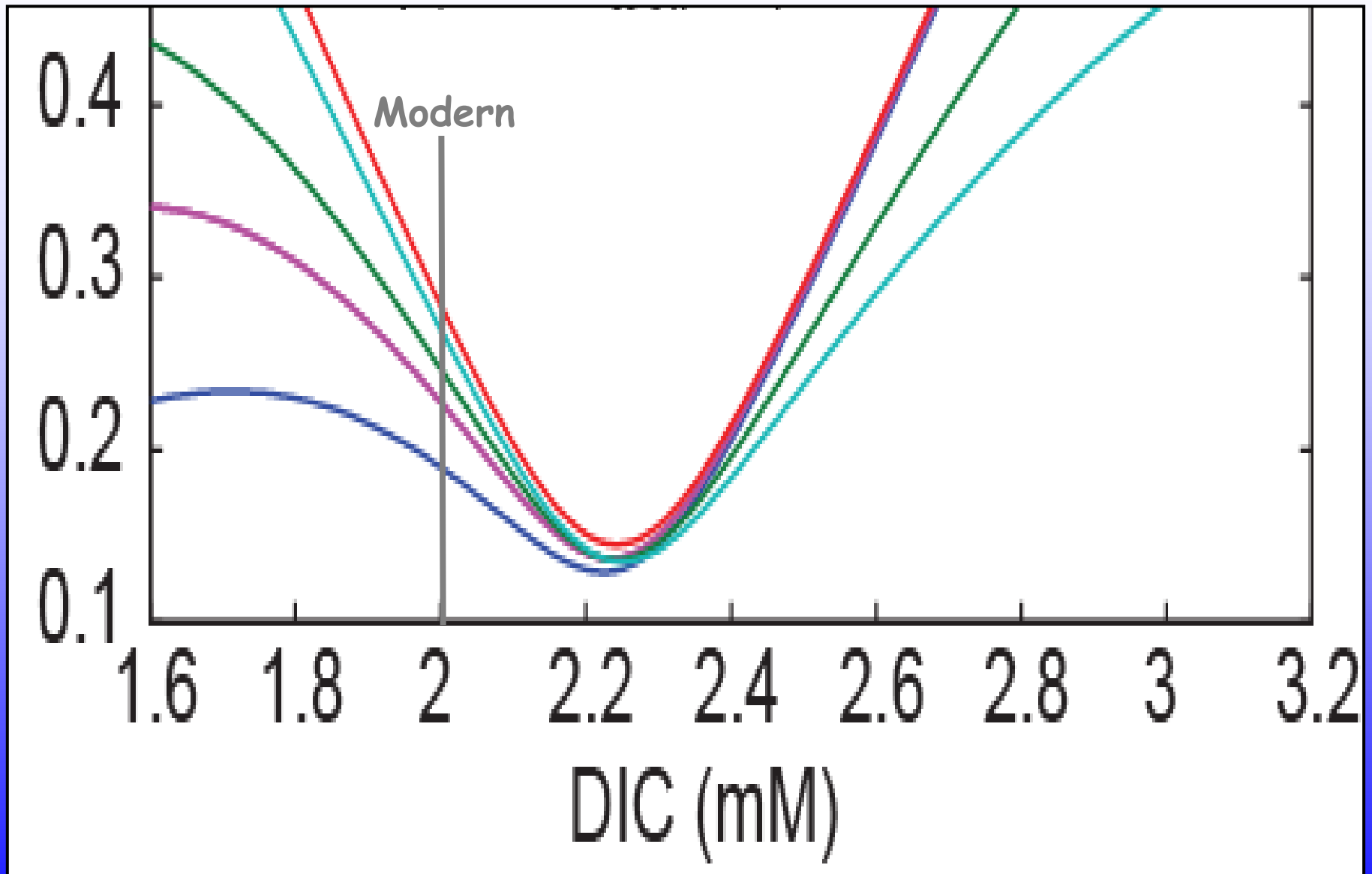
All Buffer Factors show a minimum where $DIC = Alk$
Buffer factors at $Alk = 2.25 \text{ mM}$



Higher buffer factor means larger DIC increase for the same amount of CO_2 rise

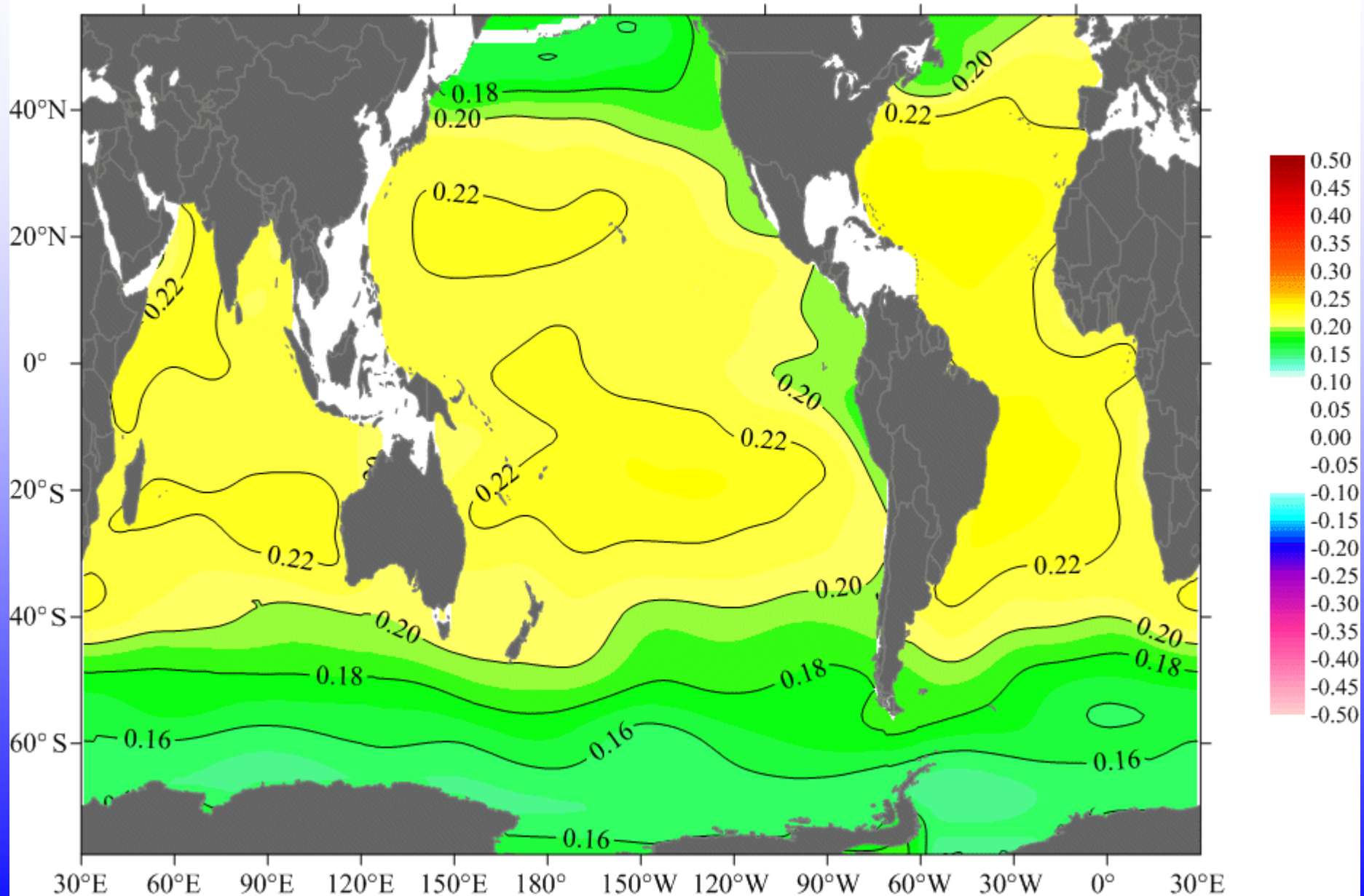


Range is from the shallow slope, but as DIC increases the slope increases



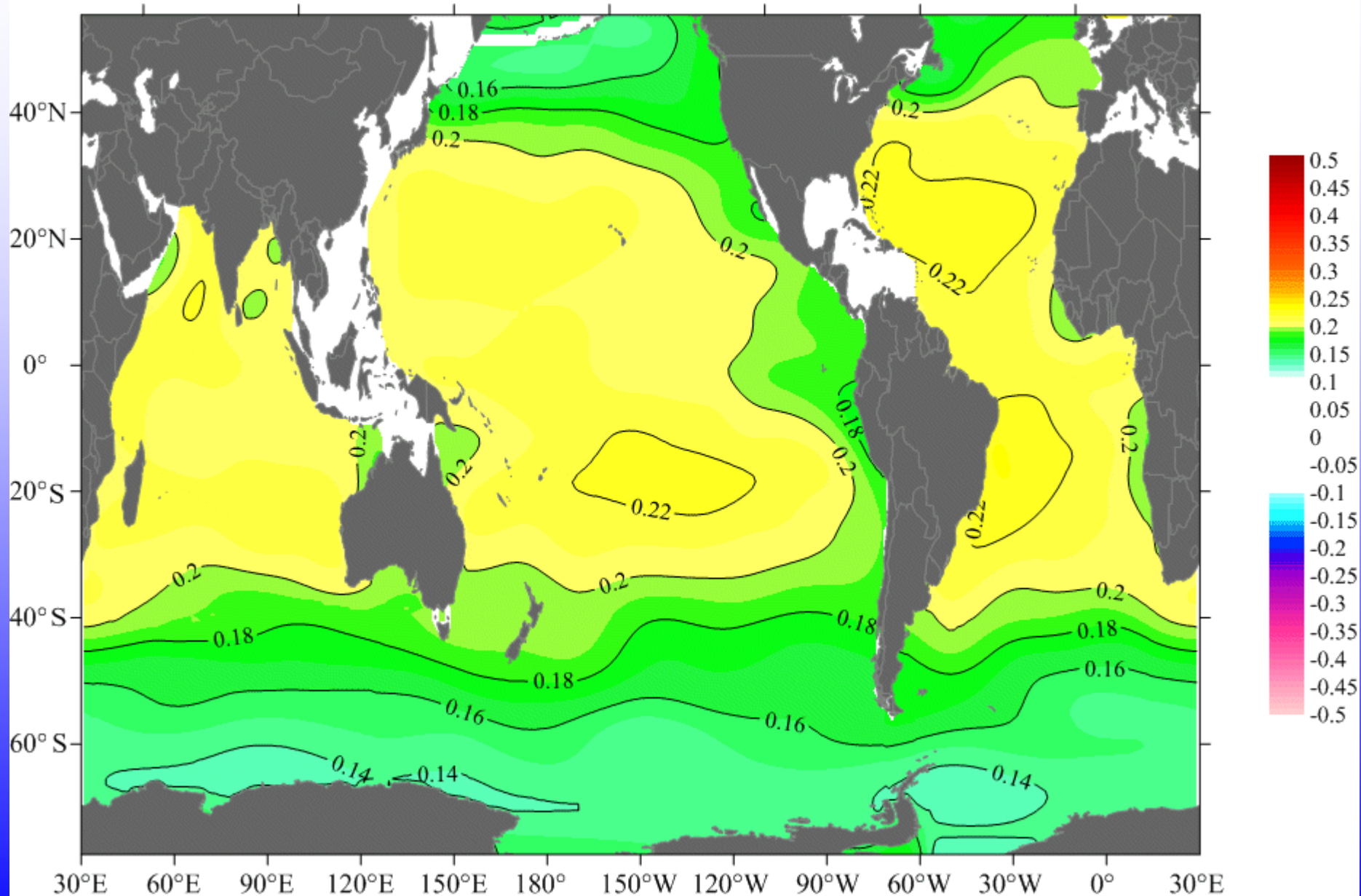
Preindustrial North Pacific ranges from 0.17-0.23 ($\Delta=.06$)

