

# Multiple stressors in coastal ocean environments – rethinking the impact of ocean acidification

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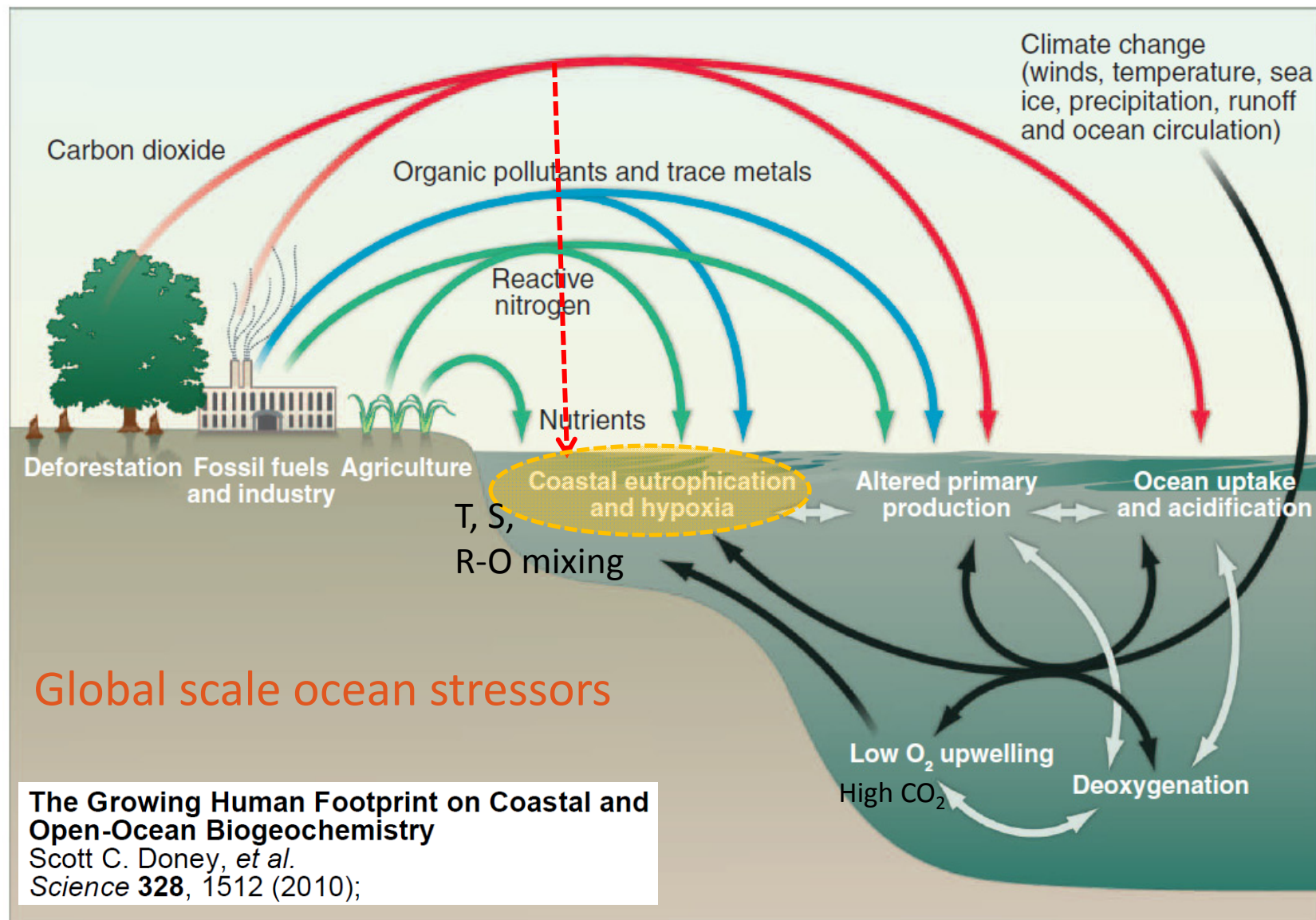
WHOI, July 16-19, 2012



# Outline

- Introduction
- Examples of acidification and low O<sub>2</sub> events in coastal waters
- Responses of ocean CO<sub>2</sub> system to multiple stressors: based on first principles
- Possible impacts on organisms, ecosystem and biogeochemical processes
- Summary





**Fig. 1.** Schematic of human impacts on ocean biogeochemistry either directly via fluxes of material into the ocean (colored arrows) or indirectly via climate change and altered ocean circulation (black arrows). The gray arrows denote the interconnections among ocean biogeochemical dynamics. Note that many ocean processes are affected by multiple stressors, and the synergistic effects of human perturbations is a key area for further research.

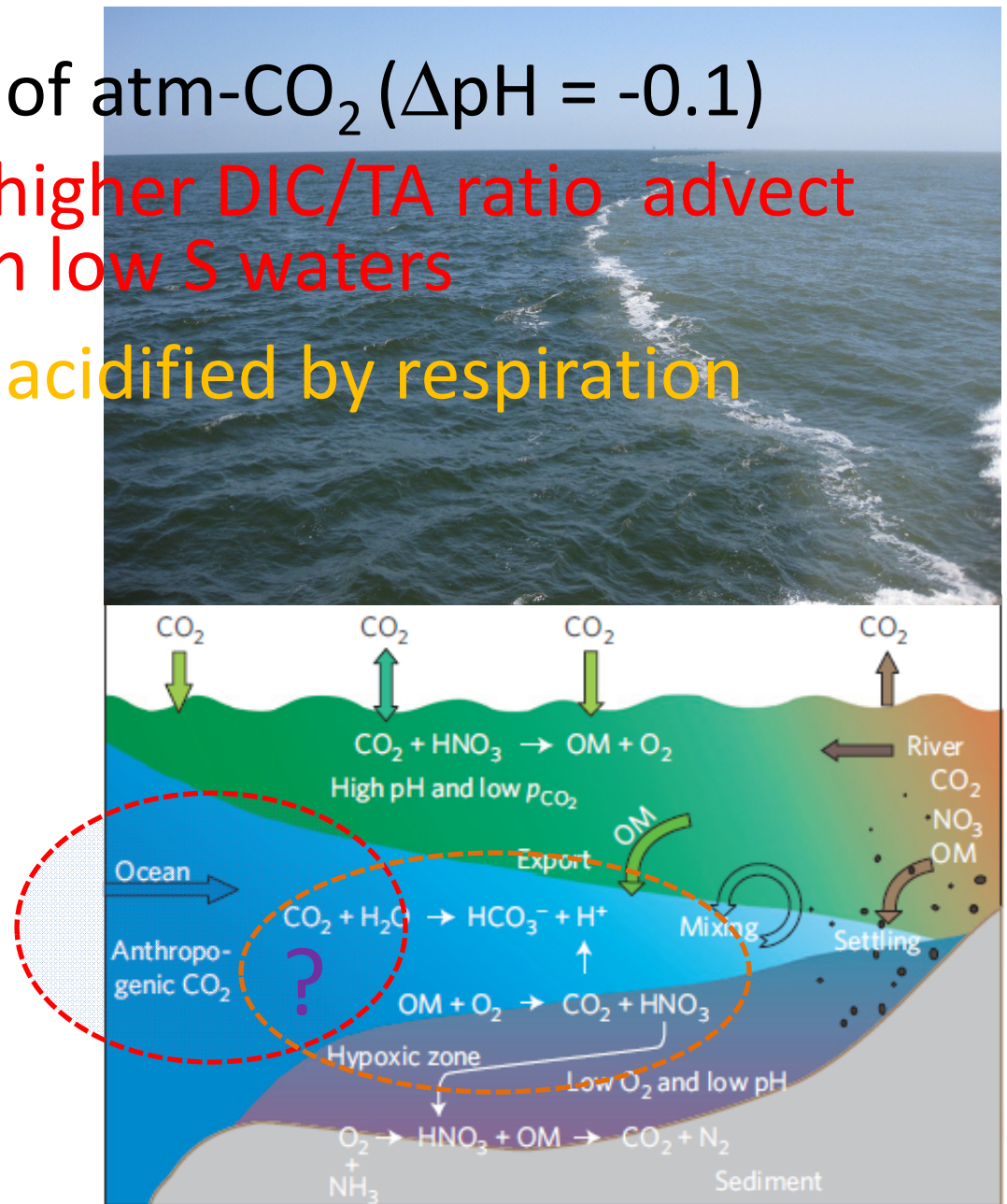
# Coastal ocean stressors— either directly or indirectly related to OA

- Temperature stress
  - Global warming; local extreme weather
- Salinity stress
  - Tidal cycle; reduced or increased freshwater input
- River end-member increase
- Nutrient stress
  - Fertilizer use ( $\text{NO}_3$ ); sewage discharge ( $\text{NH}_4$ )
- (low)  $\text{O}_2$  stress
- $\text{CO}_2$  (high and low) stress
- More frequent storm
- ...

# Ocean acidification (in coastal waters?)

- Global ocean uptake of atm- $\text{CO}_2$  ( $\Delta\text{pH} = -0.1$ )
- Source water with a higher DIC/TA ratio advect onshore and mix with low S waters
- This water is further acidified by respiration

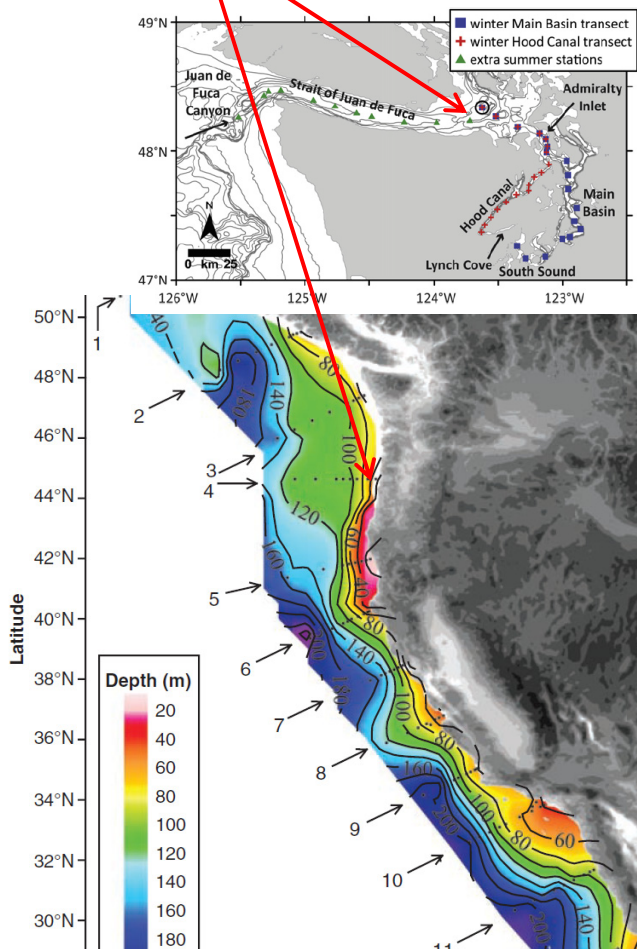
How do they interact?



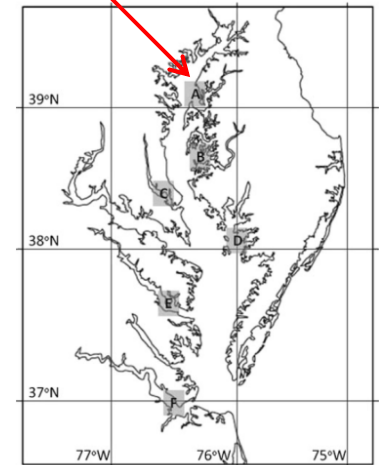
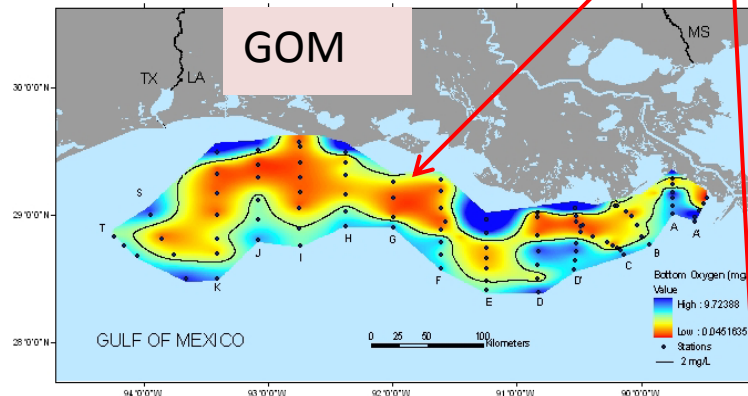


# Examples of acidification and low O<sub>2</sub> events in coastal waters

## Major upwelling impacted waters



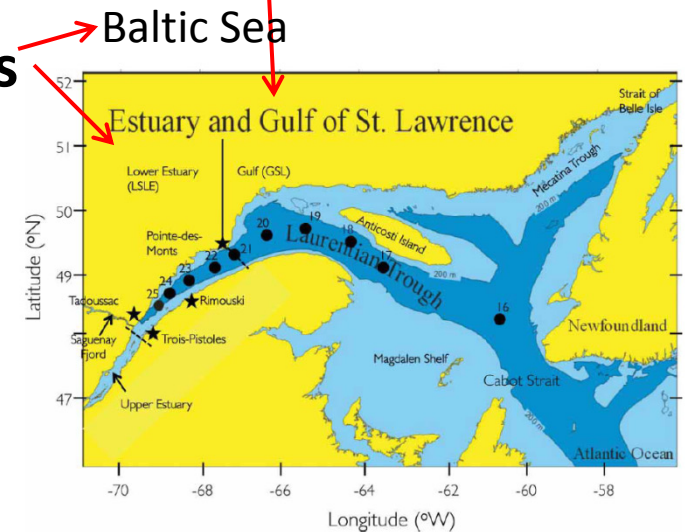
## Within and under eutrophic river plumes (warm waters)



