

Ocean Acidification and Its Effects on Marine Life

Taro Takahashi

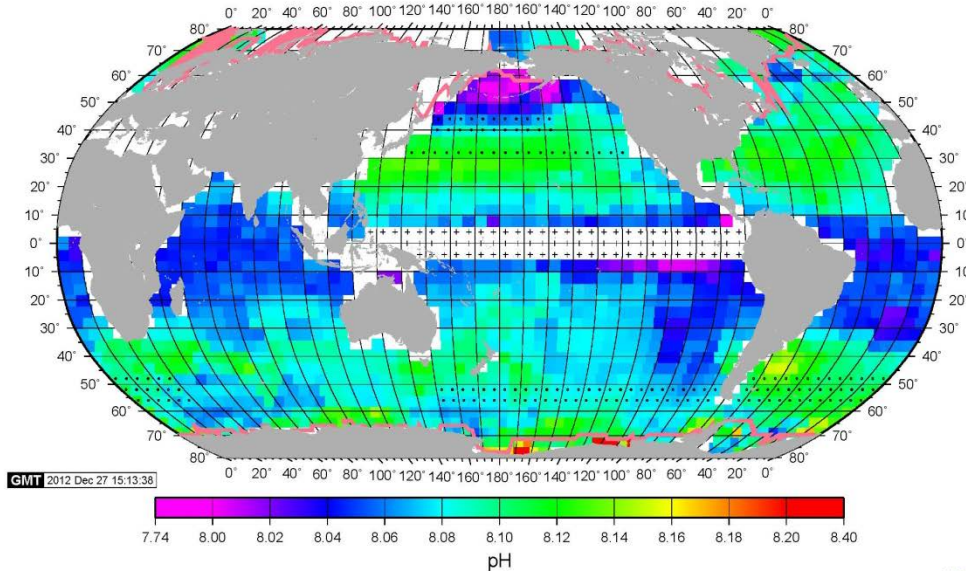
Ewing Lamont Research Professor

Lamont-Doherty Earth Observatory, Columbia University

1. What is the main cause of ocean acidification?:
 - a. Chemical reactions, pH and alkalinity of ocean water
 - b. Acidification observed at selected locations
 - c. Distribution of pH and CaCO_3 saturation over the global oceans
2. What are the effects of acidification on marine organisms?:
 - a. Effects on corals and other calcifiers
 - b. An biological study on Pacific oysters

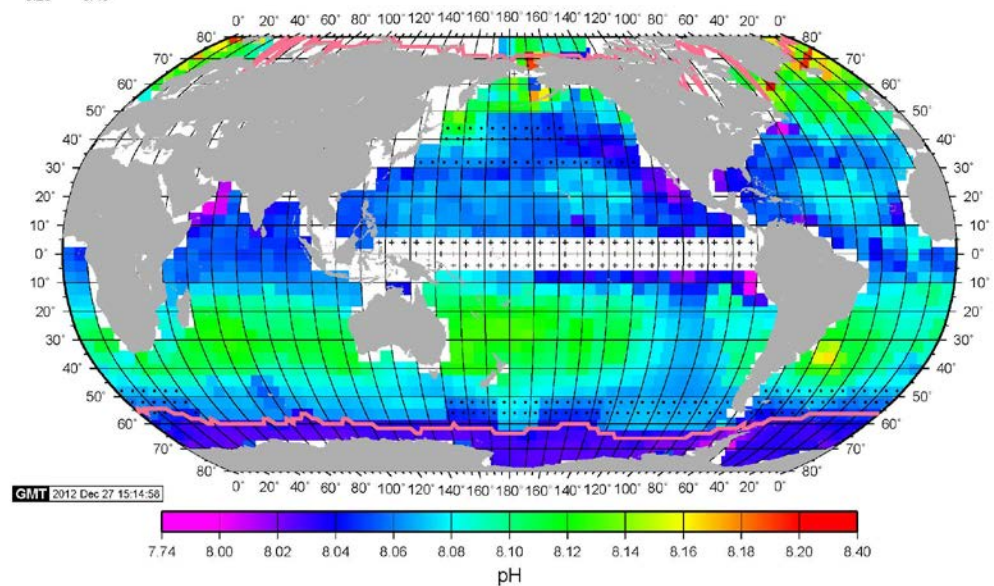
Climatological mean distribution of pH in global surface ocean water
(Takahashi et al., Marine Chem., 164, 95-125, 2014)

(A)
Calculated pH for
February, 2005



Global range of pH = 7.9 to 8.2
(1.3×10^{-8} to 6.3×10^{-9} mol H^+ /liter),
varying by a factor of 2 in the H^+
concentration.)