gamma preindustrial DIC



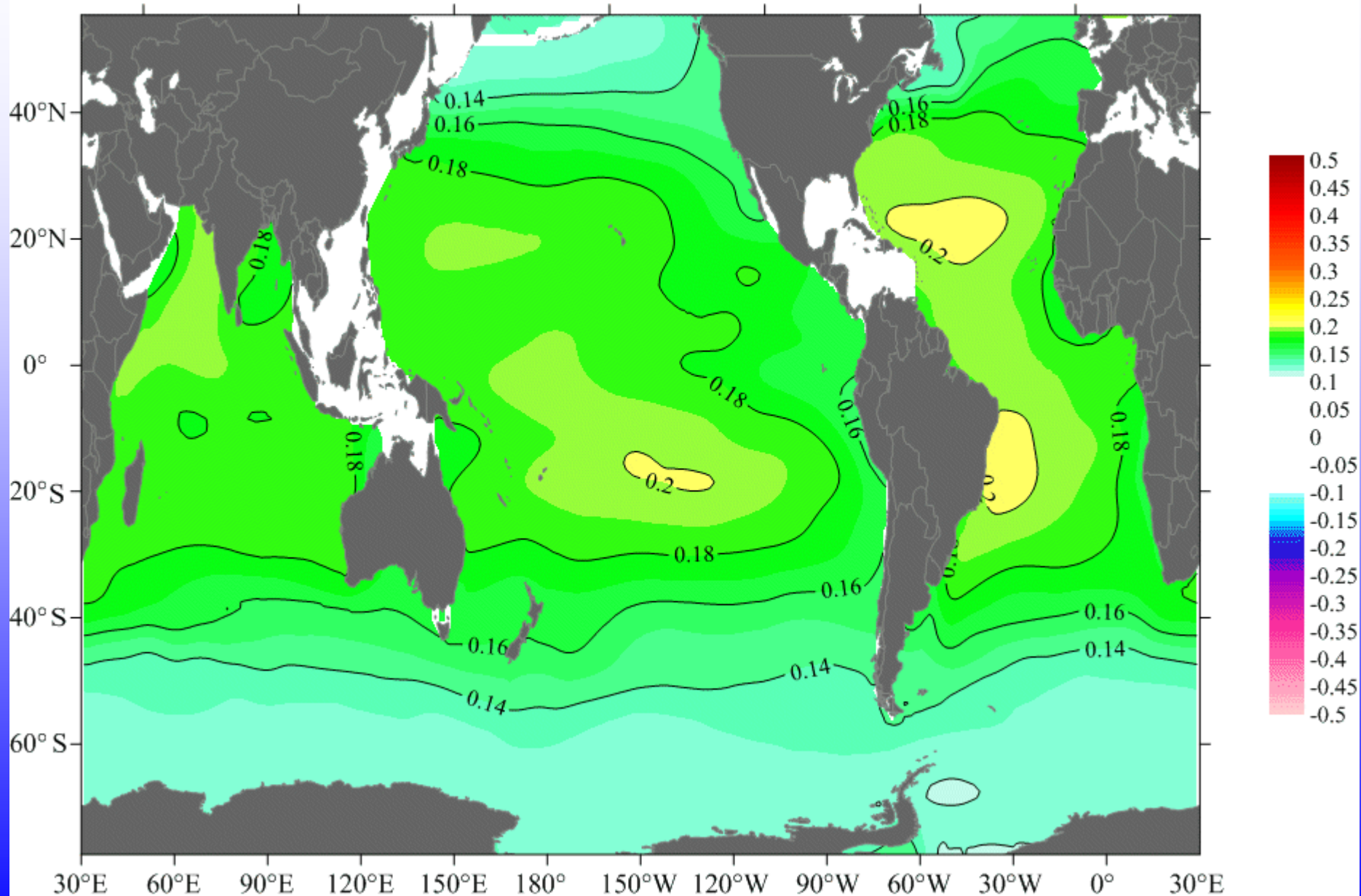
Modern North Pacific ranges from 0.15-0.21 ($\Delta=.06$)

gamma DIC



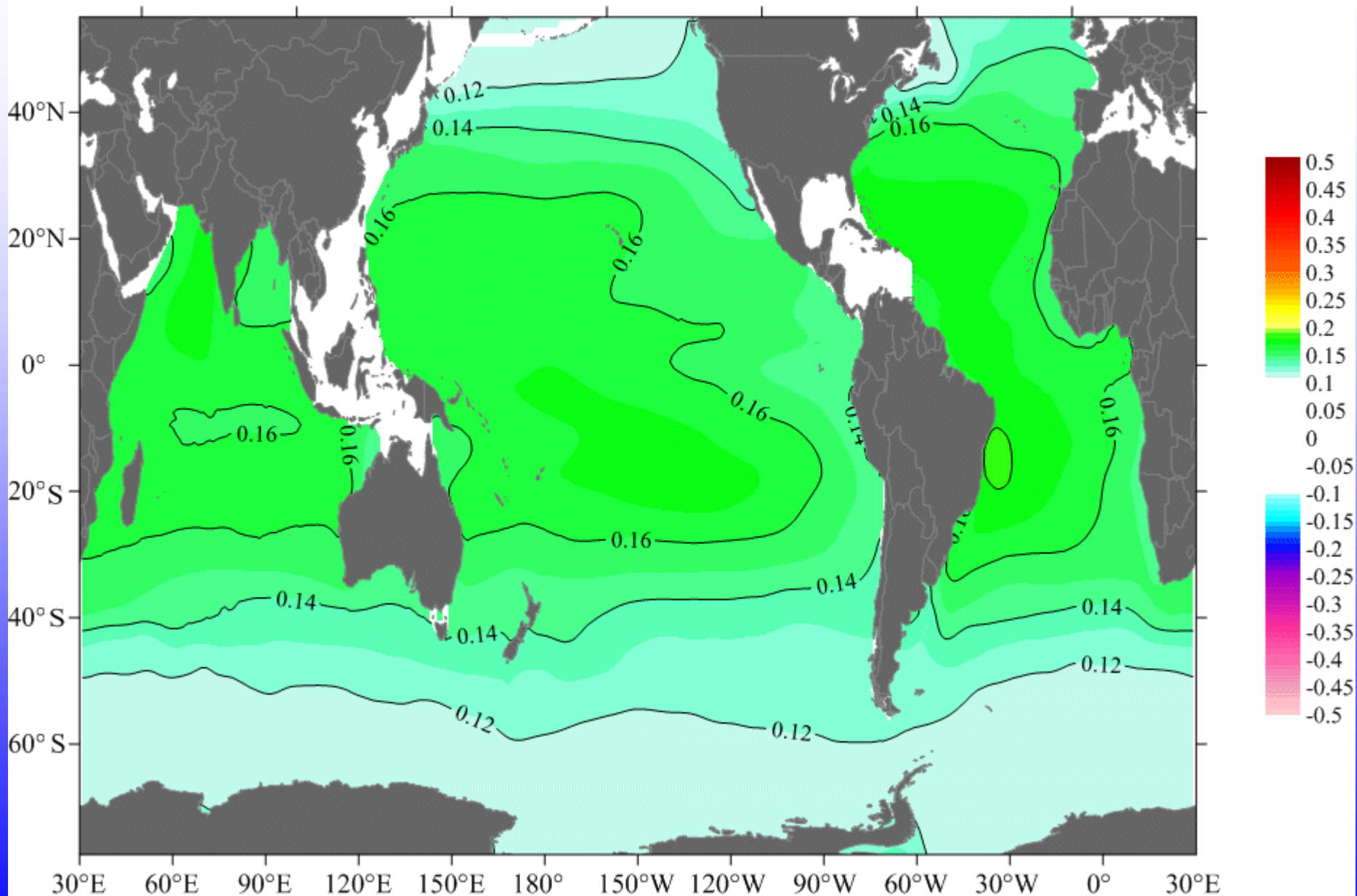
Modern North Pacific ranges from 0.13-0.19 ($\Delta=.06$)