Chesapeake Bay

## low temp waters

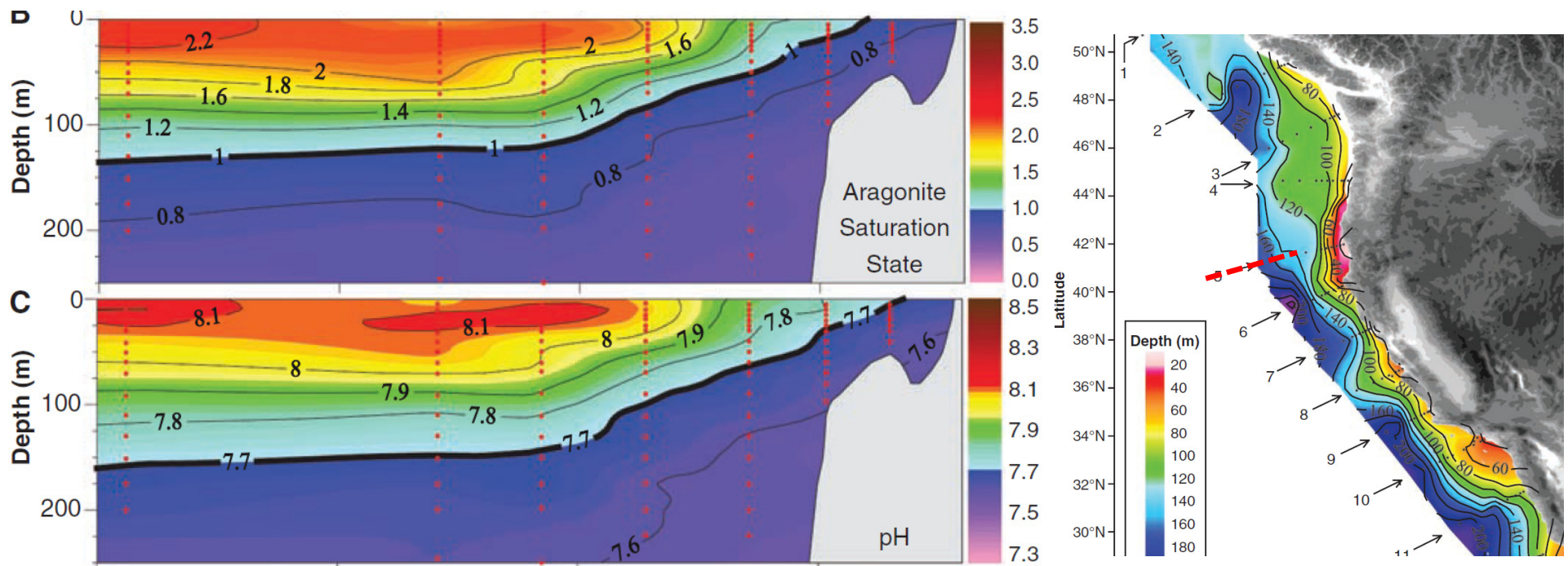
The Bering Sea and Arctic Ocean coastal waters



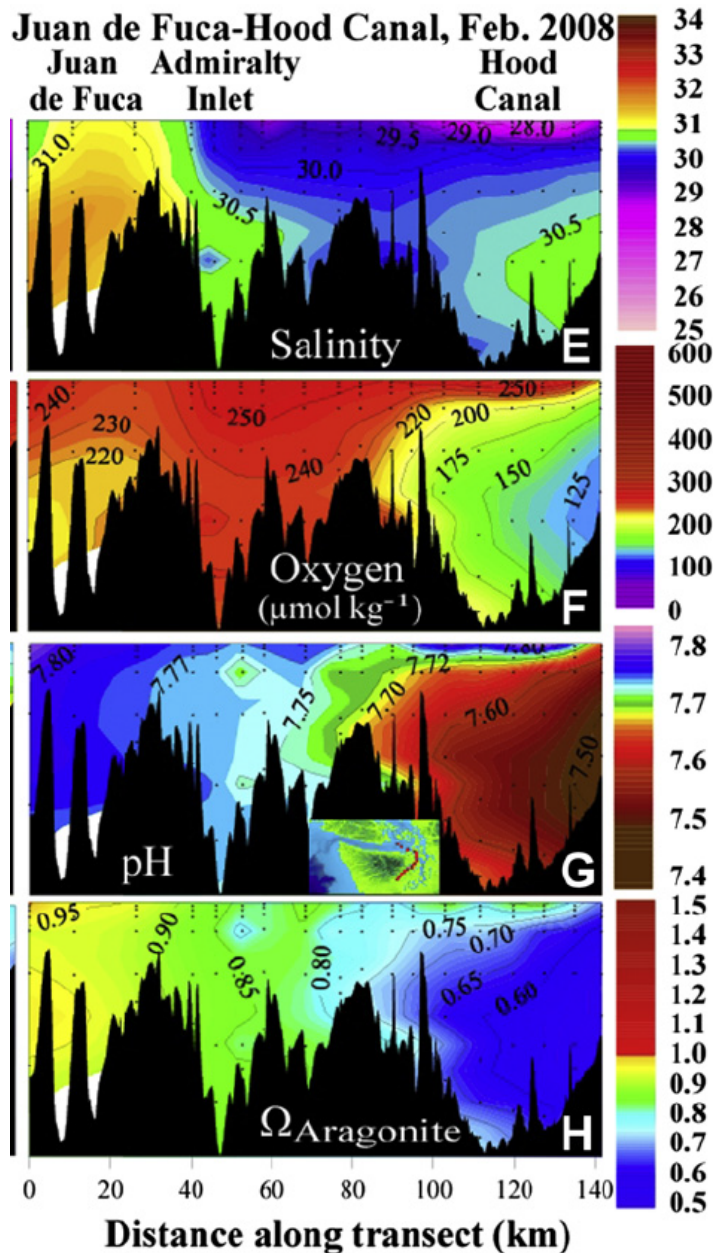
# Acidification and low O<sub>2</sub> events in coastal waters--1.

At an eastern boundary current shelf

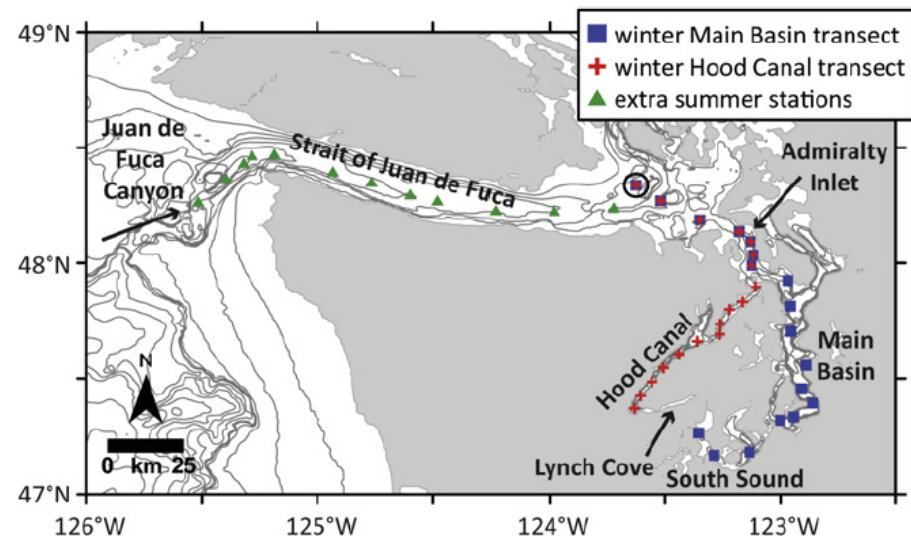
- dominated by upwelling of open ocean subsurface water with **low temp**, **low [O<sub>2</sub>]**, **low pH**, **low  $\Omega$** , and **high  $p\text{CO}_2/\text{DIC}$**  on to the shelf (Feely et al. 2008, Science)



# Acidification and low O<sub>2</sub> events in coastal waters--2.



- In an upwelling dominated submerged estuary/bay (Puget Sound)

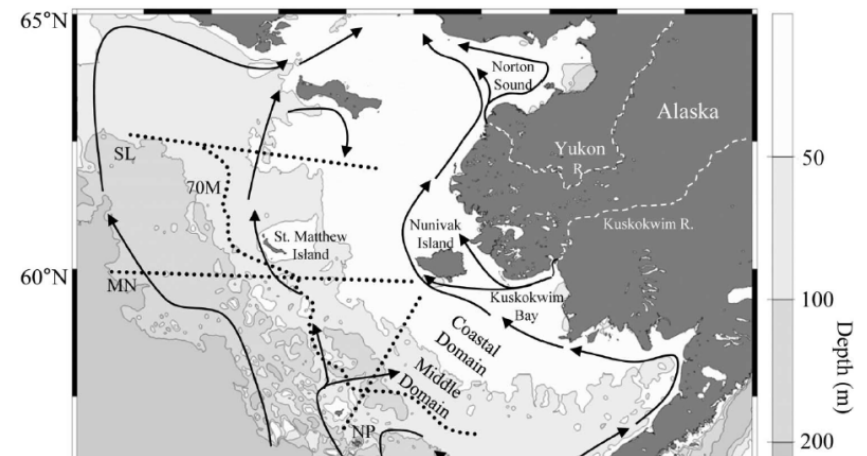
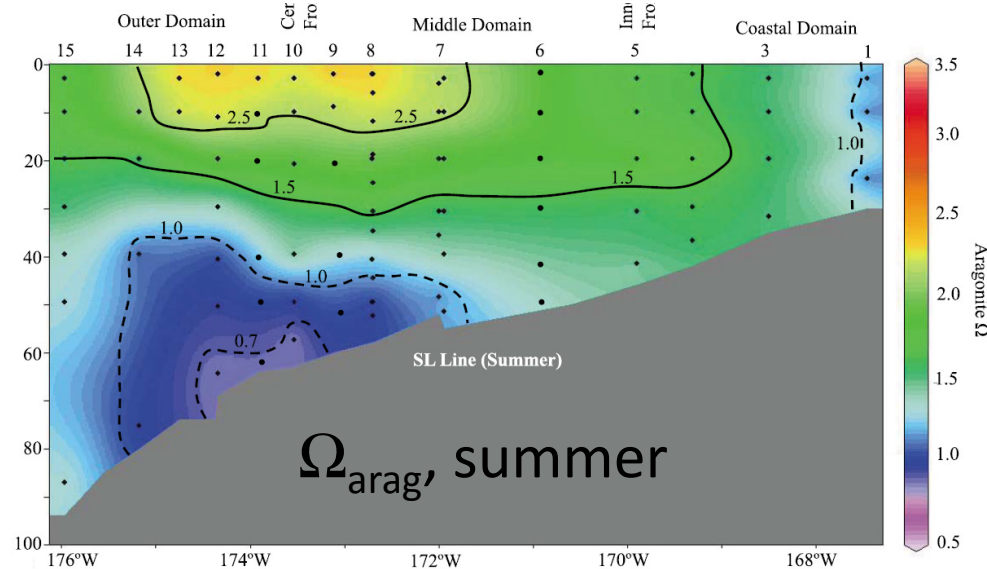
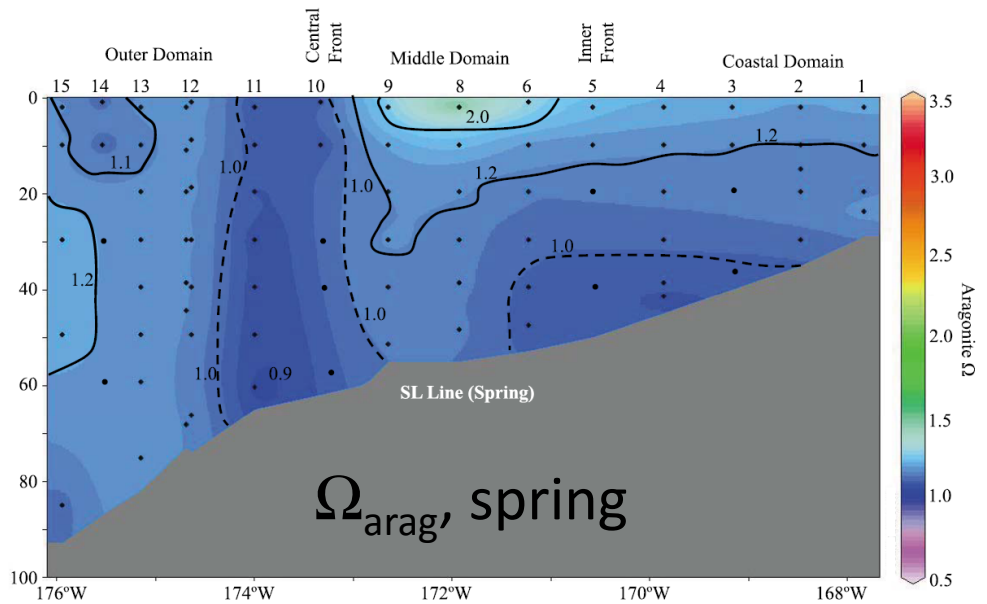