(B)
Calculated pH for
August, 2005

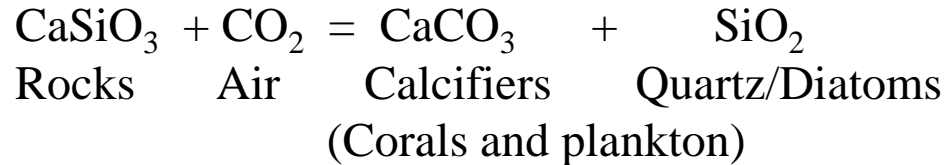


Temperate oceans =
8.05 in warmer months and
8.15 in colder months

Seasonally changes by about 25%
In the H^+ ion concentration.

CHEMICAL REACTIONS

Urey's geochemical reactions:



Regulations of H^+ ions in ocean:

From land $\text{CaSiO}_3 + \text{H}_2\text{O} = \text{Ca}^{++} + 2 \text{OH}^- + \text{SiO}_2$...make ocean more alkaline

From the air $\text{CO}_2 + \text{H}_2\text{O} = \text{HCO}_3^- + \text{H}^+$ make ocean more acidic

In the sea:

Photosynthesis $\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CHOH (organic)} + \text{O}_2$...reduces CO_2 in water,
and make seawater less acid or more alkaline.

Calcification $\text{Ca}^{++} + \text{CO}_2 + \text{H}_2\text{O} = \text{CaCO}_3 \text{ (corals)} + 2 \text{H}^+$
Growths of calcifiers make seawater more acidic,
Dissolution of lime stones neutralizes acidic waters.

DEFINITION OF pH AND OMEGA

$$\text{pH} = \log 1/(\text{H}^+) = -\log (\text{H}^+) , \text{ and } K_w = (\text{H}^+) (\text{OH}^-) = 1 \times 10^{-14}$$

Neutral waters, $\text{pH} = 7$, $\text{H}^+ = 1 \times 10^{-7}$ mole/L and $\text{OH}^- = 1 \times 10^{-7}$ mole/L

Acidic waters, $\text{pH} < 7$ and $\text{H}^+ > 1 \times 10^{-7}$ mole/L, $\text{OH}^- < 1 \times 10^{-7}$ mole/L

Soda drinks, $\text{pH} \sim 4$,

$\text{H}^+ \sim 1 \times 10^{-4}$ mole/L and $\text{OH}^- \sim 1 \times 10^{-10}$ mole/L

Alkaline waters, $\text{pH} > 7$

Human blood and seawater, $\text{pH} \sim 8$,

$\text{H}^+ \sim 1 \times 10^{-8}$ mole/L and $\text{OH}^- \sim 1 \times 10^{-6}$ mole/L.

Degree of Saturation of CaCO_3 in seawater:

Solubility product of CaCO_3 (K_{sp}) = $[\text{Ca}^{++}] [\text{CO}_3^{=}]$ at saturation

$$\Omega = [\text{Ca}^{++}]_{sw} \cdot [\text{CO}_3^{=}]_{sw} / K_{sp}$$

$\Omega = 1$, saturated

$\Omega > 1$, favors precipitation or formation of CaCO_3

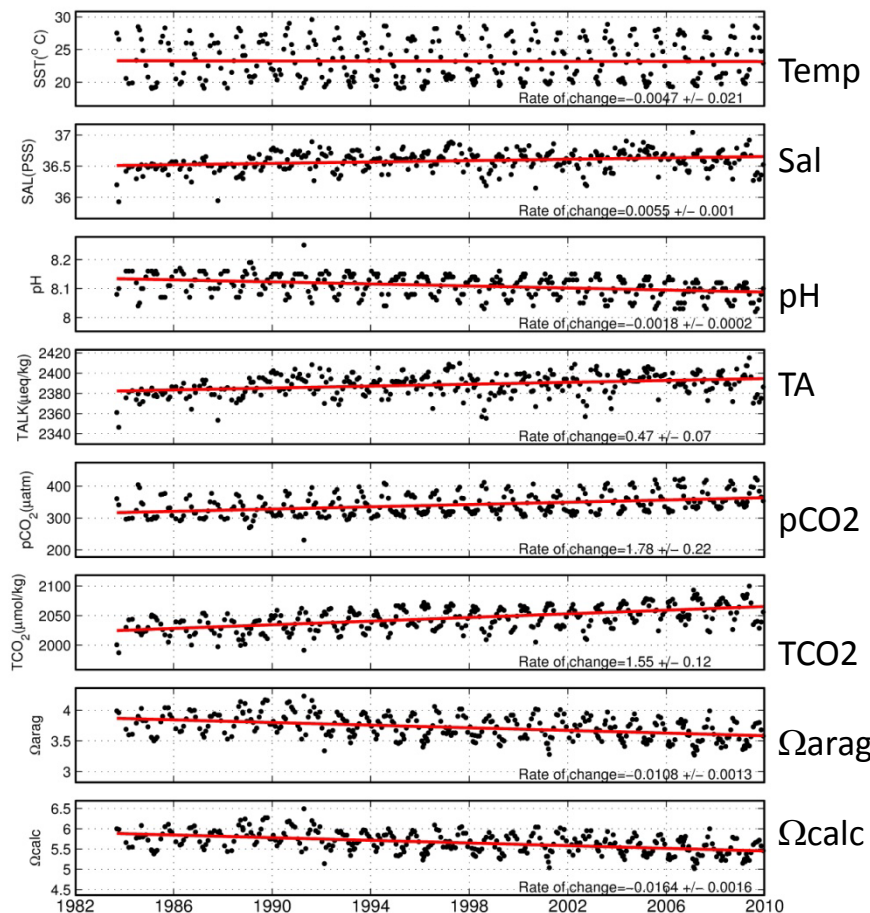
$\Omega < 1$, dissolution of CaCO_3 .