gamma DIC x 2

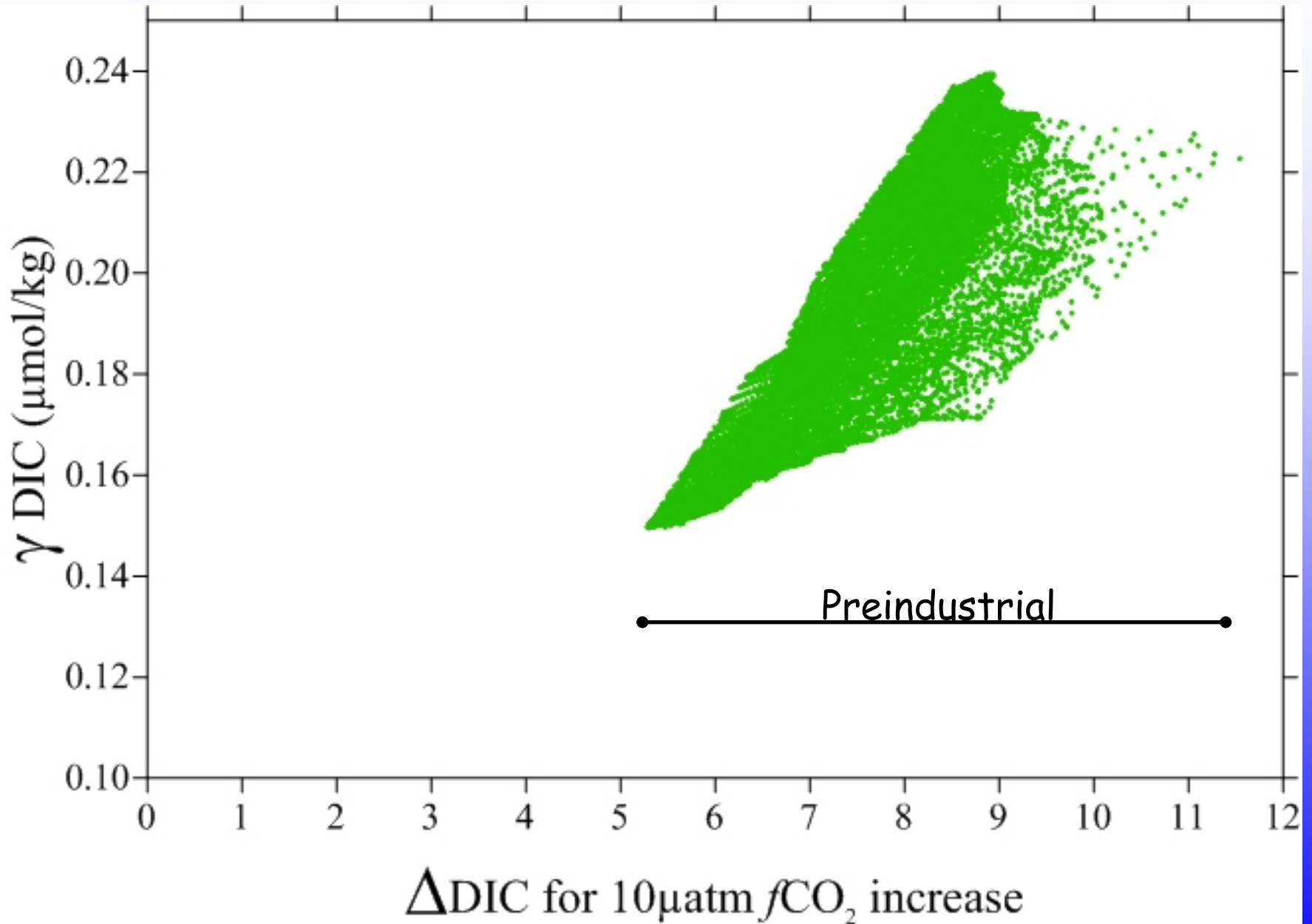


Modern North Pacific ranges from 0.11-0.17 ($\Delta=0.06$)

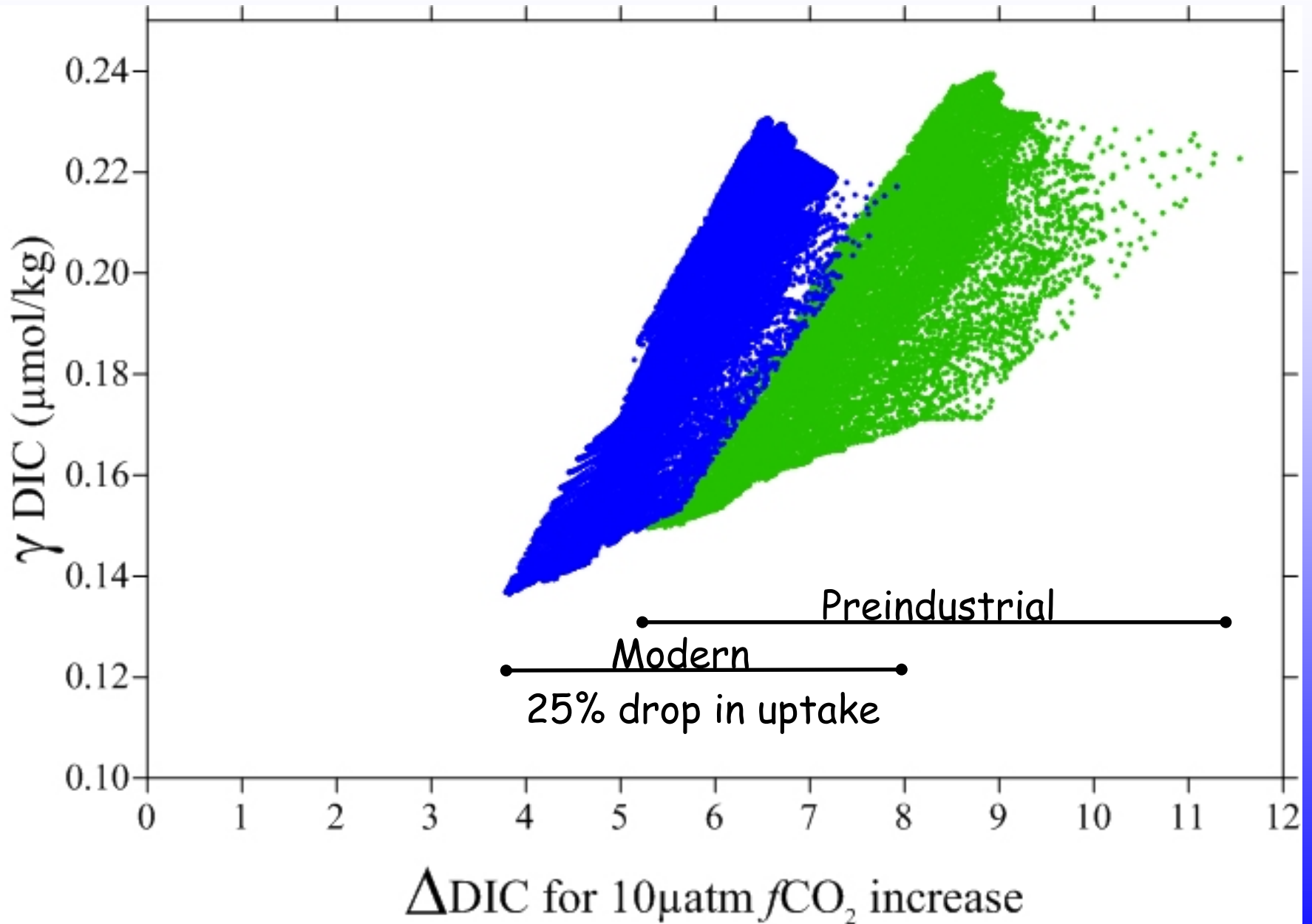
gamma DIC x 3



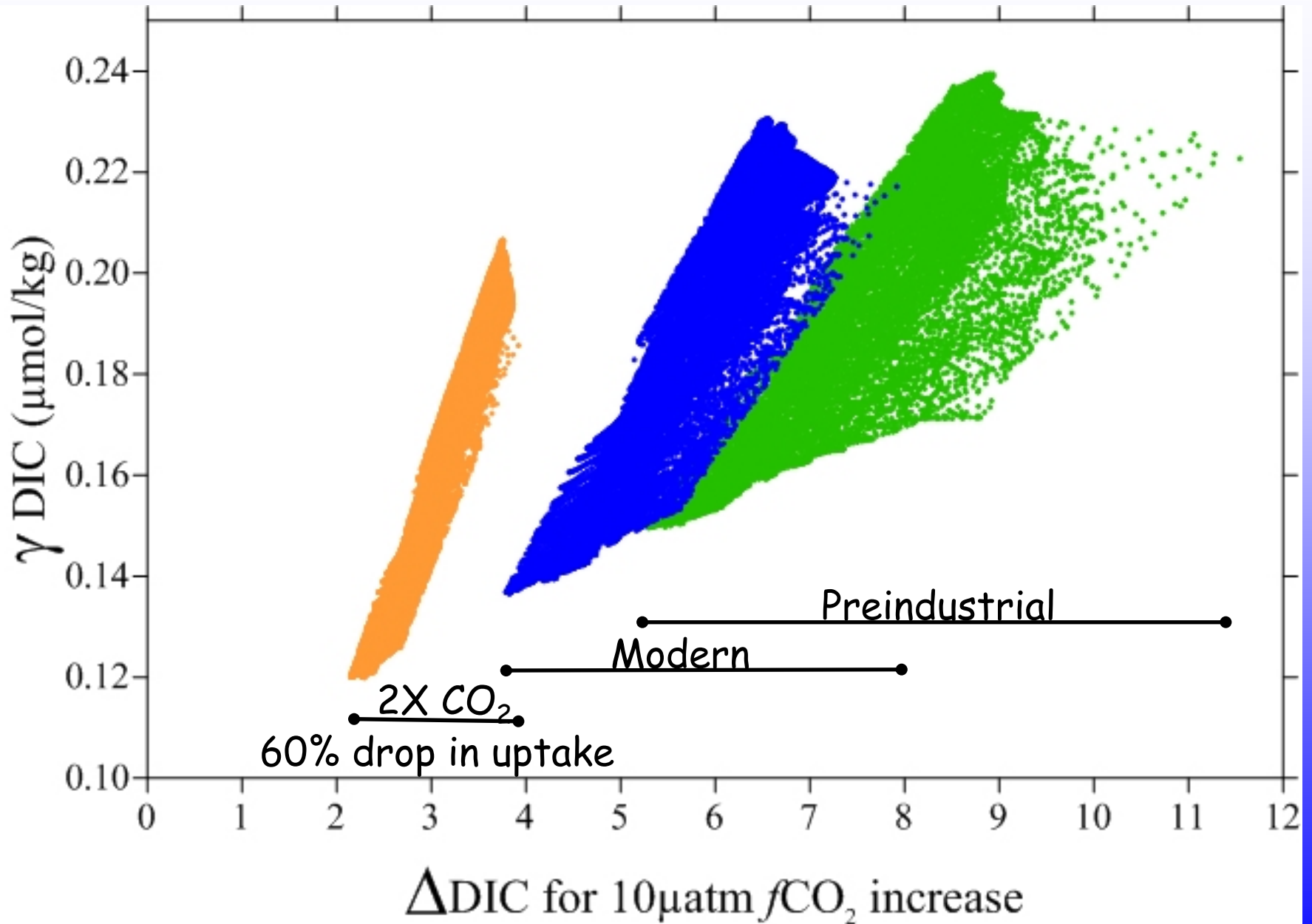
Higher buffer factor means larger DIC increase for the same amount of CO_2 rise