Feely et al. 2010, ECSS



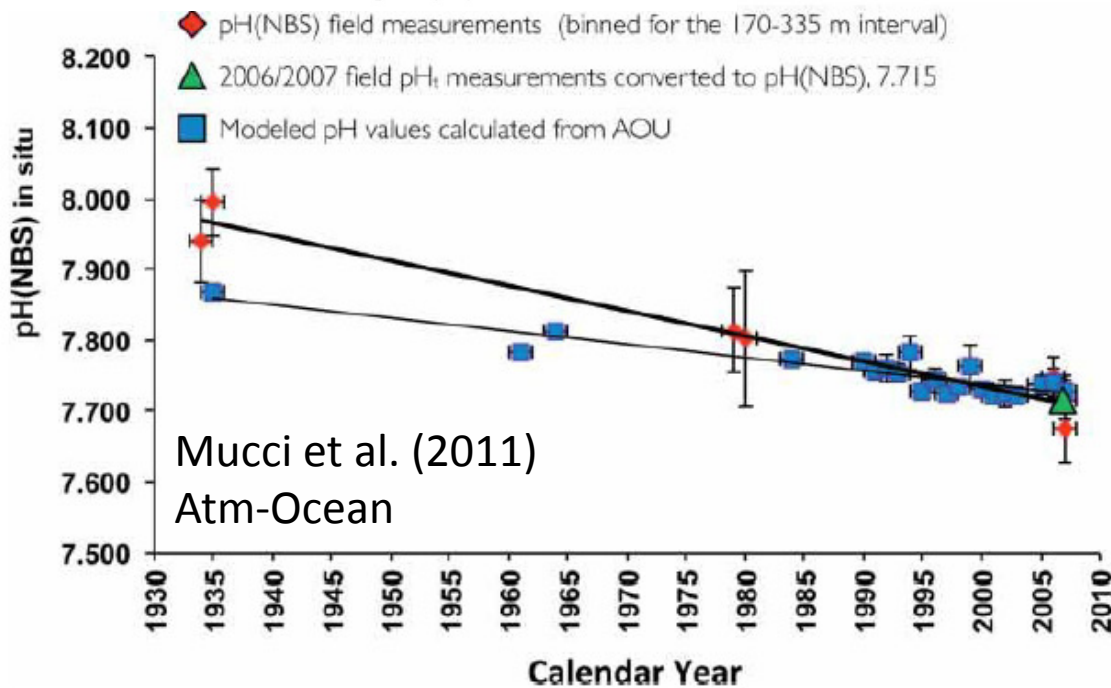
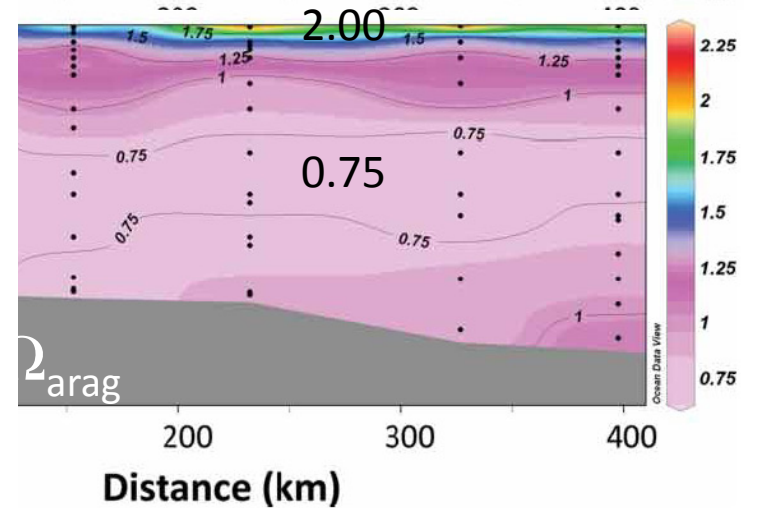
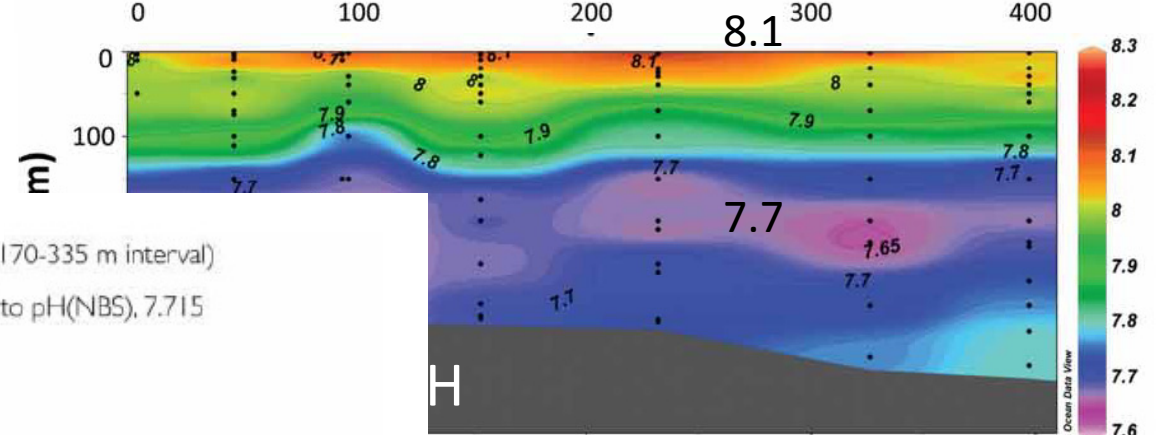
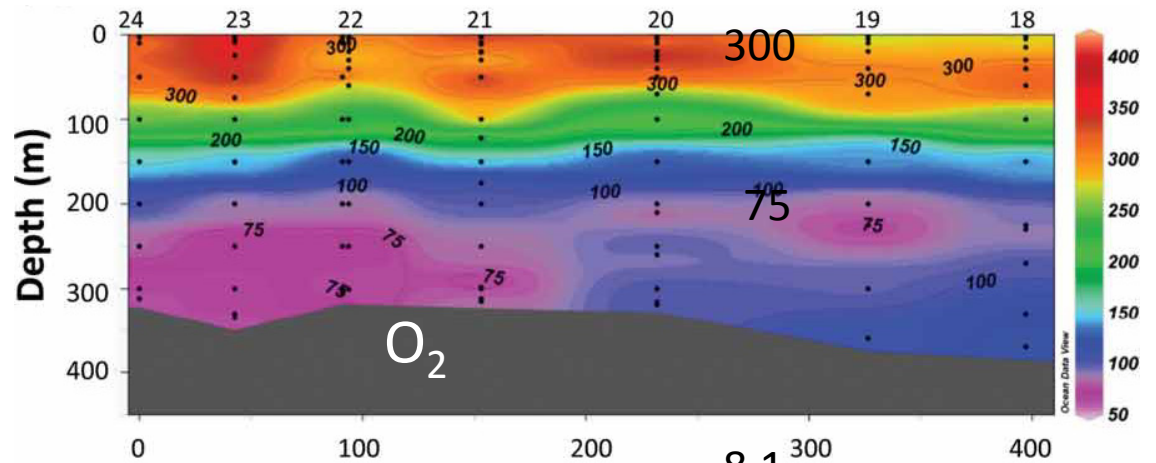
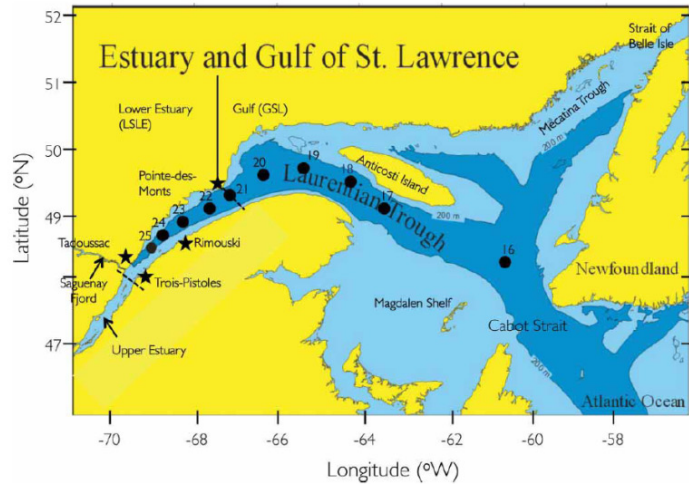
# Acidification and low O<sub>2</sub> events in coastal waters—3.

- High latitude waters (Eastern Bering Sea)



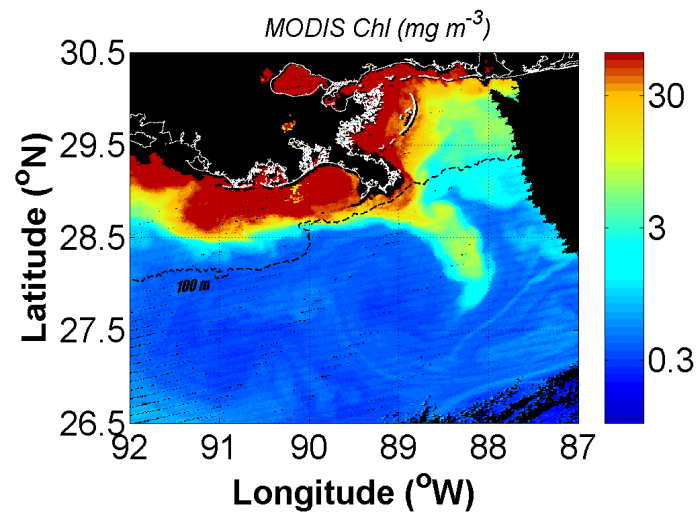
(Mathis et al. 2011; JGR)

# 4. St. Lawrence Estuary & Gulf

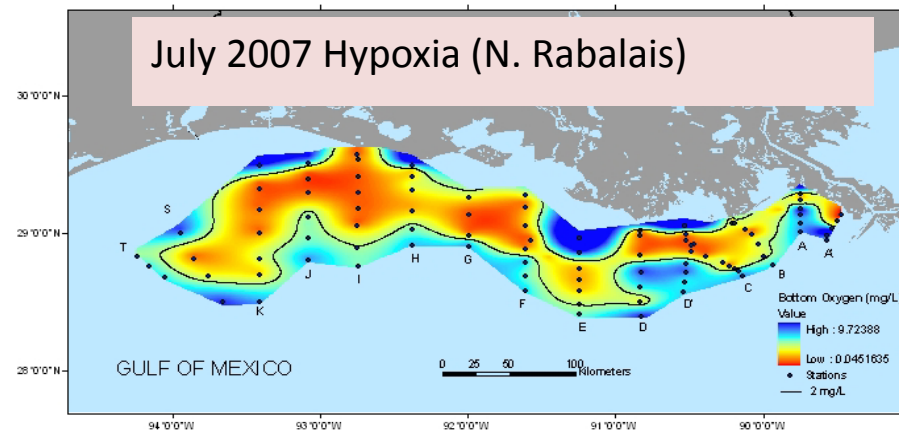


# Acidification and low O<sub>2</sub> events in coastal waters—5.

- Eutrophication-hypoxia is not only a serious regional stressor, it is also



## MR/GOM



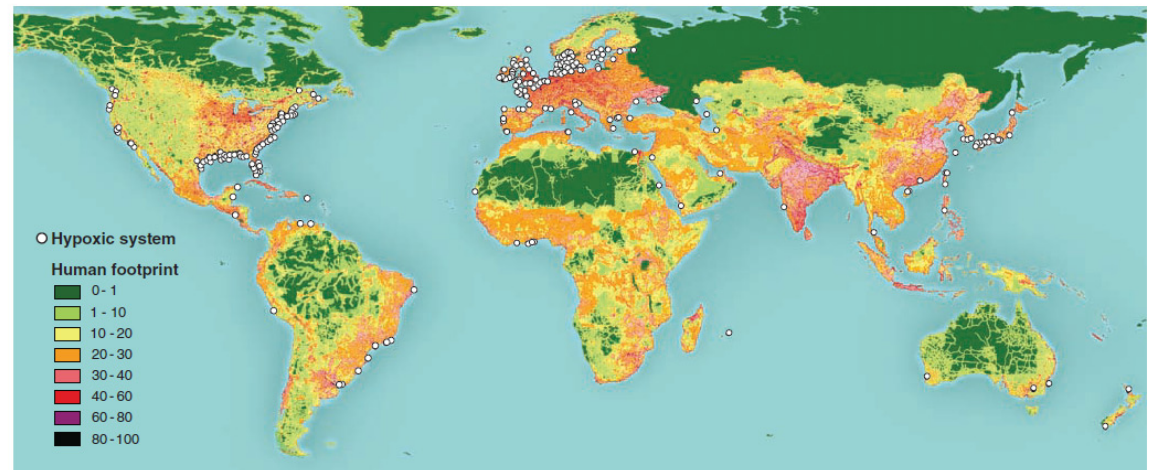
a globally threat.