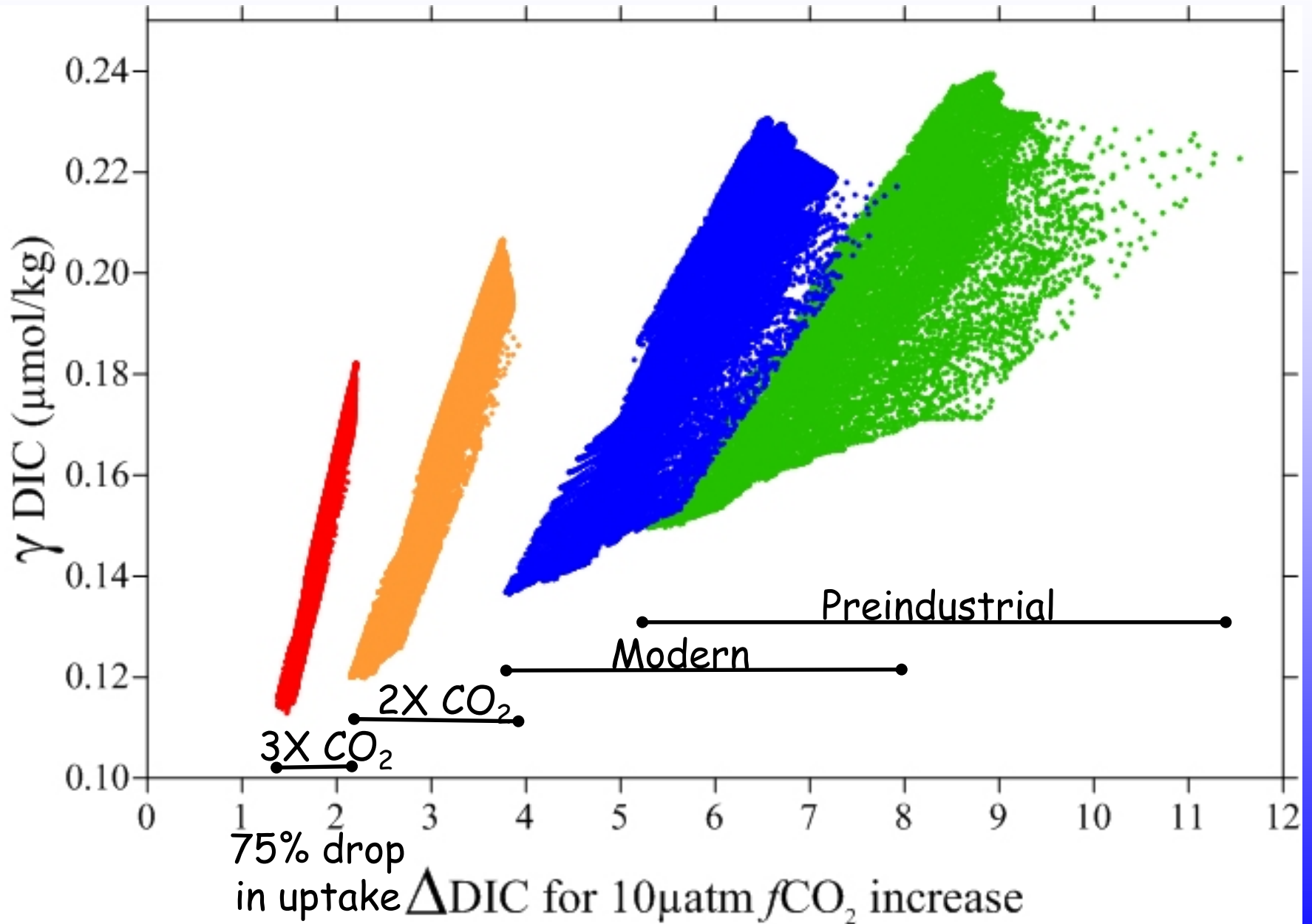
Higher buffer factor means larger DIC increase for the same amount of CO_2 rise



Higher buffer factor means larger DIC increase for the same amount of CO_2 rise

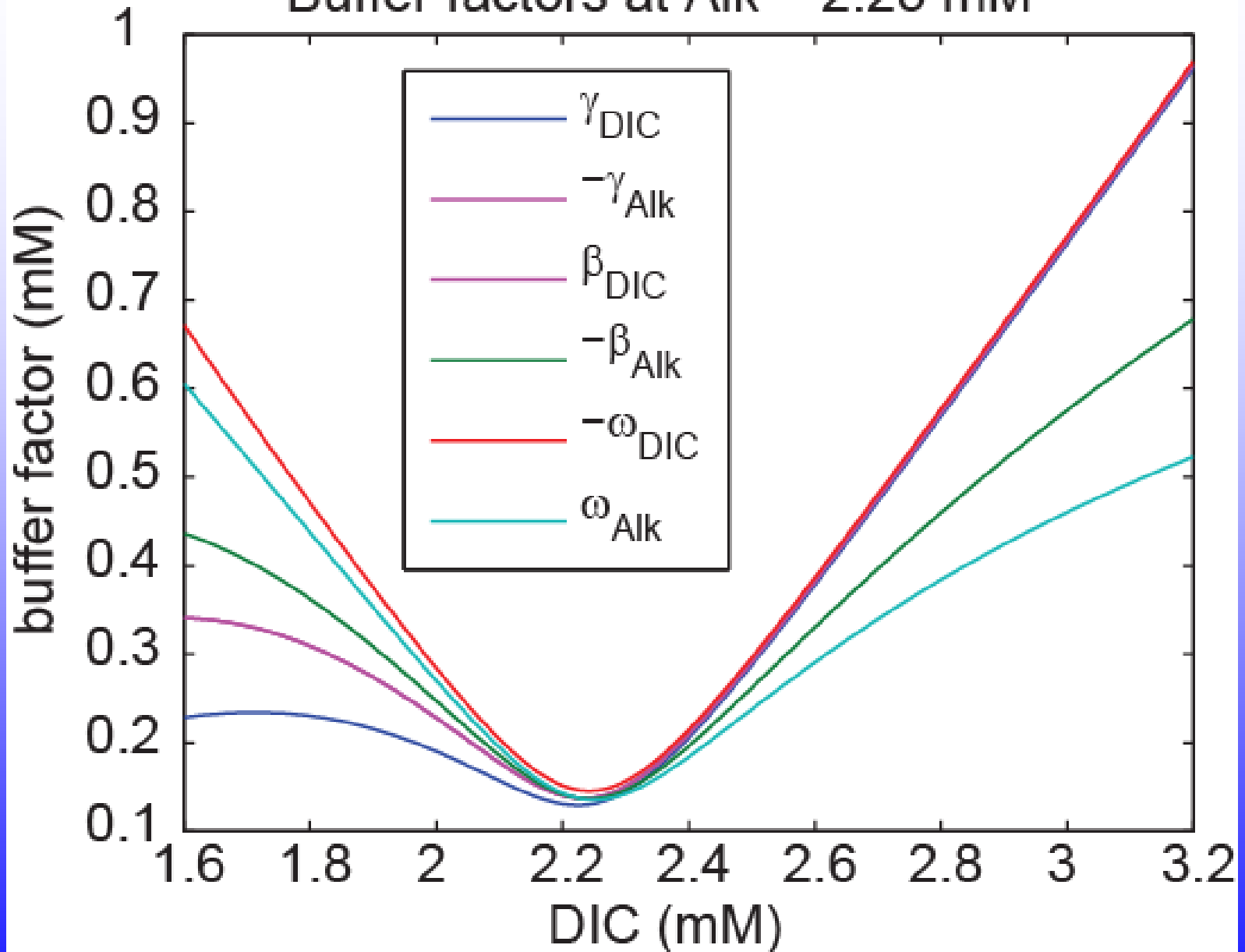


Higher buffer factor means larger DIC increase for the same amount of CO_2 rise

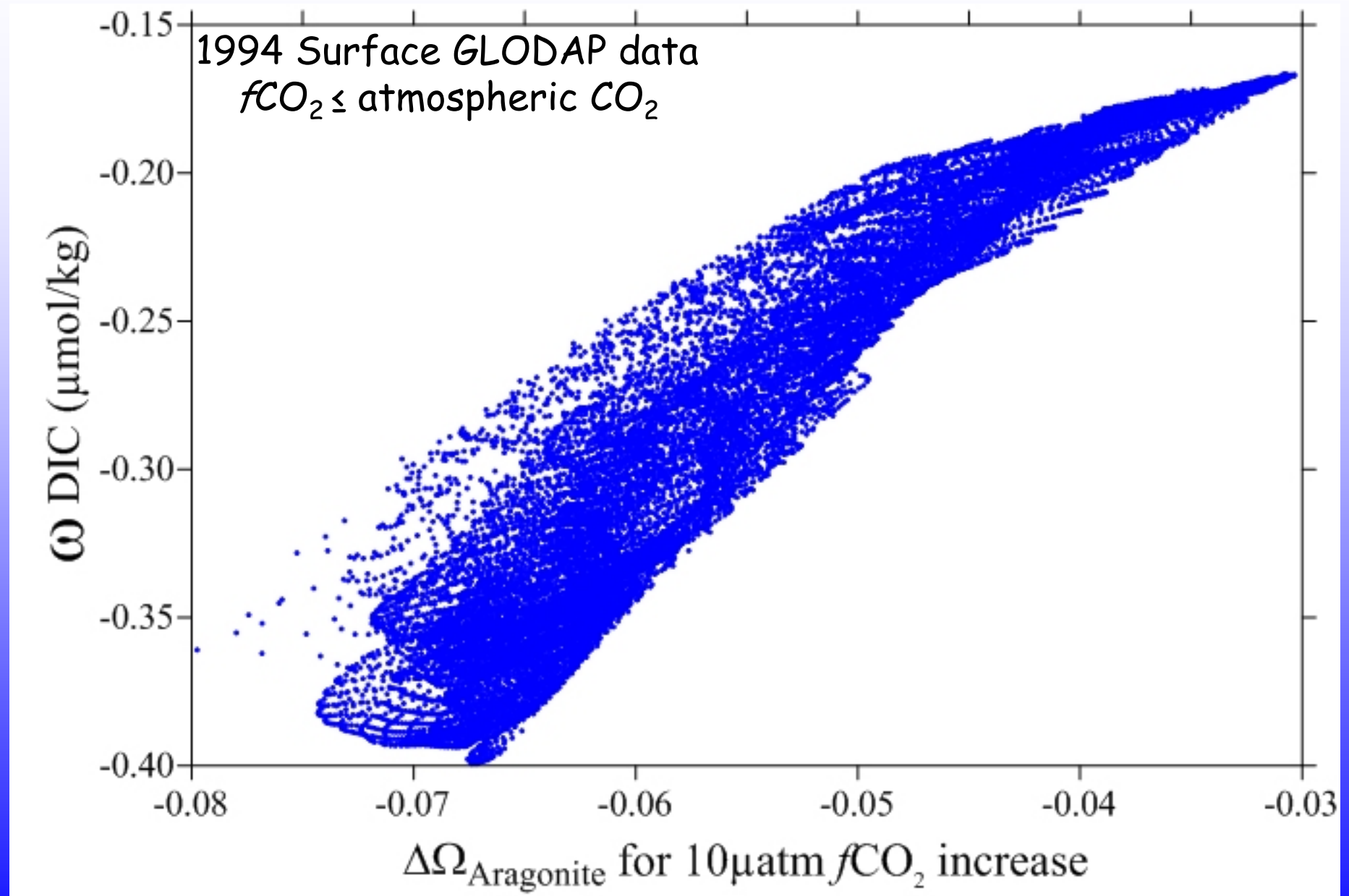


Omega-DIC has much steeper slope than gamma-DIC

Buffer factors at $Alk = 2.25$ mM

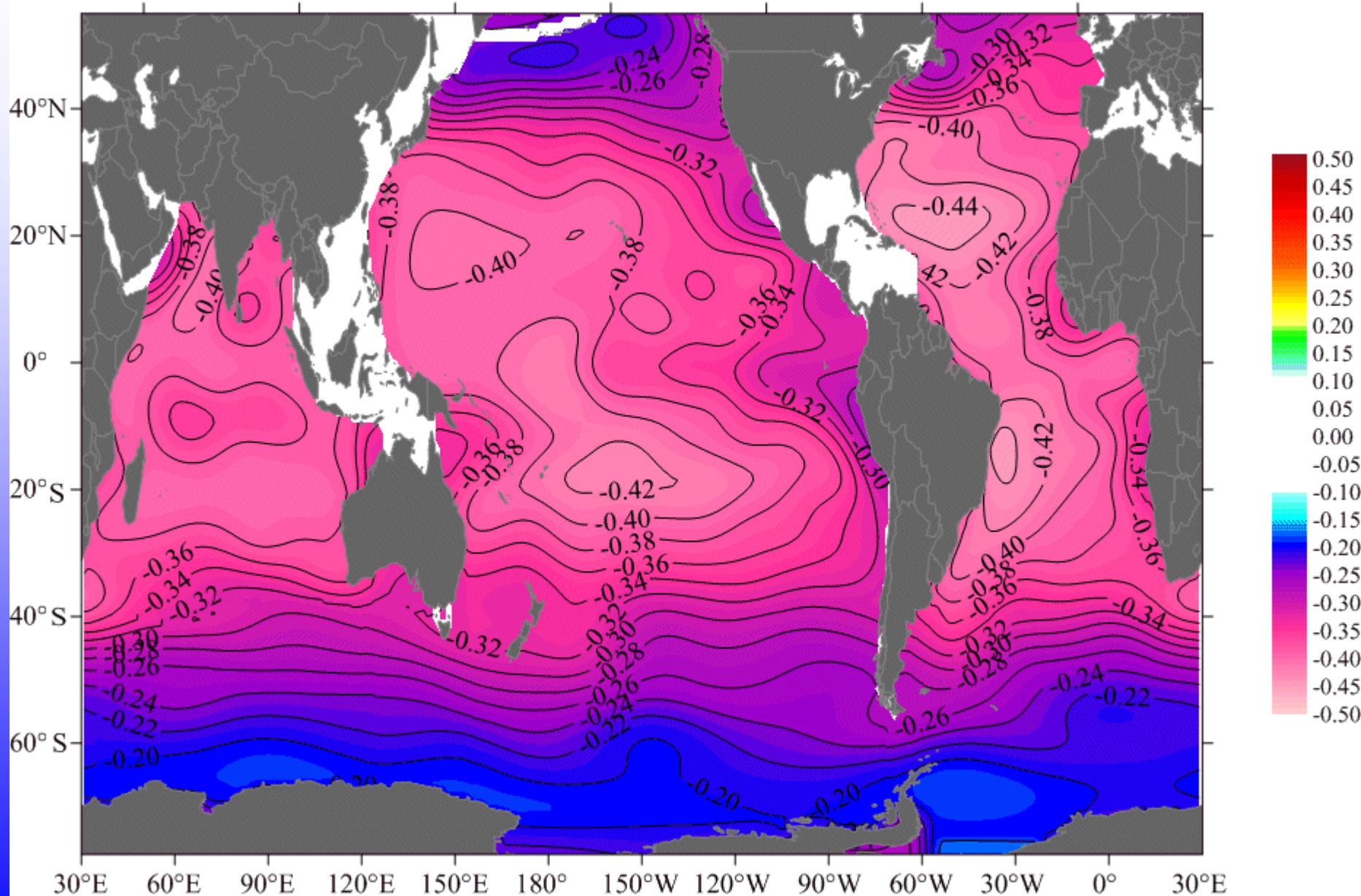


The more negative omega-DIC gets, the larger the drop in saturation state

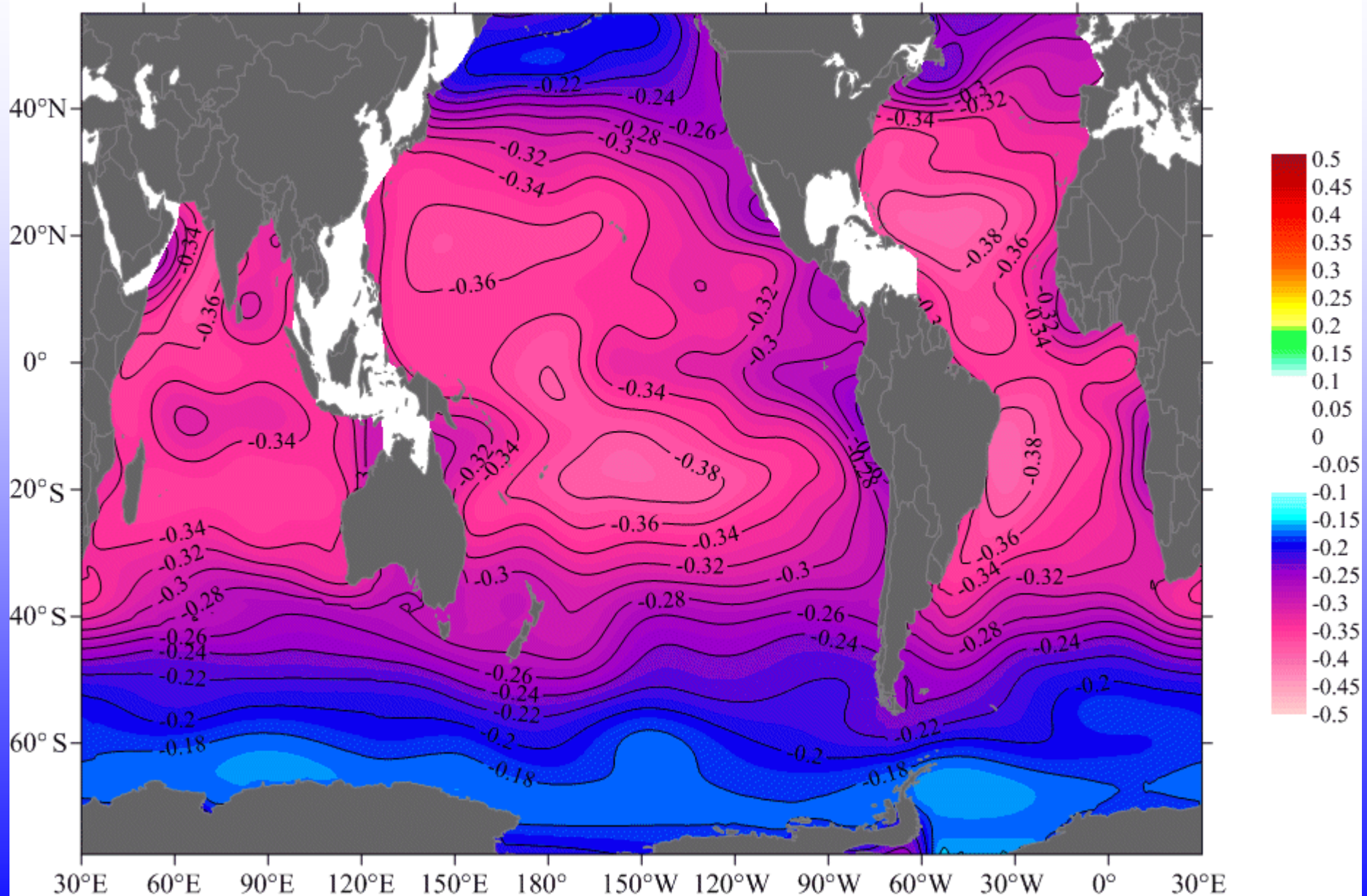


Preindustrial North Pacific ranges from -0.22-0.41 ($\Delta=.19$)