### Spreading Dead Zones and Consequences for Marine Ecosystems

Robert J. Diaz, *et al.*

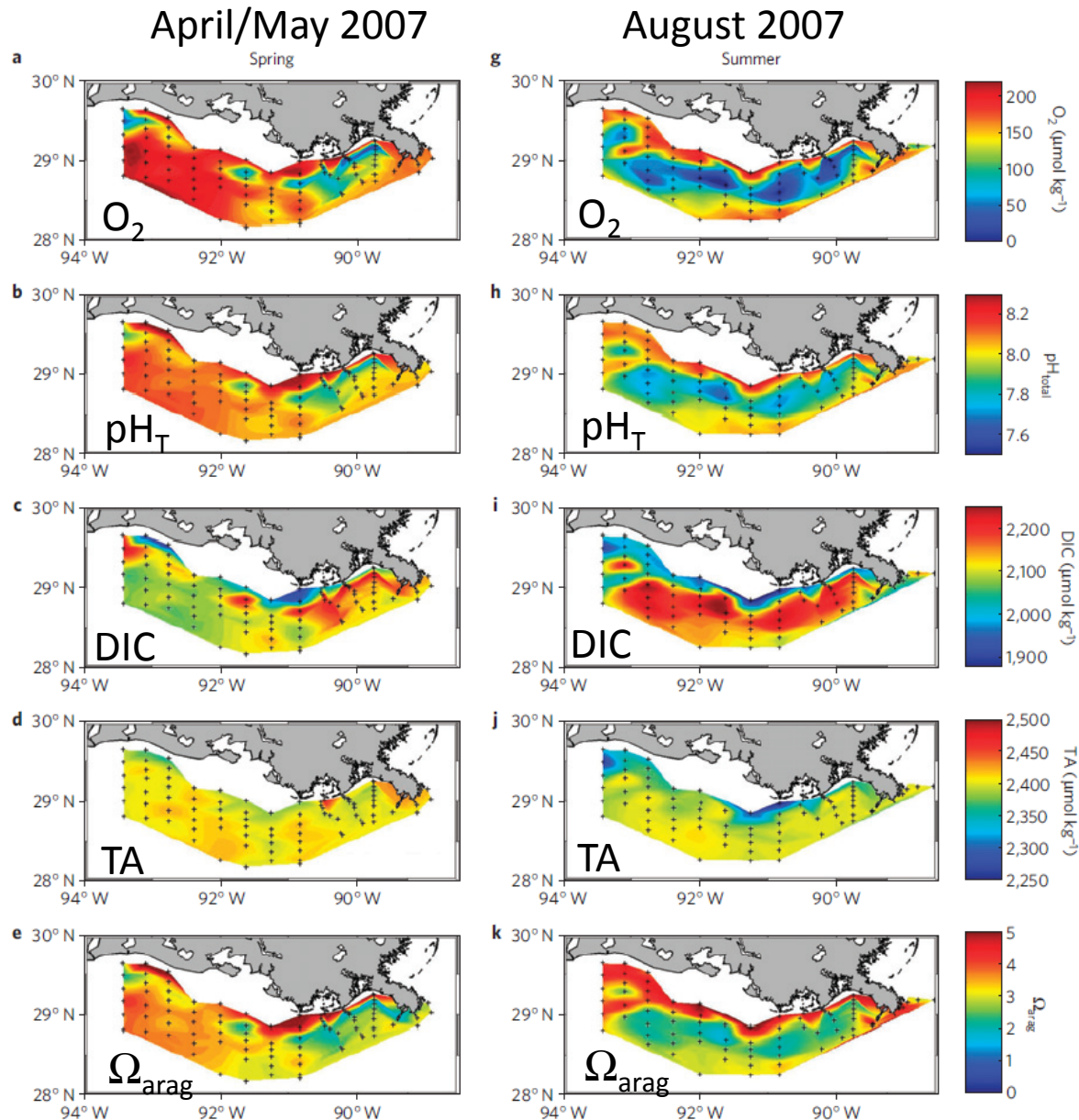
*Science* **321**, 926 (2008);

DOI: 10.1126/science.1156401





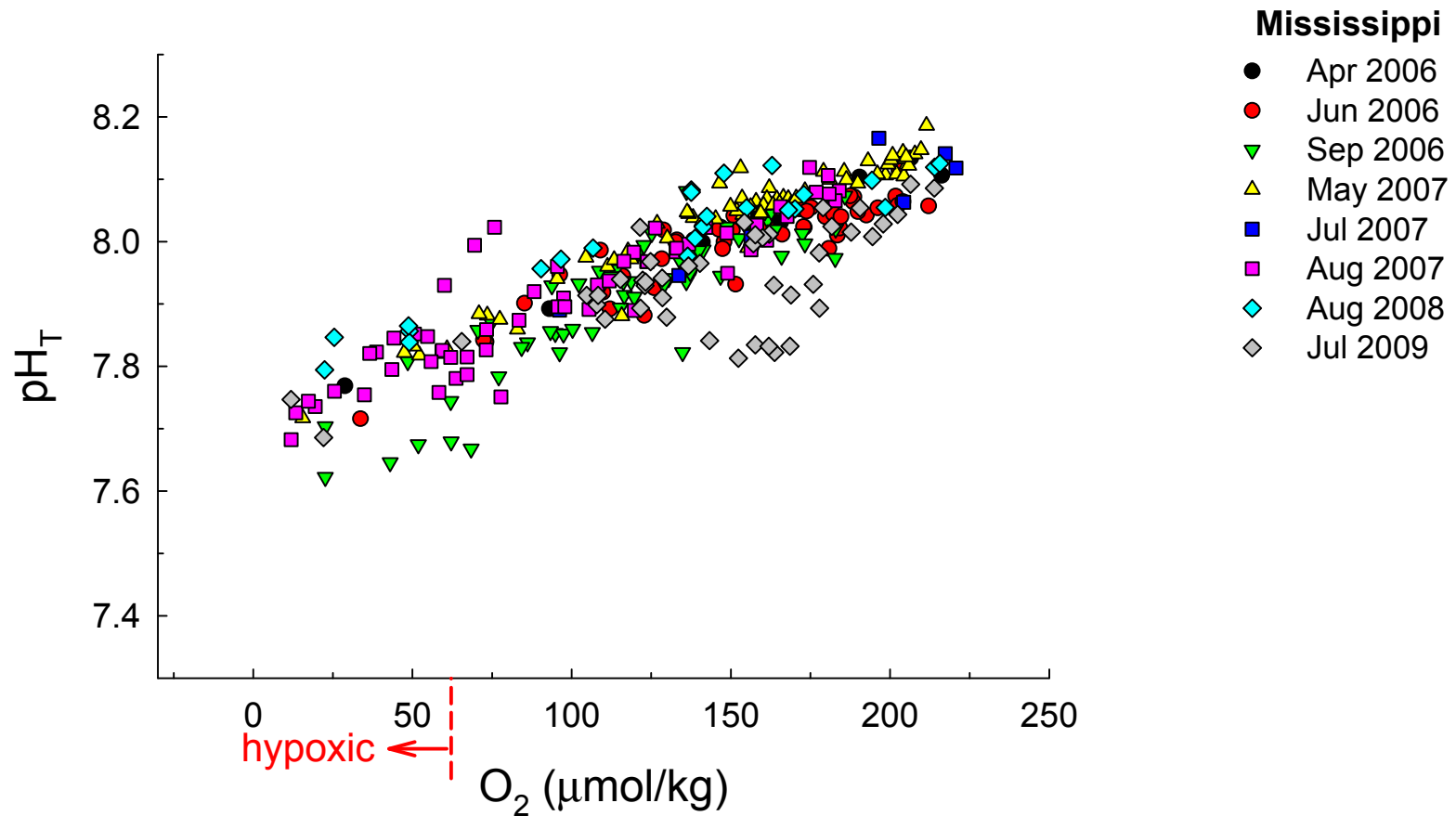
# Acidification and low O<sub>2</sub> events in coastal water--5.



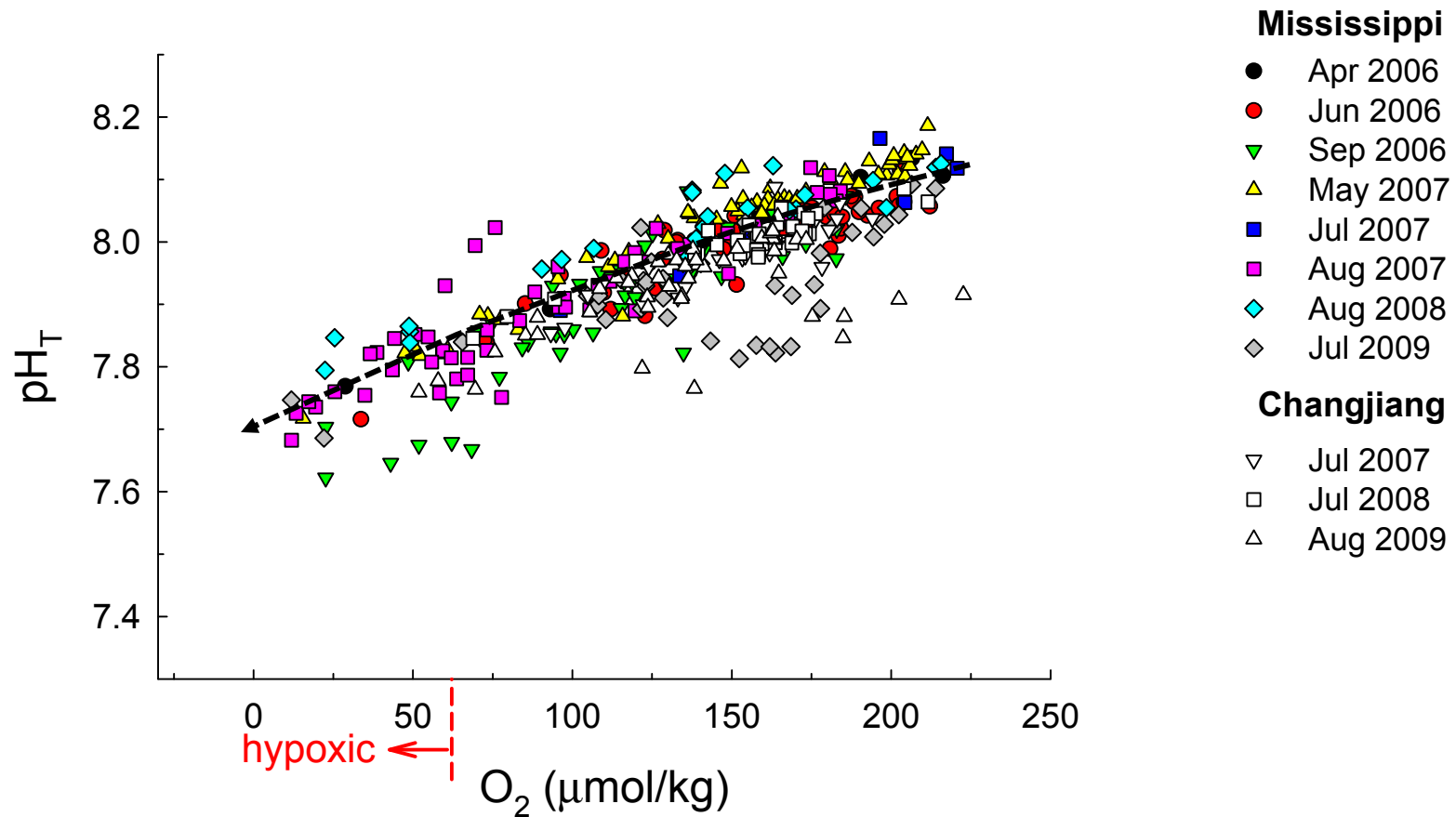
- Gulf of Mexico hypoxic water

Cai et al. 2011  
Nature Geoscience

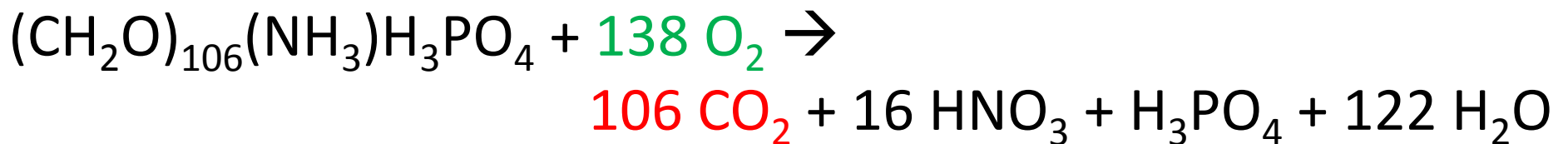
# Subsurface water pH and [O<sub>2</sub>] relationship