omega preindustrial DIC

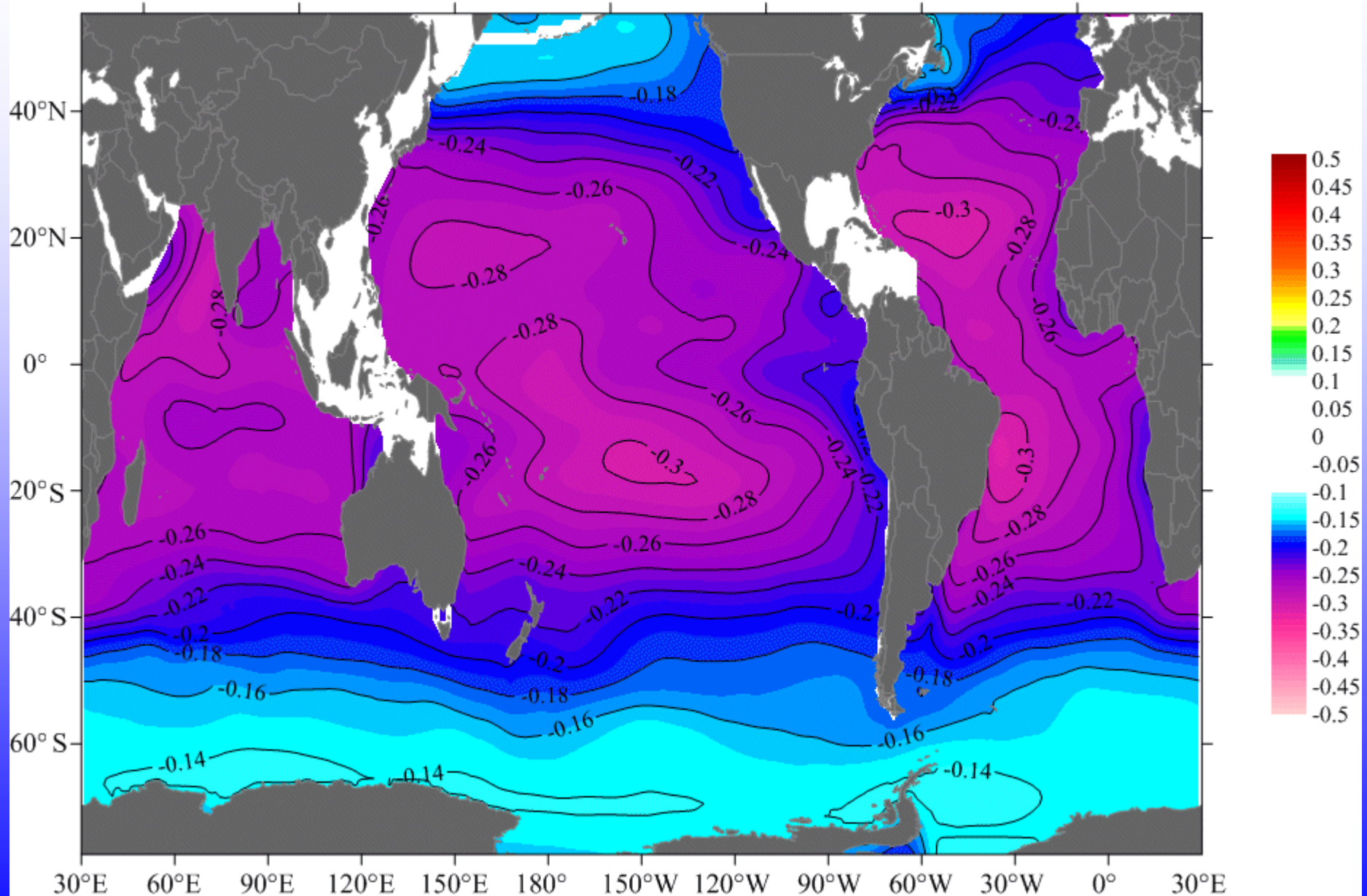


Modern North Pacific ranges from -0.20 - -0.37 ($\Delta=.17$) omega DIC



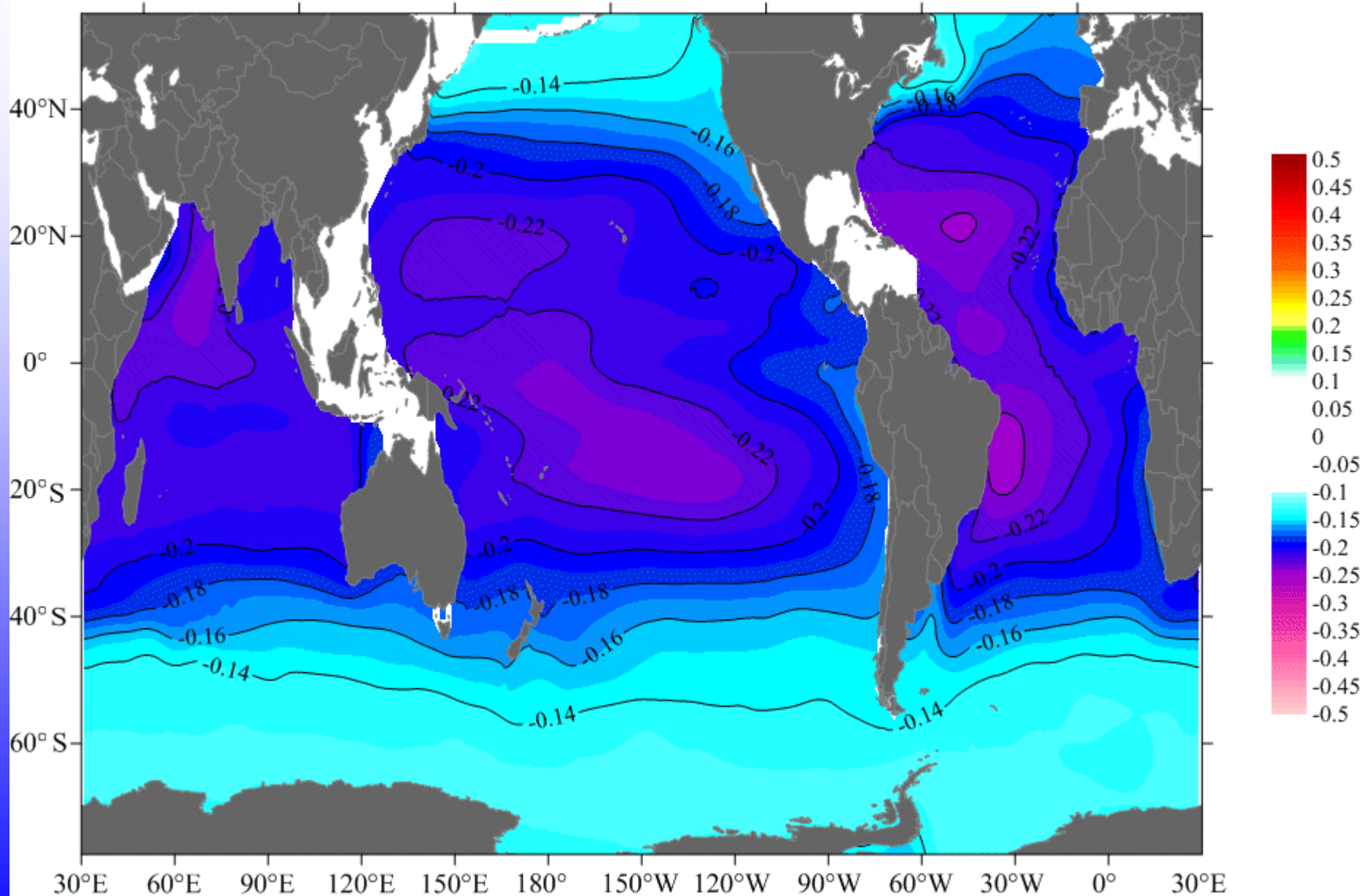
2X CO₂ North Pacific ranges from -0.15-0.28 ($\Delta=.13$)

omega DIC x 2

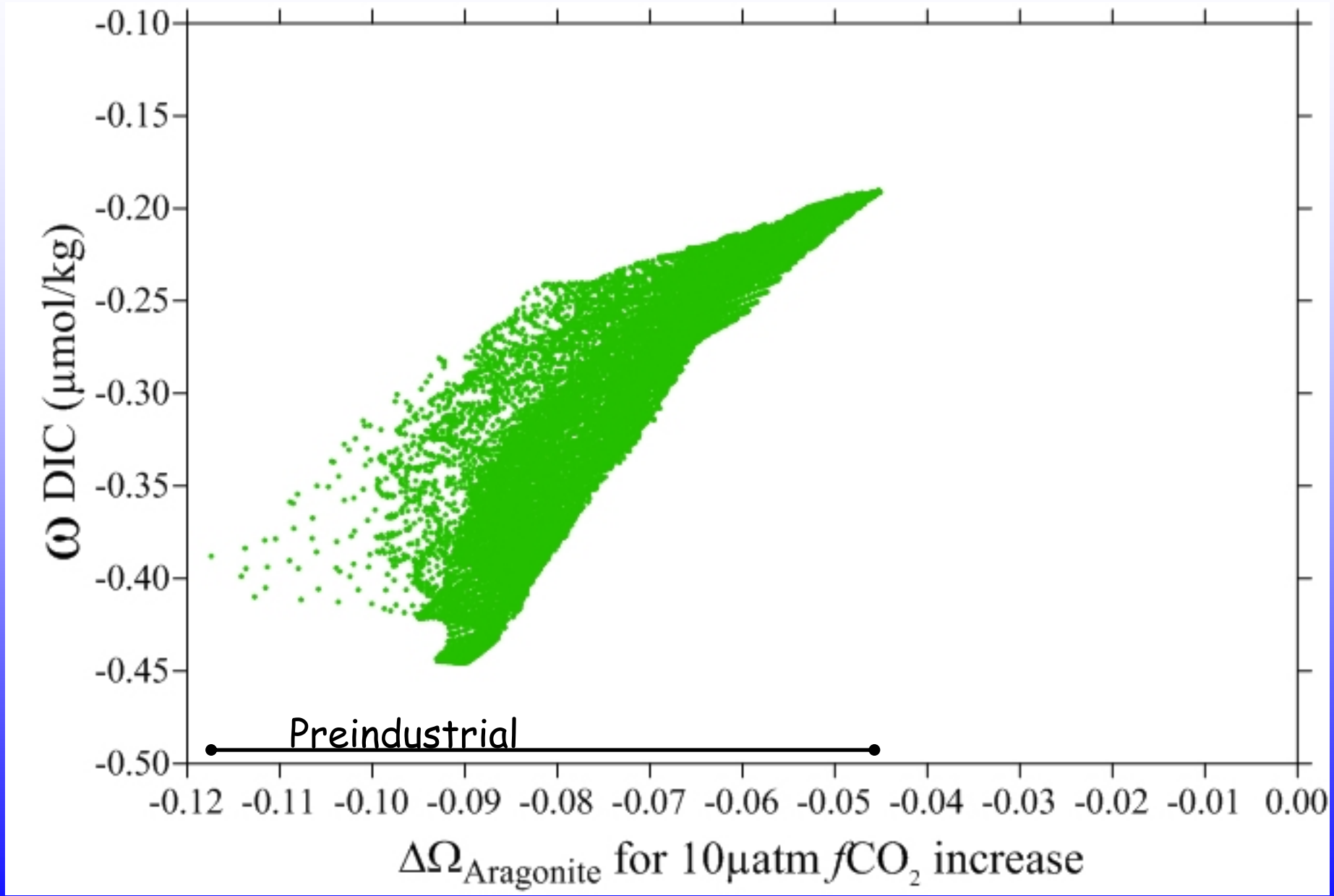


3X CO₂ North Pacific ranges from -0.14-0.22 ($\Delta=.08$)

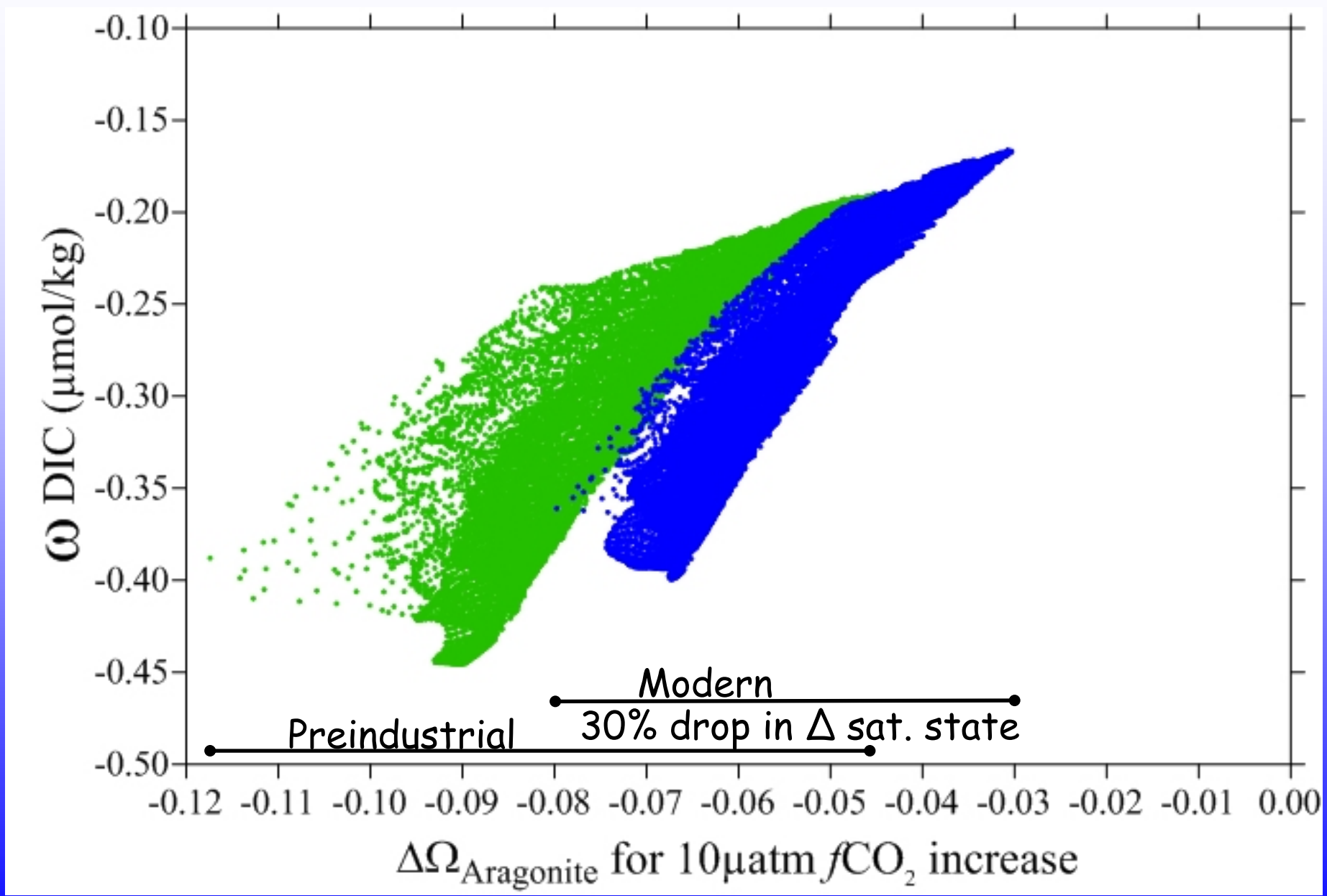
omega DIC x 3



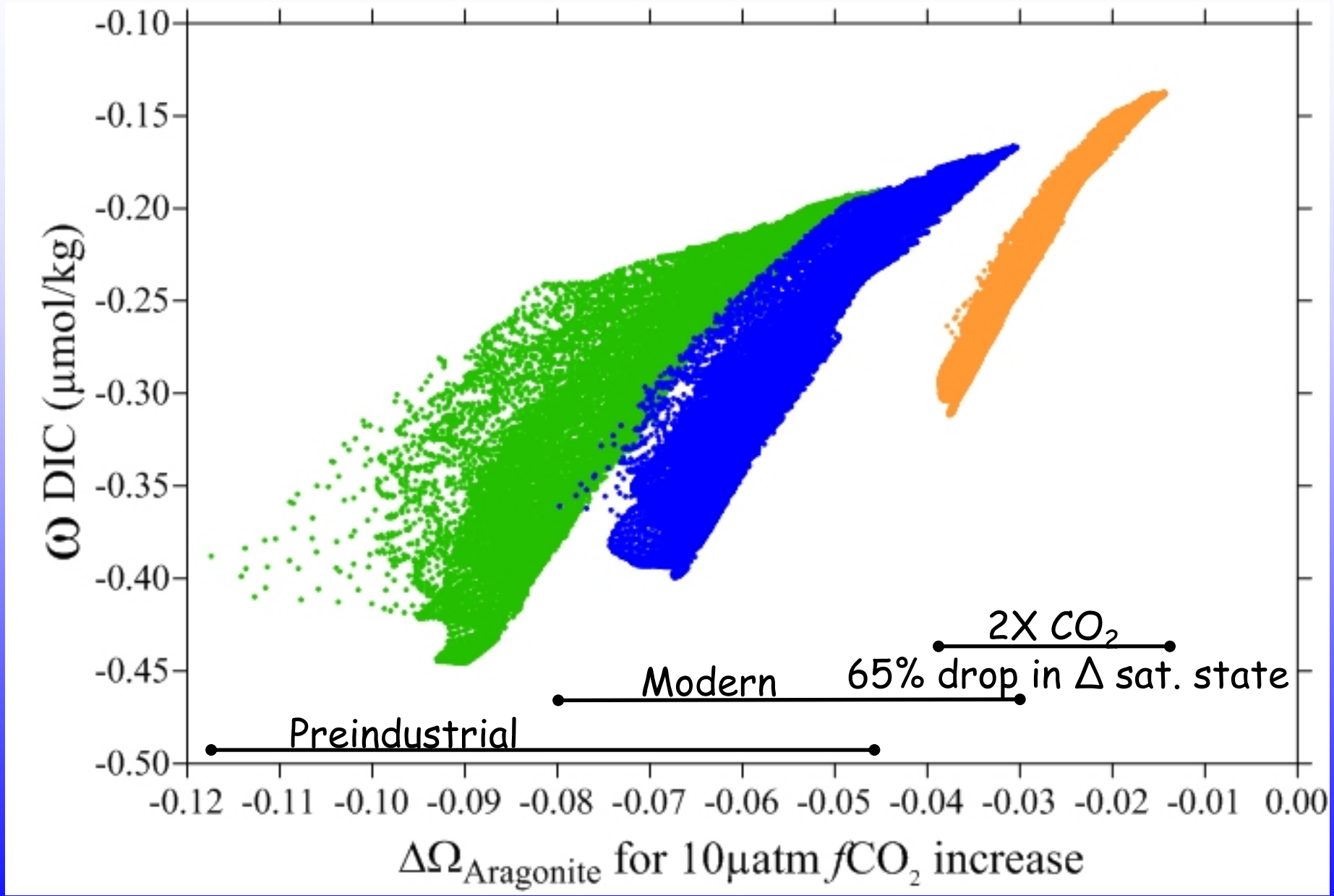
The more negative omega-DIC gets, the larger the drop in saturation state



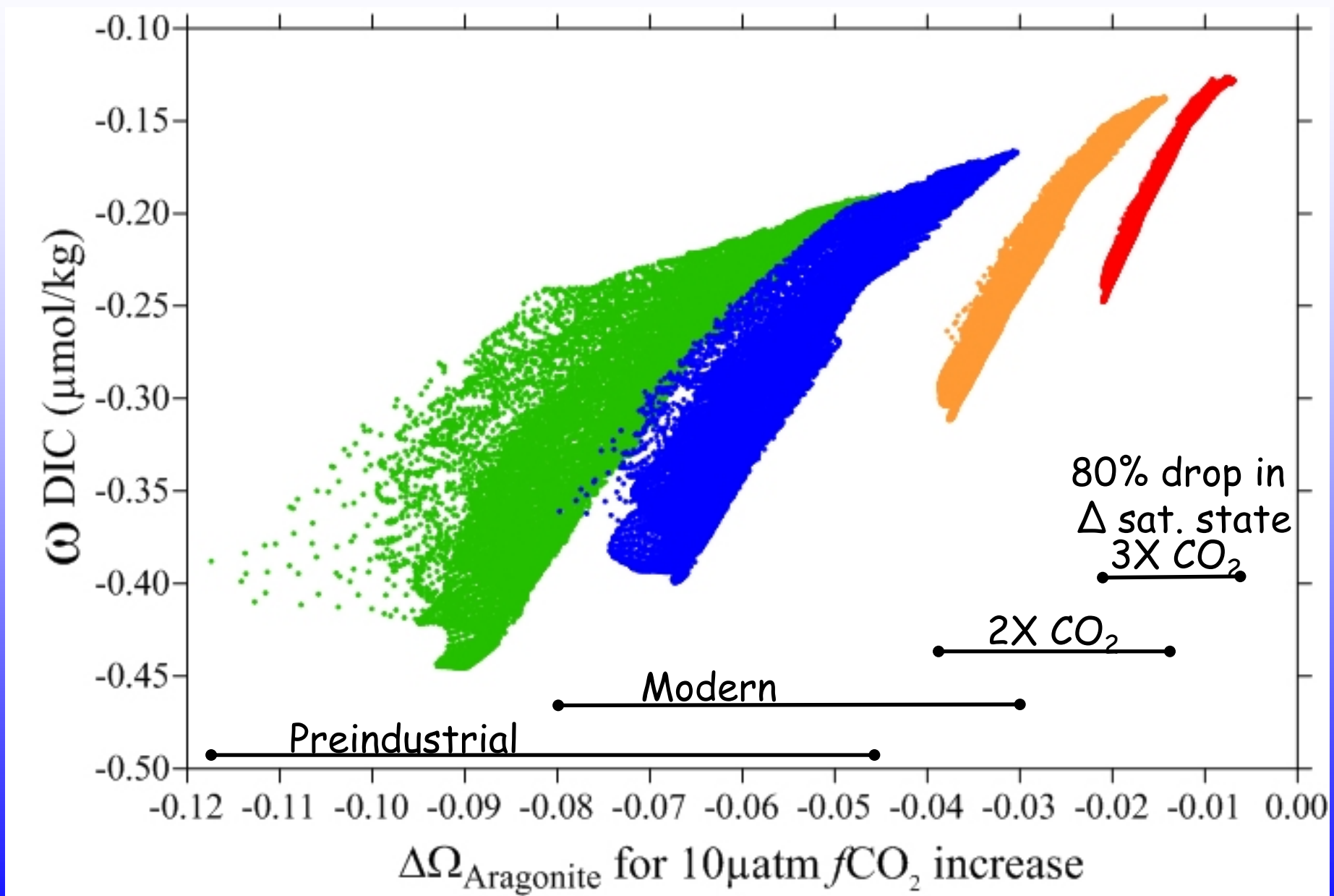
The more negative omega-DIC gets, the larger the drop in saturation state