# Subsurface water pH and [O<sub>2</sub>] relationship



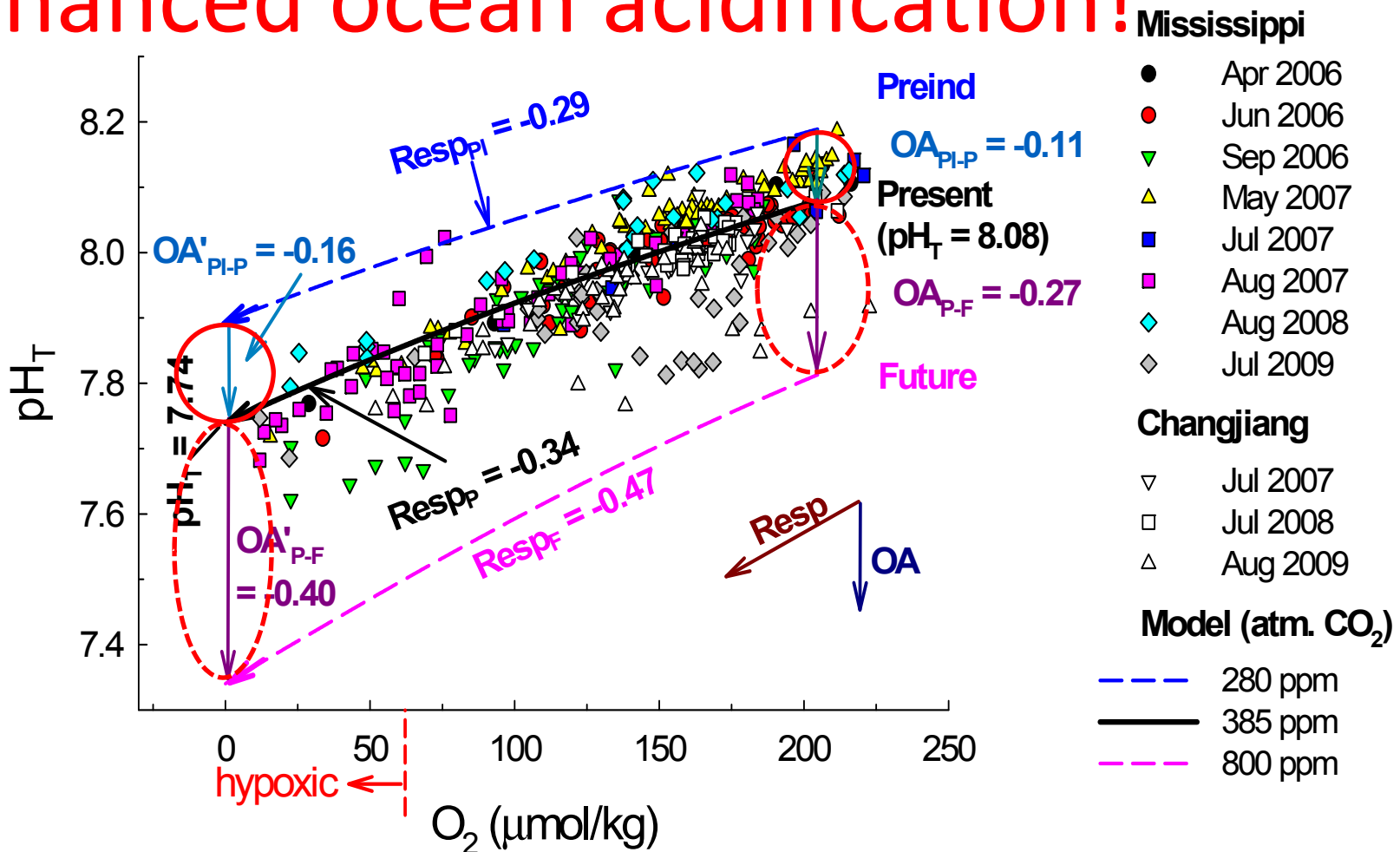
Cai et al. (2011)





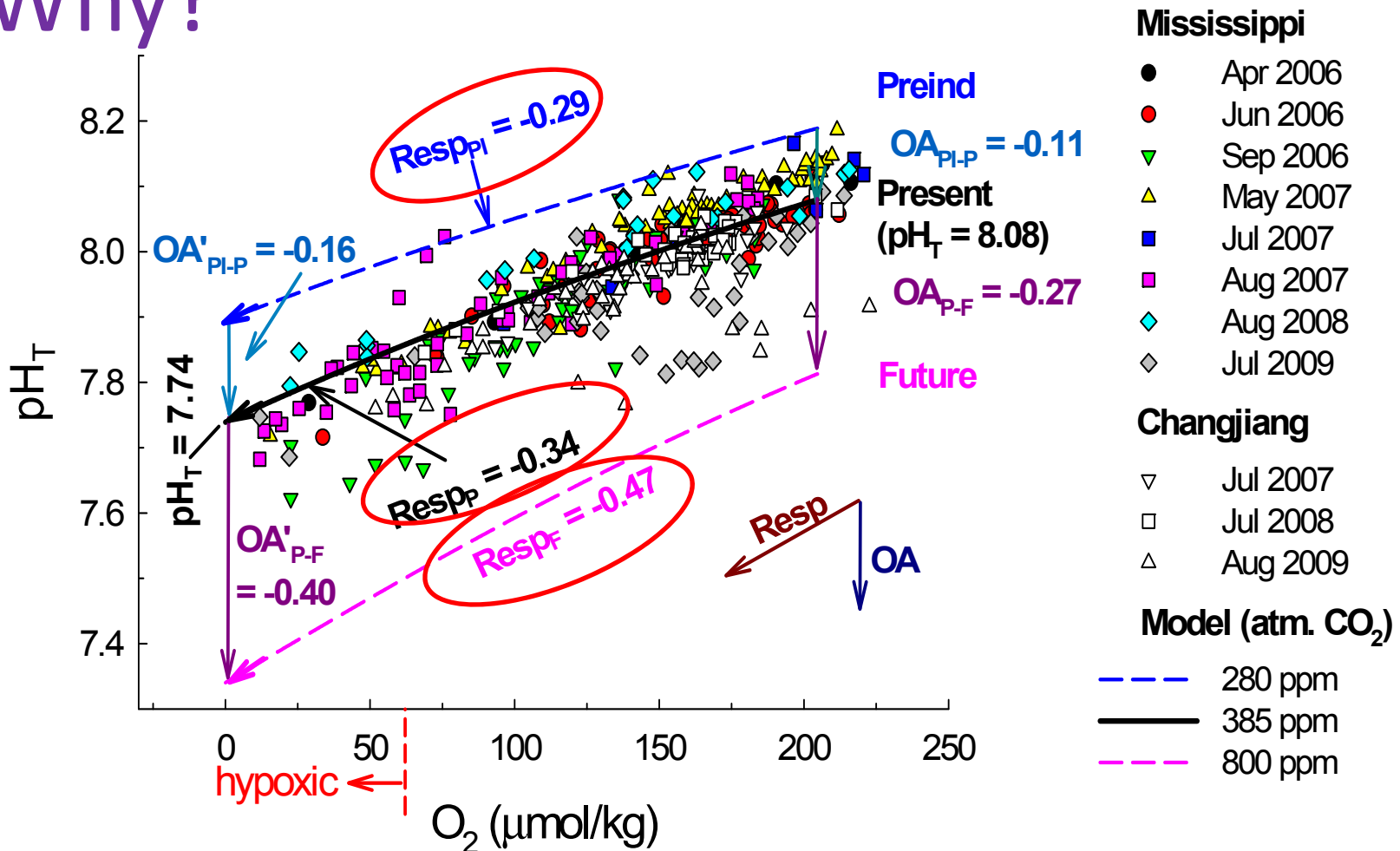
# How do anthropogenic CO<sub>2</sub> and CO<sub>2</sub> from respiration interact?

## Enhanced ocean acidification!

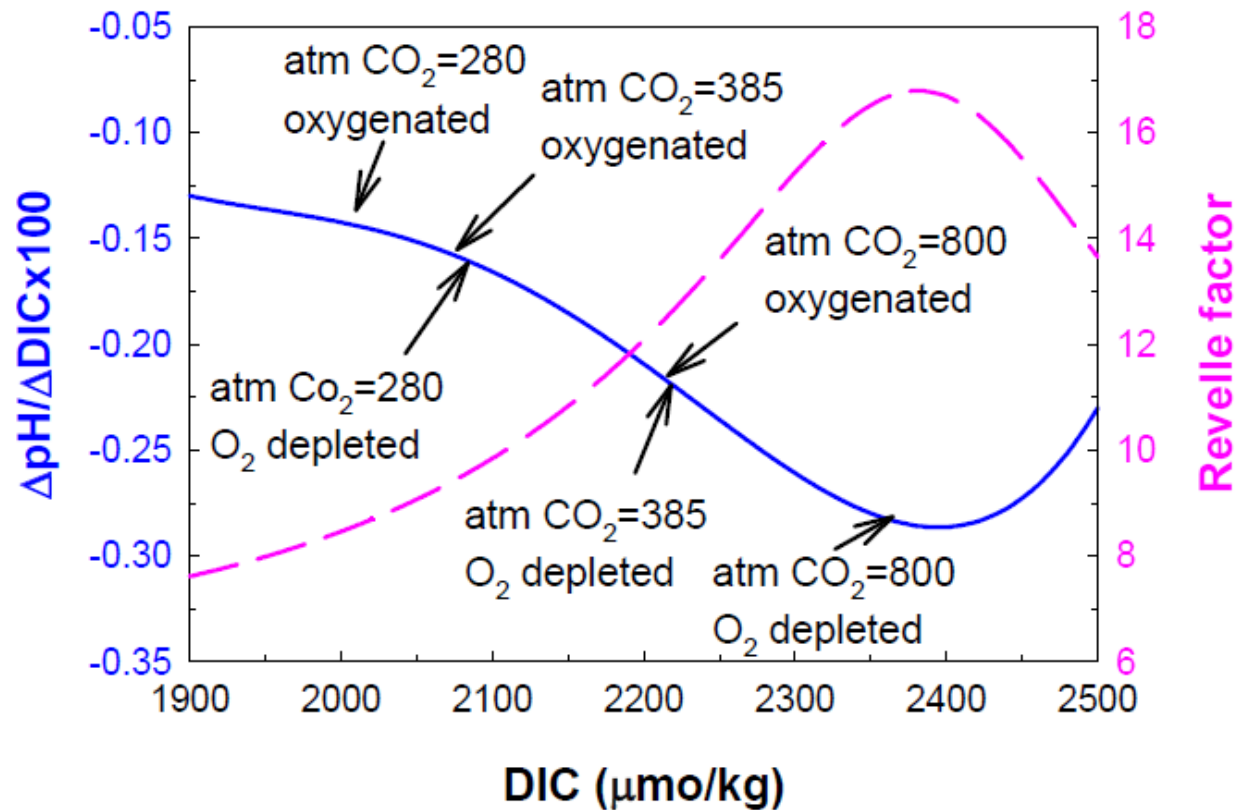


# Respiratory CO<sub>2</sub>-driven acidification is **enhanced** by anthropogenic CO<sub>2</sub>

Why?



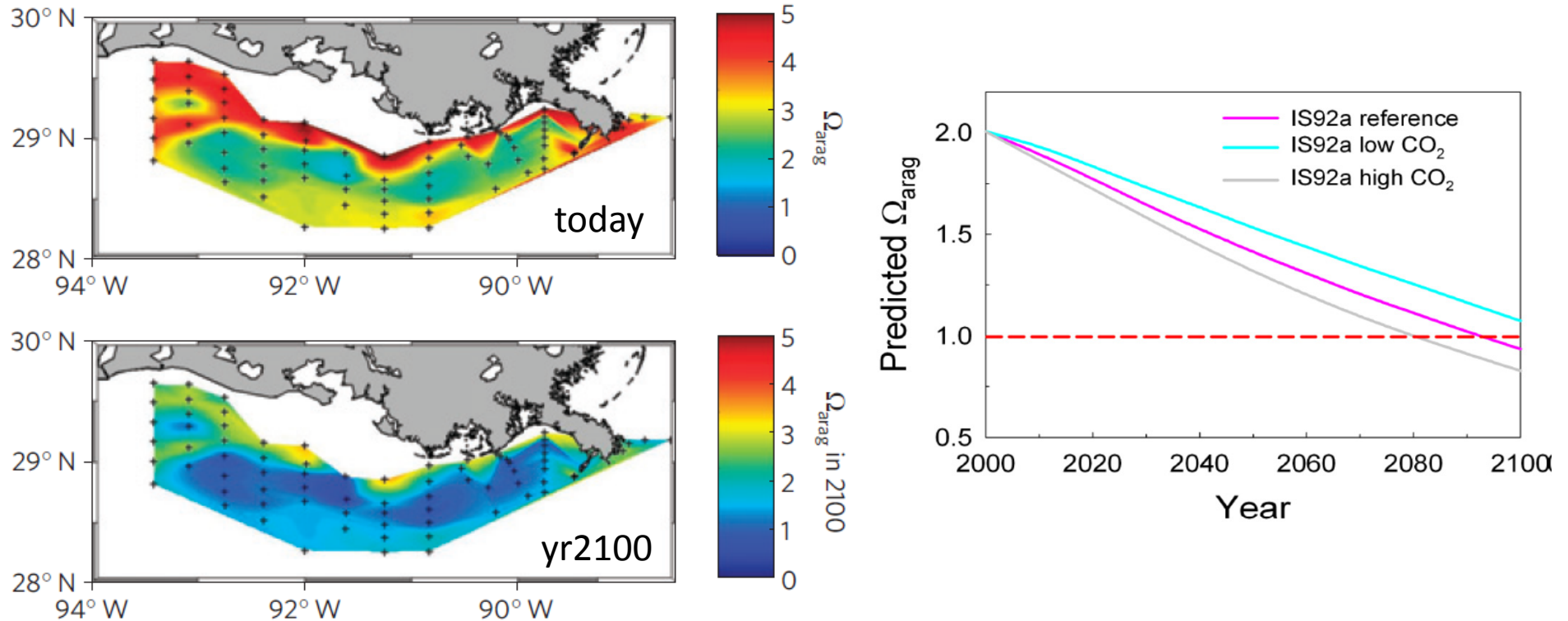
# Weakening of buffer capacity in CO<sub>2</sub>-enriched waters



Cai et al. (2011)  
Nature Geoscience



# Impact on carbonate saturation state



- with the same hypoxia level, by year 2100, large areas of GOM will be driven to under-saturation with respect to aragonite!