The more negative omega-DIC gets, the larger the drop in saturation state

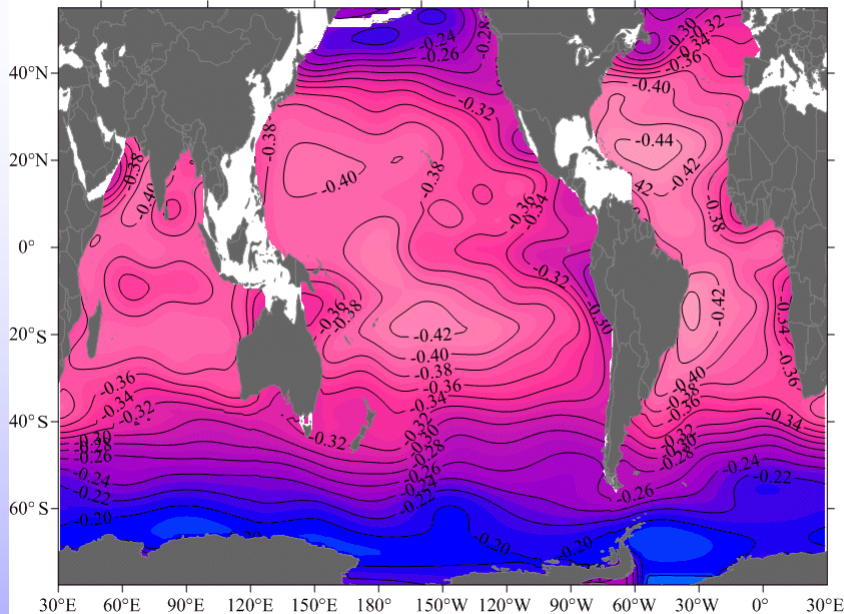


The more negative omega-DIC gets, the larger the drop in saturation state

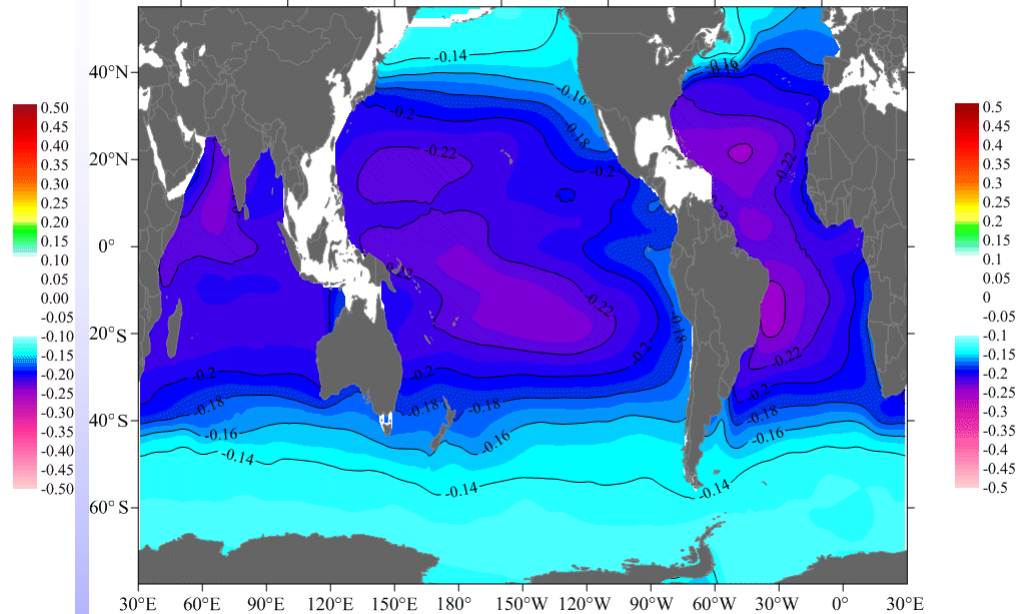


As we move to higher CO_2 levels, the spatial gradients get smaller

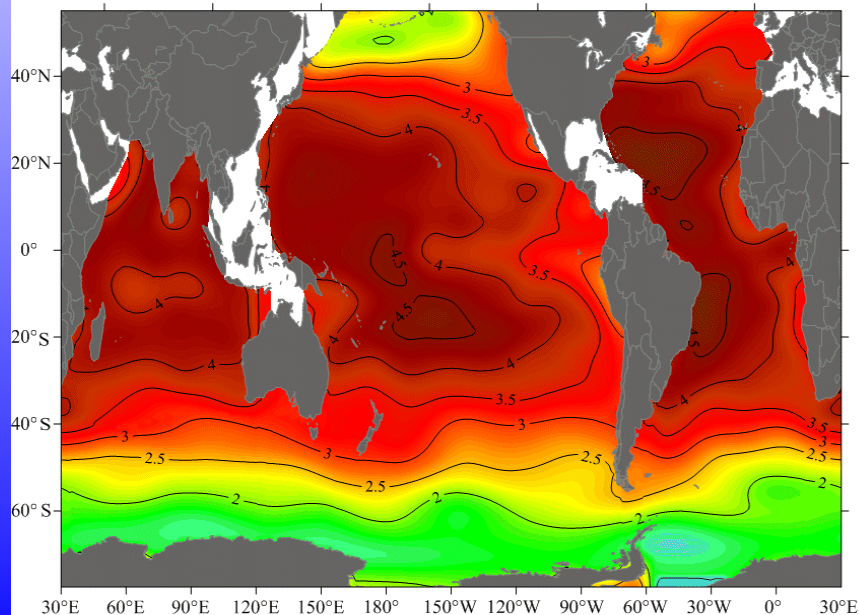
omega preindustrial DIC



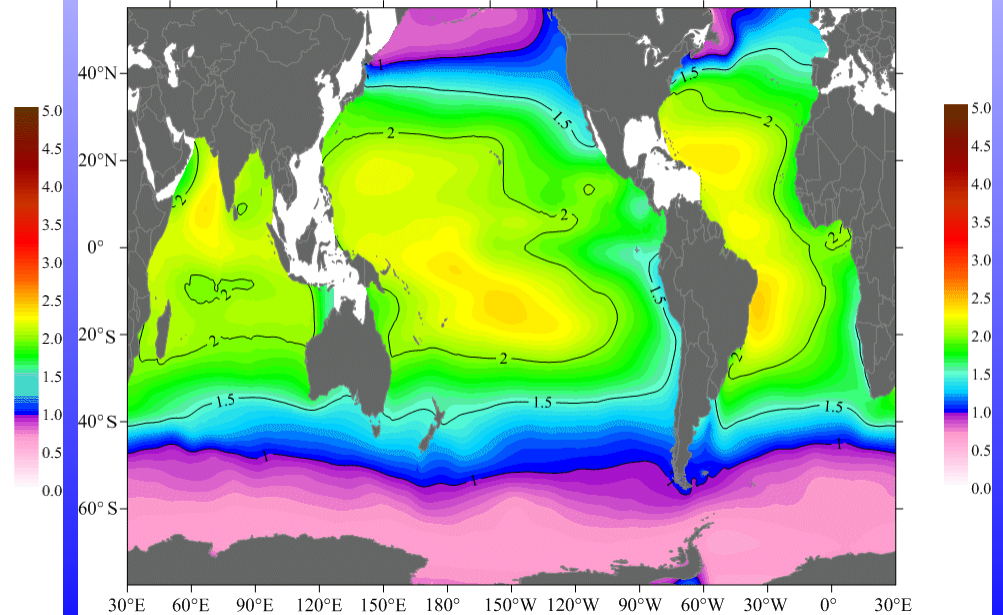
omega DIC x 3



Pre-industrial $\Omega_{\text{Aragonite}}$ Saturation State



$\Omega_{\text{Aragonite}}$ Saturation State x 3



Conclusions

1. Detailed studies of the inorganic carbon system are helping us to better understand the physical and biological processes in the ocean.
2. An understanding of the chemistry of inorganic carbon in the ocean is fundamental to understanding ocean acidification and the role of the ocean in the global carbon cycle.
3. At least two carbon parameters must be measured to constrain the ocean carbon system.
4. Each of the parameters is affected by ocean processes to a differing degree.
5. Rising CO_2 levels and global climate change will affect the processes controlling the distribution of carbon in the ocean, but what will be the net effect from the full range of forcing?
6. Additional carbon studies and sustained carbon measurements are needed to better understand the evolution of the ocean carbon system and ocean acidification.

Thank You!

Andrew will now go into more detail on CO_2 chemistry and the measurable carbon parameters



The R/V Thomas G. Thompson arriving in Papeete, Tahiti
for the beginning of P16N February 2006

Several Independent Approaches are Converging on an Estimate of the Anthropogenic CO₂ Uptake

Table 1. Summary of Recent Estimates of the Oceanic Uptake Rate of Anthropogenic CO₂ for the Period of the 1990s and Early 2000s

Method	Estimate (Pg C a ⁻¹)	Time Period	Authors
Estimates Based on Oceanic Observations			
Ocean Inversion (10 models)	-2.2 ± 0.3	Nominal 1995	this study and Mikaloff - Fletcher et al. [2006]
Ocean Inversion (3 models)	-1.8 ± 0.4	Nominal 1990	Gloor et al. [2003]
Air-sea pCO ₂ difference (adjusted) ^a	-1.9 ± 0.7	Nominal 2000 ^b	Takahashi et al. [2008]
Air-sea pCO ₂ difference (adjusted) ^{a,c}	-2.0 ± 60%	Nominal 1995	Takahashi et al. [2002]
Estimates Based on Atmospheric Observations			
Atmospheric O ₂ /N ₂ ratio	-1.9 ± 0.6	1990–1999	Manning and Keeling [2006]
Atmospheric O ₂ /N ₂ ratio	-2.2 ± 0.6	1993–2003	Manning and Keeling [2006]
Atmospheric O ₂ /N ₂ ratio	-1.7 ± 0.5	1993–2002	Bender et al. [2005]
Atmospheric CO ₂ inversions (adjusted) ^a	-1.8 ± 1.0	1992–1996	Gurney et al. [2004]
Estimates Based on Oceanic and Atmospheric Observations			
Air-sea ¹³ C disequilibrium	-1.5 ± 0.9	1985–1995	Gruber and Keeling [2001]
Deconvolution of atm. δ ¹³ C and CO ₂	-2.0 ± 0.8	1985–1995	Joos et al. [1999a]
Joint atmosphere-ocean inversion	-2.1 ± 0.2	1992–1996	Jacobson et al. [2007b]
Estimates Based on Ocean Biogeochemistry Models			
OCMIP-2 (13 models)	-2.4 ± 0.5	1990–1999	Watson and Orr [2003]
OCMIP-2 (4 “best” models) ^d	-2.2 ± 0.2	1990–1999	Matsumoto et al. [2004]

^a Adjusted by 0.45 Pg C a⁻¹ to account for the outgassing of natural CO₂ that is driven by the carbon input by rivers.

^b The estimate for a nominal year of 1995 would be less than 0.1 Pg C a⁻¹ smaller.

^c Corrected for wrong windspeeds used in published version; see http://www.ldeo.columbia.edu/res/pi/CO2/carbondioxide/pages/air_sea_flux_rev1.html.

^d These models were selected on the basis of their ability to simulate correctly, within the uncertainty of the data, the observed oceanic inventories and regional distributions of chlorofluorocarbon and bomb radiocarbon.