# Responses of ocean CO<sub>2</sub> system to multiple stresses: from first principles

- Salinity
- Temperature
- River-Ocean mixing
- Metabolic CO<sub>2</sub> consumption and release
- N cycle (NO<sub>3</sub> and NH<sub>4</sub>)
- More frequent storm
- ...

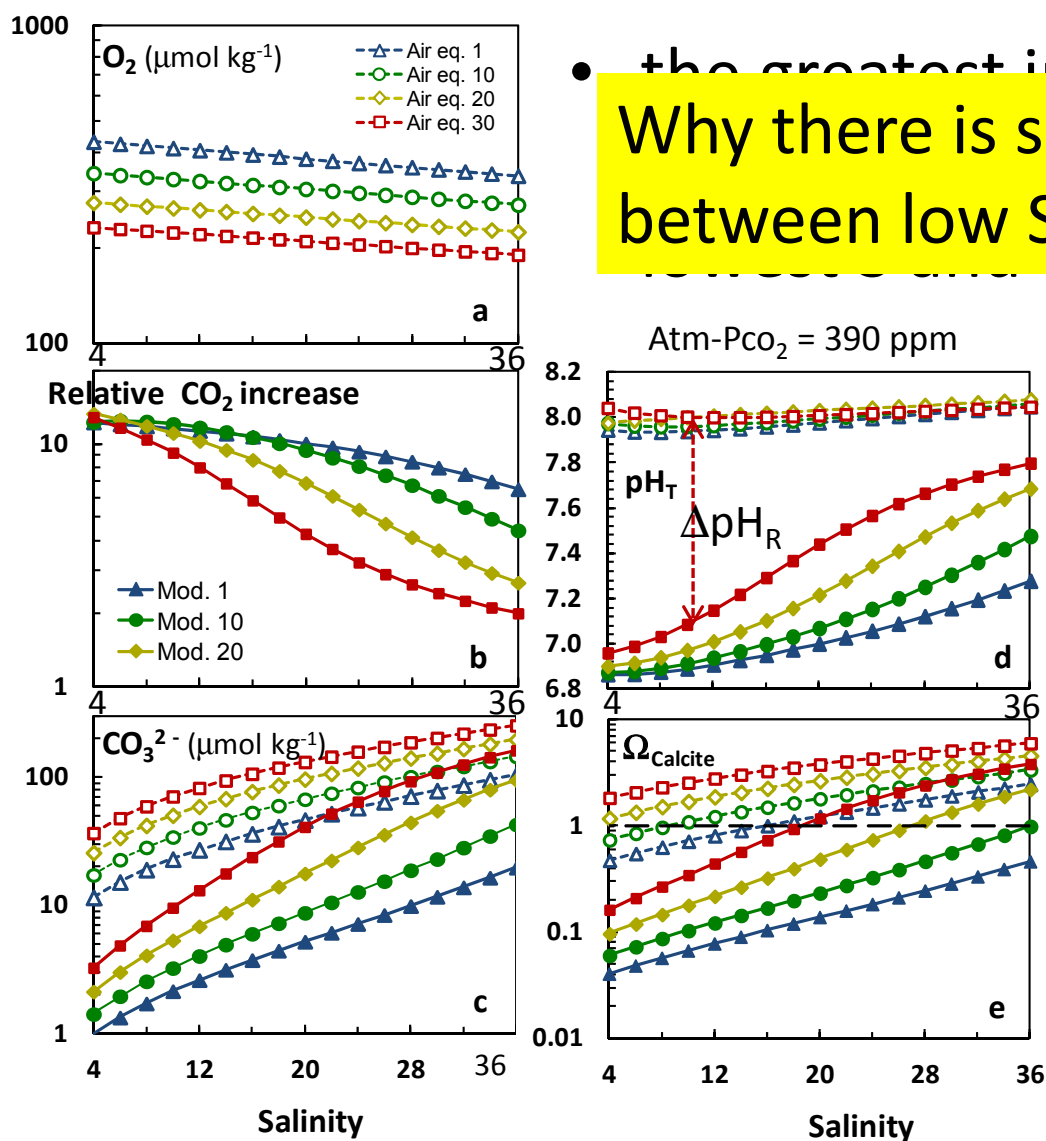
# A simple model

--examining the impact of **respiration** on pH,  $p\text{CO}_2$  and  $\Omega$  under various conditions (T, S, ...)

- Initial partial pressure ( $p\text{CO}_2$  and  $p\text{O}_2$ ) is set by the atmosphere
- **Alk is known**
  - River end-member = 1.0 mmol/kg
  - Ocean end-member = 2.3 mmol/kg
- **Bottom water is no longer in contact with the atmosphere**
- Metabolic processes follows the Redfield CN ratio...  
$$(\text{CH}_2\text{O})_{106}(\text{NH}_3)\text{H}_3\text{PO}_4 + 138\text{O}_2 \rightarrow 106\text{CO}_2 + 16\text{HNO}_3 + \text{H}_3\text{PO}_4 + 122\text{H}_2\text{O}$$



# Effects of T & S on respiratory-driven CO<sub>2</sub> acidification (over a complete consumption of O<sub>2</sub>)

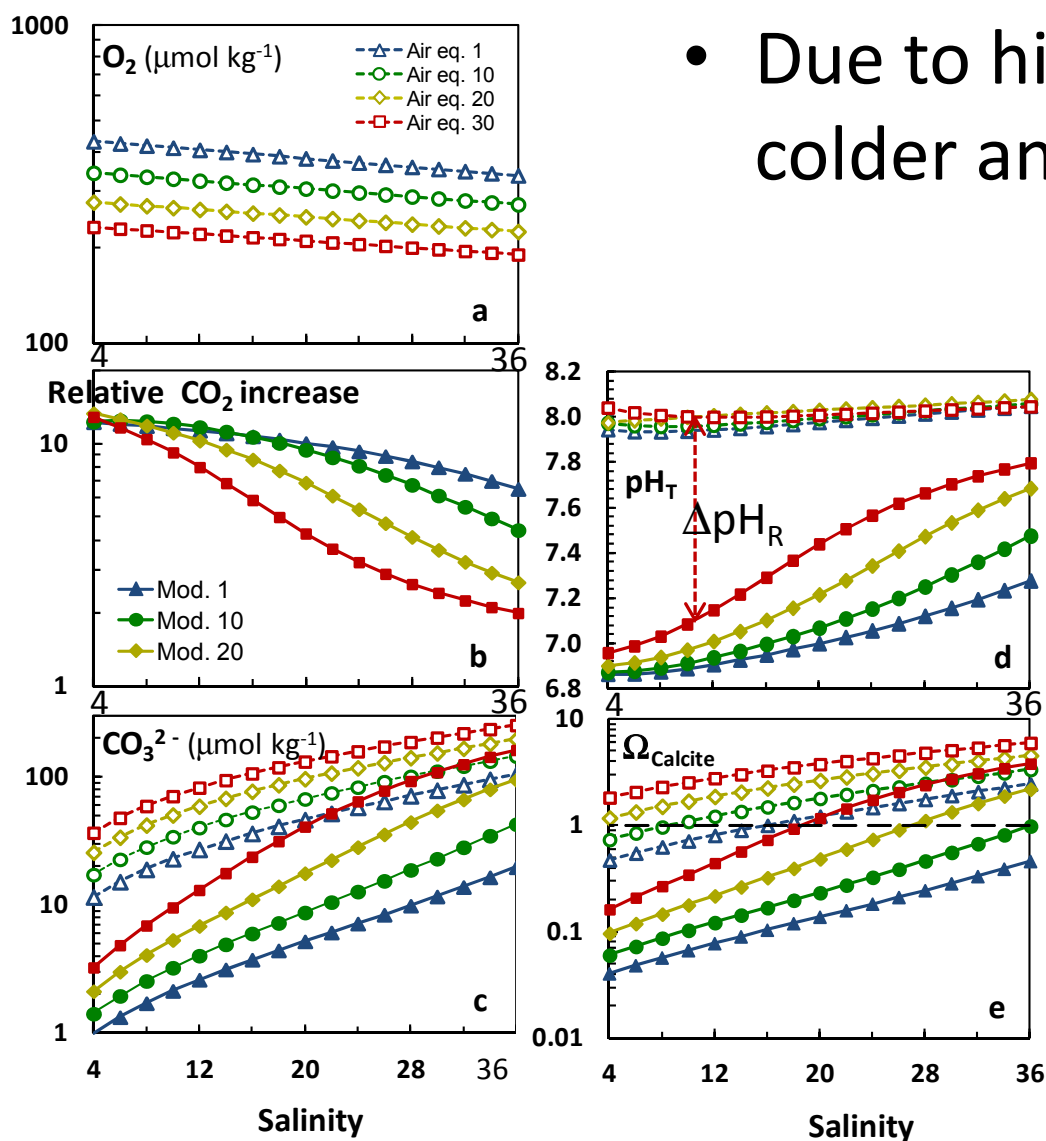


- the greatest increases in [CO<sub>2</sub>] (12-fold)
- Why there is such a big difference between low ST and high ST?

- at higher S & T, less increase in Rel.[CO<sub>2</sub>] and decrease in pH (0.25–0.77 at S=36)
- [CO<sub>3</sub><sup>2-</sup>] decreases by 12-fold (low S & T) and 1.6-fold (high T & S)

(Sunda and Cai, ES&T, under review)

# Effects of T & S on respiratory driven CO<sub>2</sub> acidification (over a complete consumption of O<sub>2</sub>)

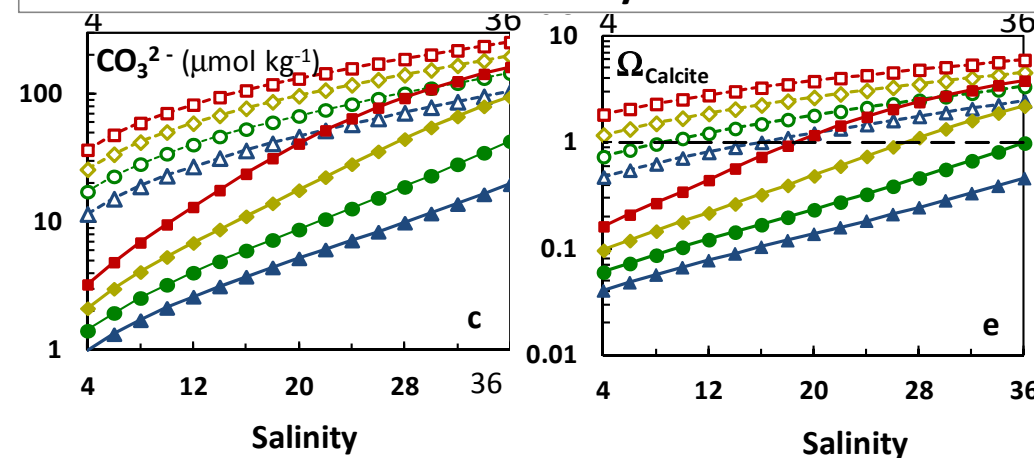
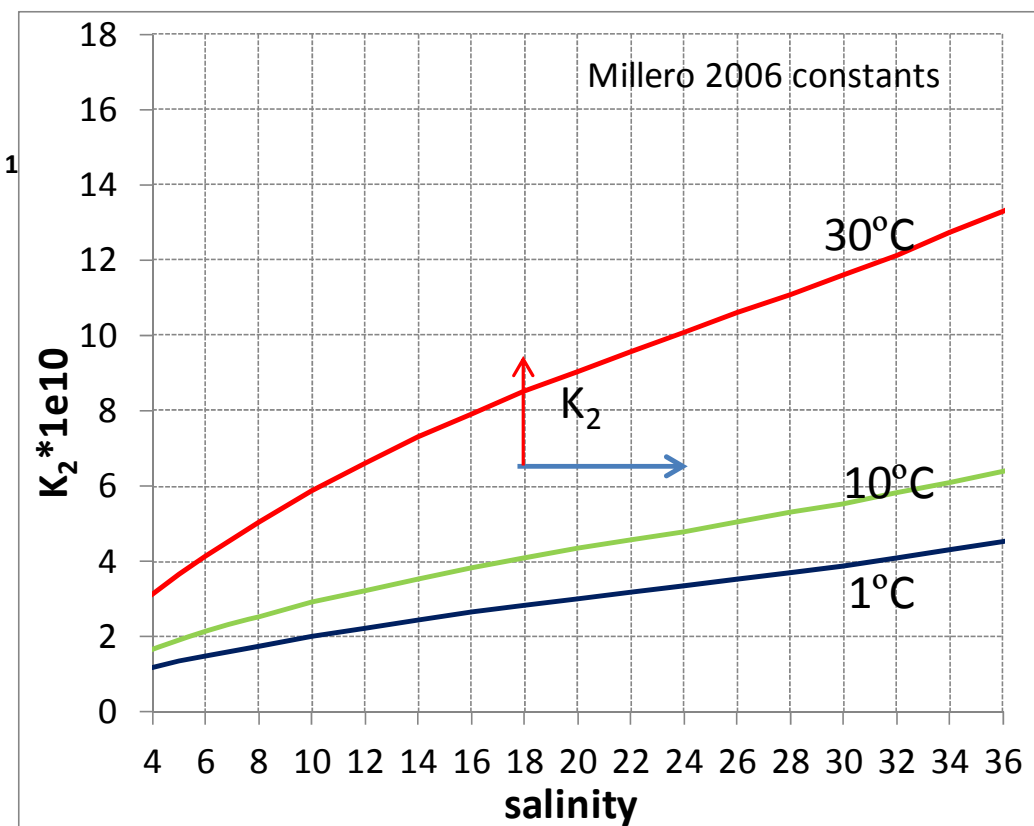


- Due to higher solubility of O<sub>2</sub> in colder and less saline waters?

- A 2.3-fold increased in O<sub>2</sub> solubility increase the resp-CO<sub>2</sub> release
- But the effect is small due to a higher (2.9X) initial [CO<sub>2</sub>] & lower initial pH at lower T and S (ΔpH from 1.07 to 1.10).

(Sunda and Cai, ES&T, under review)

# Effects of T & S on respiratory driven CO<sub>2</sub> acidification sumption of O<sub>2</sub>)



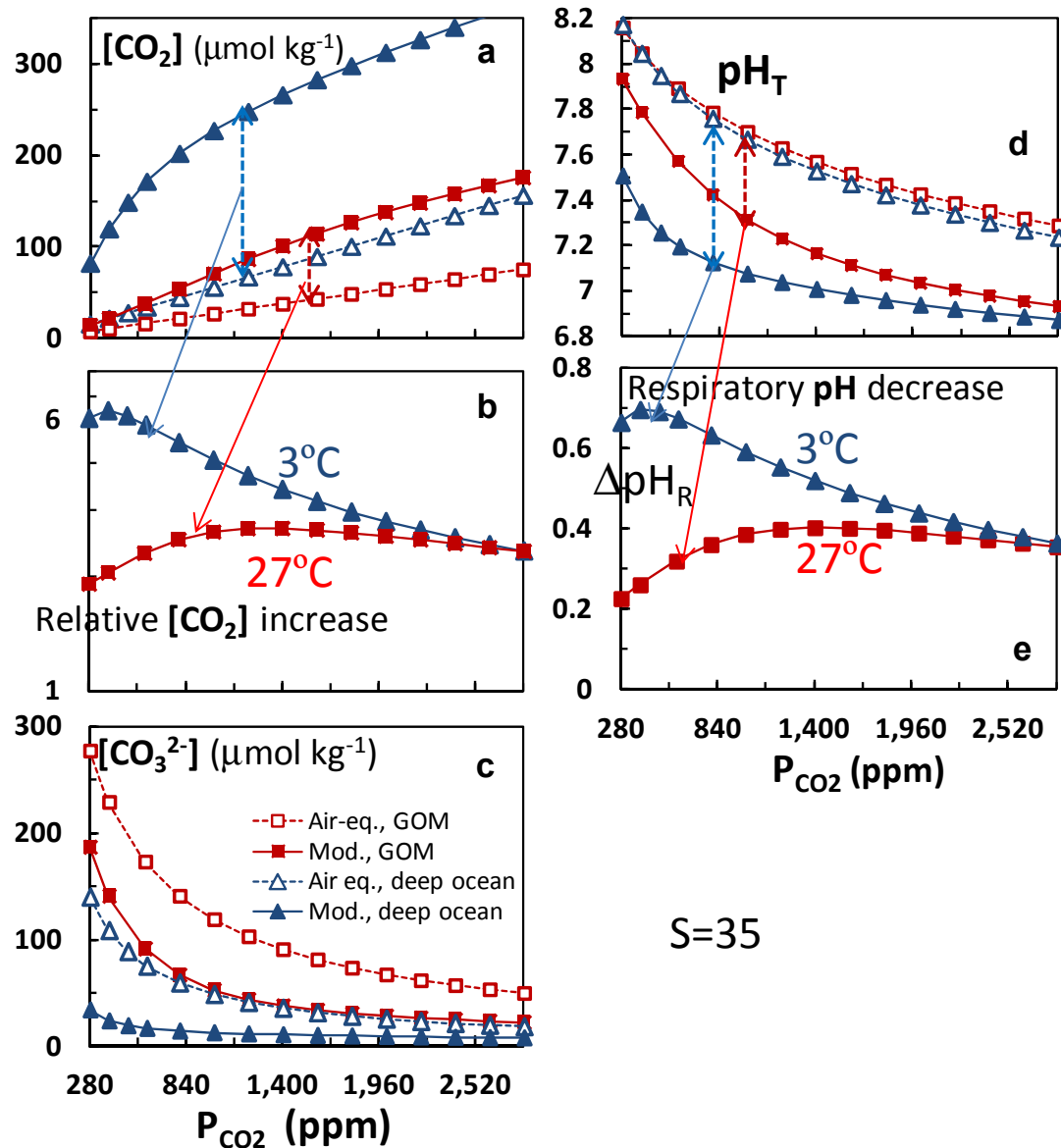
- The different initial  $[\text{CO}_3^{2-}]$  is responsible for the very different sensitivity to salinity and temp

– Higher TA at high sal (2.4 mM vs. ~1.2 mM)

– Mainly, a change in dissociation constants

(Sunda and Cai, ES&T, under review)

# Will increasing $\text{Atm-}P_{\text{CO}_2}$ amplify or suppress respiratory- $\text{CO}_2$ acidification ( $\Delta\text{pH}_R$ )?



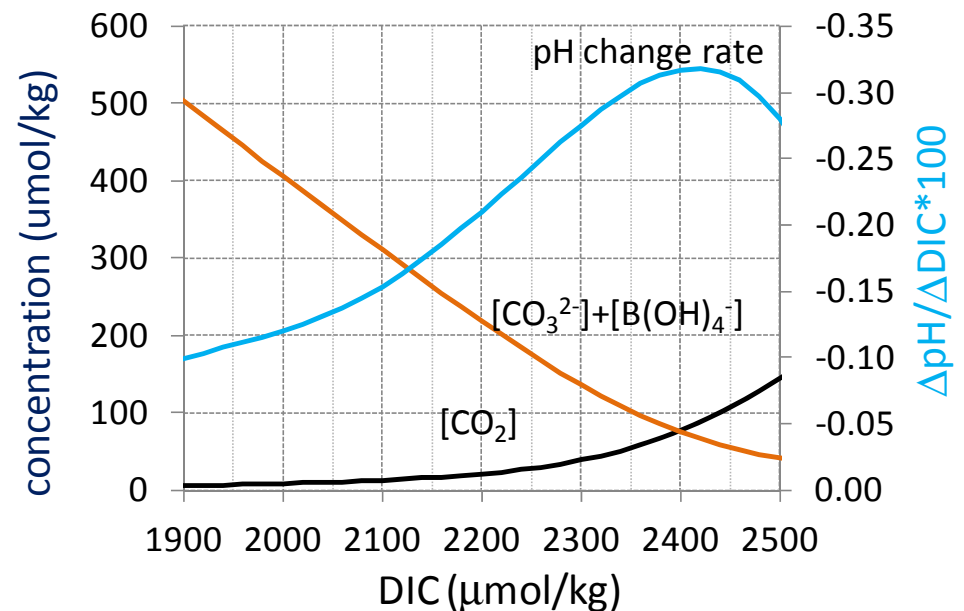
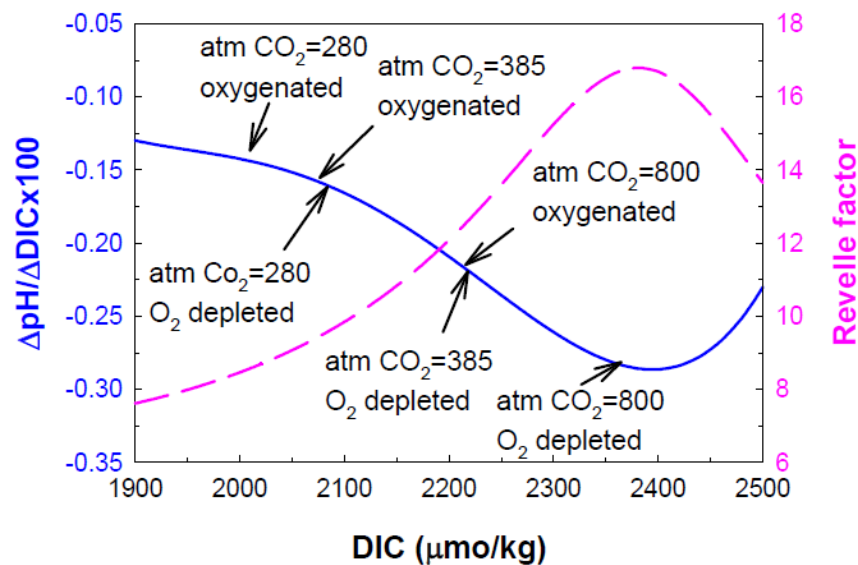
- For high T & S waters (GOM), amplify
- For low T (arctic waters), at the max. point, start to suppress
- Initial  $[\text{CO}_3^{2-}]$  is the key

(Sunda and Cai, ES&T, under review)

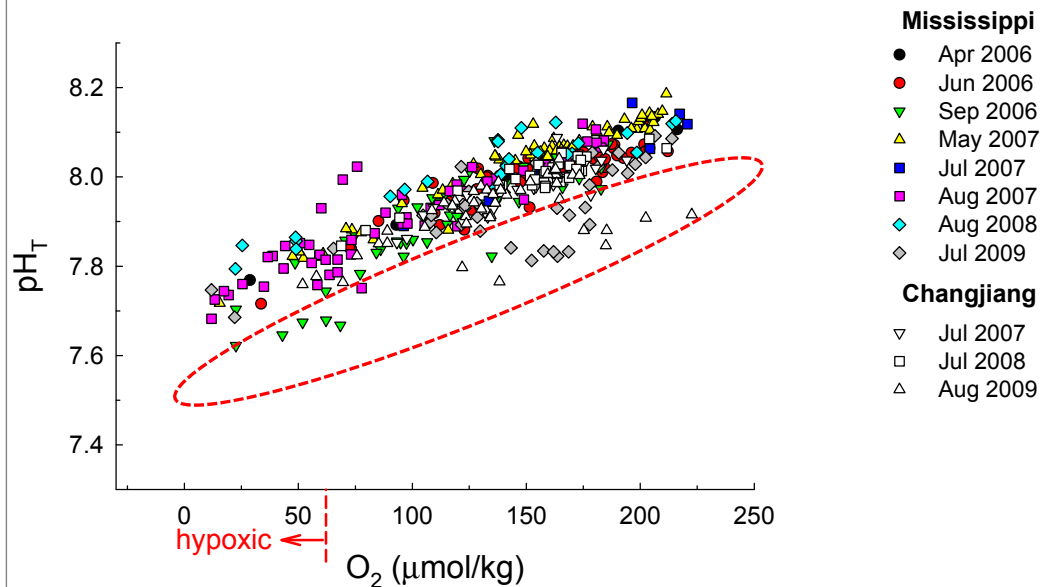
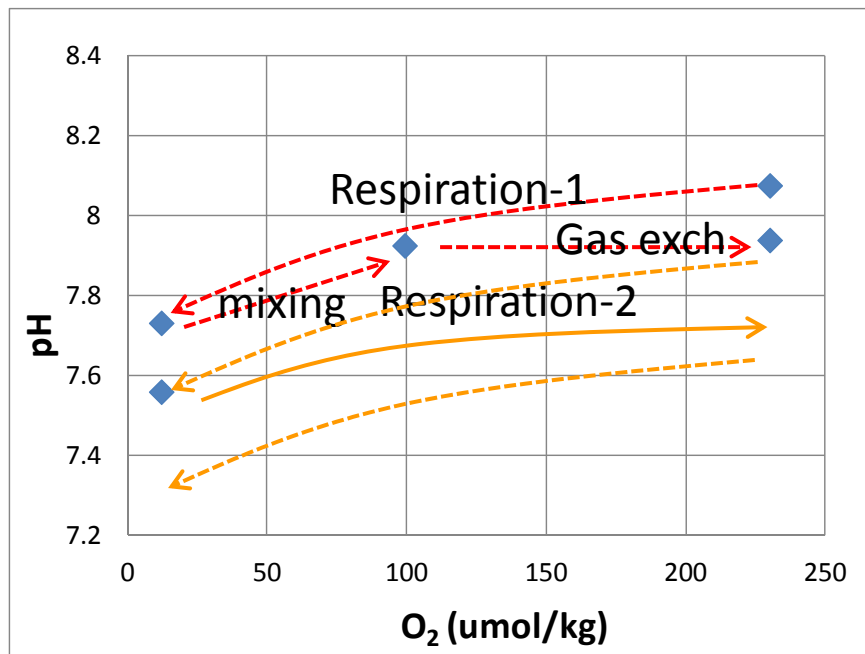
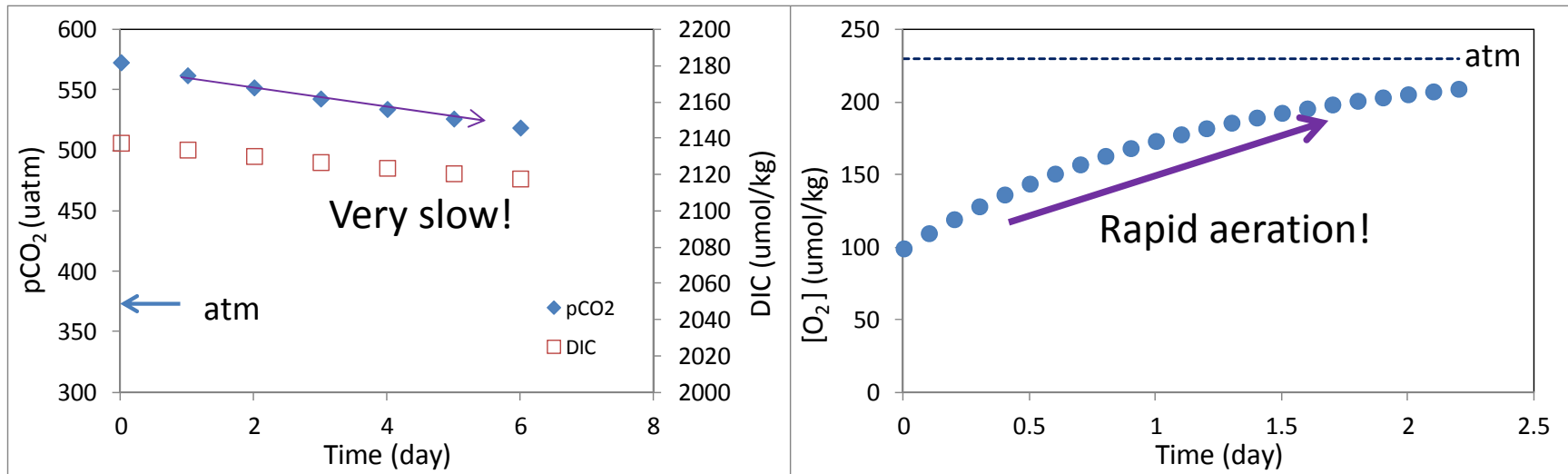


# What is so magic about this point of $\max-\Delta\text{pH}_R$ ?

- Where the system has minimum buffering capacity
- A point where  $\text{DIC} = \text{TA}$  or  $[\text{CO}_2] = [\text{CO}_3^{2-}] + \text{B}(\text{OH})^-$   
 $[\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + \text{B}(\text{OH})^-$



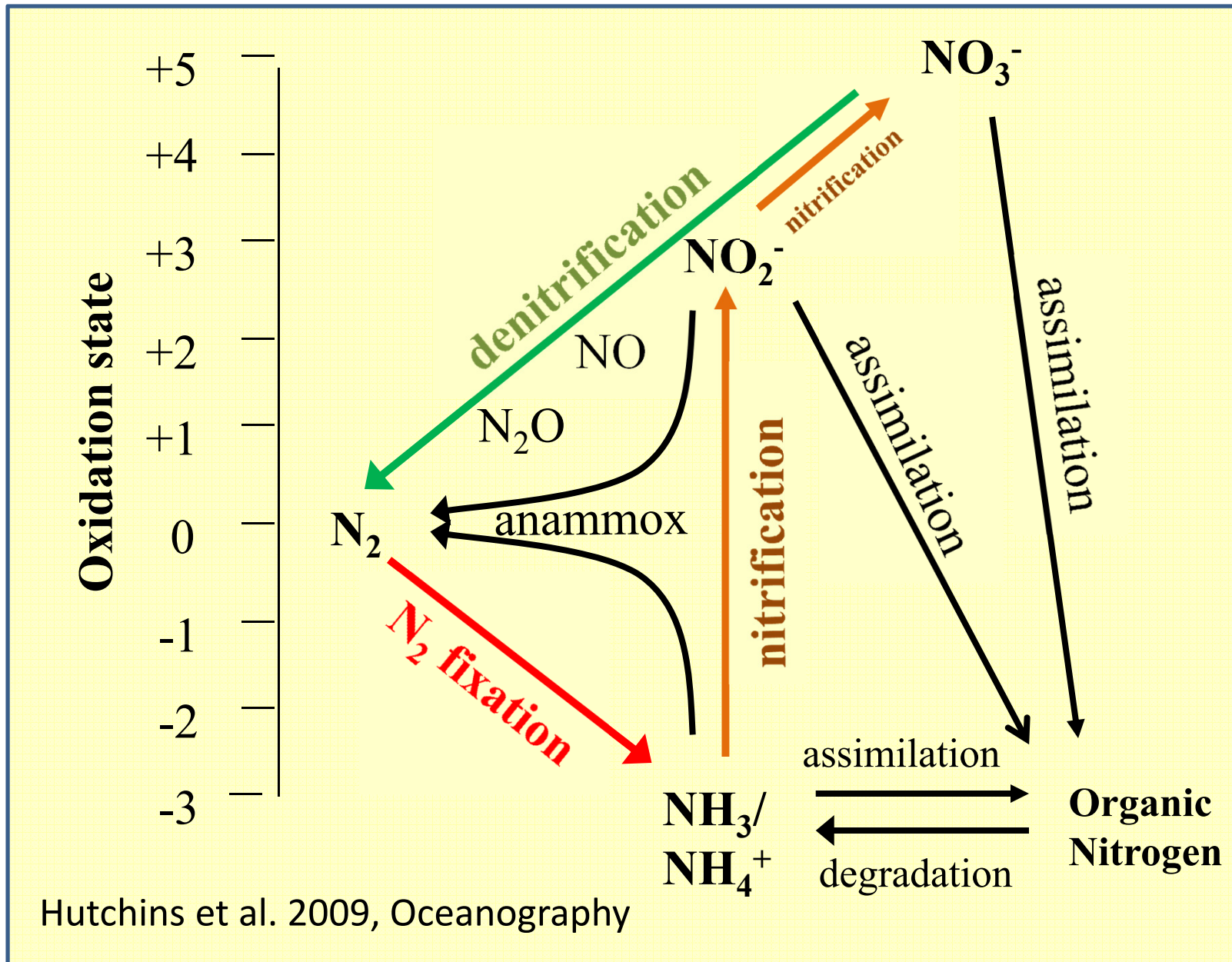
# How can a storm make bottom waters even more acidic?



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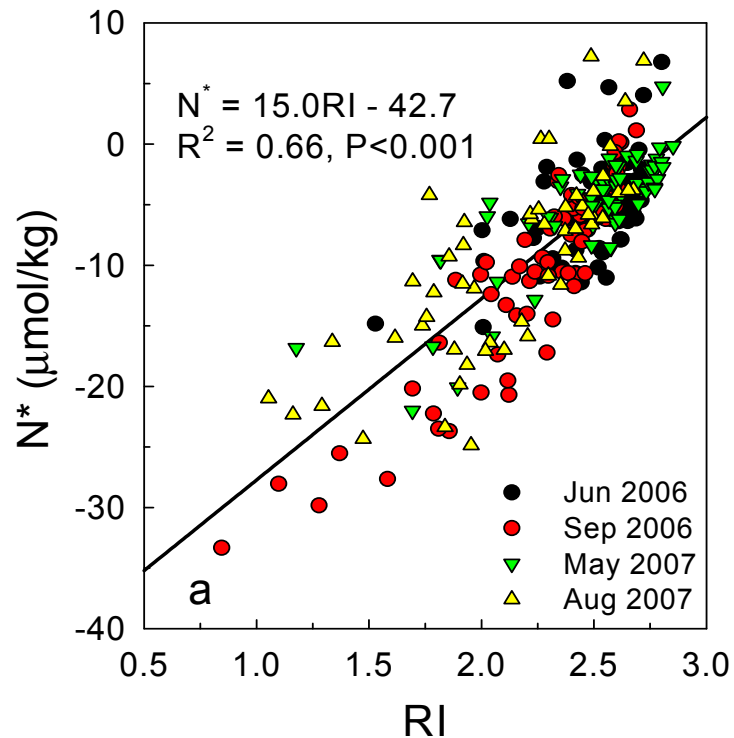
# Possible impacts on the marine nitrogen cycle





# Enhanced denitrification?

$$N^* = [\text{NO}_3]_{\text{obs}} - 16/106 * \Delta\text{DIC}$$



Cai unpublished data

$$\text{RI} = \log(p\text{O}_2/p\text{CO}_2)$$

(Brewer & Piltzer 2009)

Cai unpublished data

# Summary

- Respiration often plays a more important role in acidifying coastal bottom waters today, but
- Anthropogenic CO<sub>2</sub> uptake from the atmosphere will play an increasingly important role in acidifying coastal bottom waters.
- There is a strong enhancement of acidification in CO<sub>2</sub>-enriched waters, and such effects vary greatly with salinity and temperature, with a greater effect in low T and S water (decreasing) and a smaller effect in high T and S water (increasing).
- Storm on pH and N cycle...

# Ocean Stress Guide

What the ocean will experience this century without urgent and substantial reduction in greenhouse gas emissions.

processes depend on organisms  
on the stressor & ecosystems

Turley et al. Hot, Sour and Breathless –  
Ocean under stress. PML

SIO, EPOCA,  
OCEANA, BIOACID  
UK OA Res Prog

Stressor	Causes	Result	Direct effects	Impacts	Feedback to climate
<b>Warming</b> <ul style="list-style-type: none"> <li>● A relatively mature study area in terms of physical changes and physiology but poorly studied at ecosystem and biogeochemical level</li> </ul>	<ul style="list-style-type: none"> <li>● Increasing greenhouse gas emissions to the atmosphere</li> </ul>	<ul style="list-style-type: none"> <li>● Temperature increase, particularly in near-surface waters</li> <li>● Less ocean mixing due to increased stratification</li> <li>● Increased run-off and sea-ice melt will also contribute to stratification in Arctic waters</li> </ul>	<ul style="list-style-type: none"> <li>● Decreased carbon dioxide solubility</li> <li>● Increased speed of chemical and biological processes</li> <li>● Reduced natural nutrient re-supply in more stratified waters</li> </ul>	<ul style="list-style-type: none"> <li>● Stress to organism physiology, including coral bleaching</li> <li>● Extensive migration of species</li> <li>● More rapid turnover of organic matter</li> <li>● Nutrient stress for phytoplankton, particularly in warm waters</li> <li>● Changes to biodiversity, food webs and productivity, with potential consequences for fisheries, coastal protection and tourism</li> </ul>	<ul style="list-style-type: none"> <li>● Reduced ocean uptake of carbon dioxide due to solubility effect</li> <li>● Increased oxygen consumption, carbon dioxide production and decrease in oxygen transfer to the deep ocean</li> <li>● Potential decrease in the export of carbon to the ocean's interior</li> <li>● Decreasing productivity except in the Arctic</li> </ul>
<b>Acidification</b> <ul style="list-style-type: none"> <li>● Developed as a research topic in past decade</li> </ul>	<ul style="list-style-type: none"> <li>● Increasing atmospheric carbon dioxide emissions</li> <li>● Coastal nutrient enrichment, methane hydrates and acid gases from industrial emissions may also contribute locally</li> </ul>	<ul style="list-style-type: none"> <li>● Unprecedented rapid change to ocean carbonate chemistry</li> <li>● Much of the ocean will become corrosive to shelled animals and corals, with effects starting in the Arctic by 2020</li> </ul>	<ul style="list-style-type: none"> <li>● Reduced calcification, growth and reproduction rates in many species</li> <li>● Changes to the carbon and nitrogen composition of organic material</li> </ul>	<ul style="list-style-type: none"> <li>● Impeded shell or skeletal growth and physiological stress in many species, including juvenile stages</li> <li>● Change to biodiversity and ecosystems, and the goods and services they provide</li> <li>● Cold and upwelling waters currently supporting key fisheries and aquaculture likely to be especially vulnerable</li> </ul>	<ul style="list-style-type: none"> <li>● Reduced ocean uptake of carbon dioxide due to chemical effects</li> <li>● Changes to the export of carbon to the ocean's interior</li> <li>● Higher oxygen use throughout the water column due to changing composition of organic material</li> </ul>
<b>Deoxygenation</b> <ul style="list-style-type: none"> <li>● Emerging issue, poorly studied</li> </ul>	<ul style="list-style-type: none"> <li>● Reduced oxygen solubility due to warming</li> <li>● Decreased oxygen supply to the ocean interior due to less mixing</li> <li>● Nutrient rich land run-off stimulating oxygen removal locally</li> </ul>	<ul style="list-style-type: none"> <li>● Less oxygen available for respiration especially in productive regions, and in the ocean interior</li> <li>● Extended areas of low and very low oxygen</li> </ul>	<ul style="list-style-type: none"> <li>● Reduced growth and activity of zooplankton, fish and other oxygen-using organisms</li> </ul>	<ul style="list-style-type: none"> <li>● Stress to oxygen-using organisms</li> <li>● Risk of species loss in low oxygen areas</li> <li>● Shift to low oxygen-tolerant organisms, especially microorganisms and loss of ecosystem services in these areas</li> </ul>	<ul style="list-style-type: none"> <li>● Enhanced production of the two greenhouse gases methane and nitrous oxide</li> </ul>
<b>All three together</b> <ul style="list-style-type: none"> <li>● Few studies</li> </ul>	<ul style="list-style-type: none"> <li>● Increasing greenhouse gas emissions, especially carbon dioxide, to the atmosphere</li> </ul>	<ul style="list-style-type: none"> <li>● More frequent occurrence of waters that will not only be warmer but also have higher acidity and less oxygen content</li> </ul>	<ul style="list-style-type: none"> <li>● Damage to organism physiology, energy balance, shell formation: e.g. coral reef degradation</li> </ul>	<ul style="list-style-type: none"> <li>● Ocean acidification can reduce organisms' thermal tolerance, increasing the impact of warming</li> <li>● Combined effects further increase risk to food security and industries depending on healthy and productive marine ecosystems</li> </ul>	<ul style="list-style-type: none"> <li>● Major change to ocean physics, chemistry and ecosystems</li> <li>● Risk of multiple positive feedbacks to atmosphere, increasing the rate of future climate change</li> </ul>