Time Trends Observed at the Bermuda Time Series (BATS) and Hawaii Ocean Time-series (HOT) Stations

H⁺ concentrations in surface ocean increase at a rate of 4.5% per decade or about 50% per century.

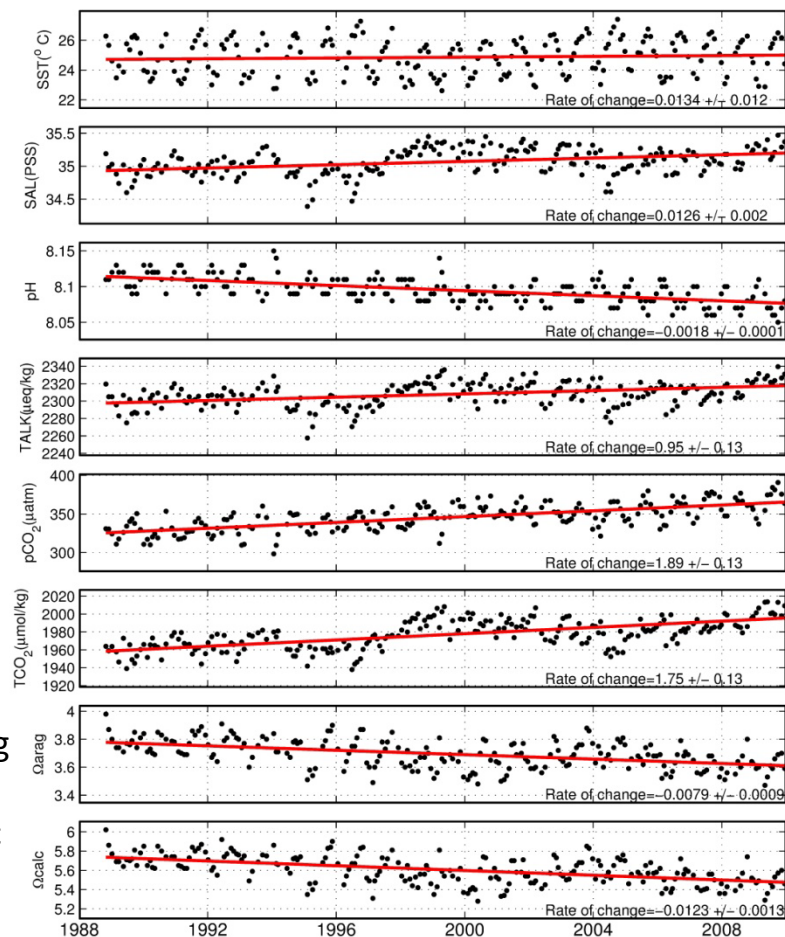
BATS

pCO₂ = +1.78 uatm/yr, pH = -0.0018 /yr
TA = +0.47 ueq/kg/yr, TCO₂ = +1.55 umol/kg/yr



HOT

pCO₂ = +1.89 uatm/yr, pH = -0.0018 /yr
TA = +0.95 ueq/kg/yr, TCO₂ = +1.75 umol/kg/yr

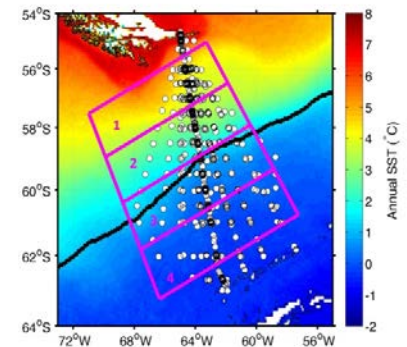
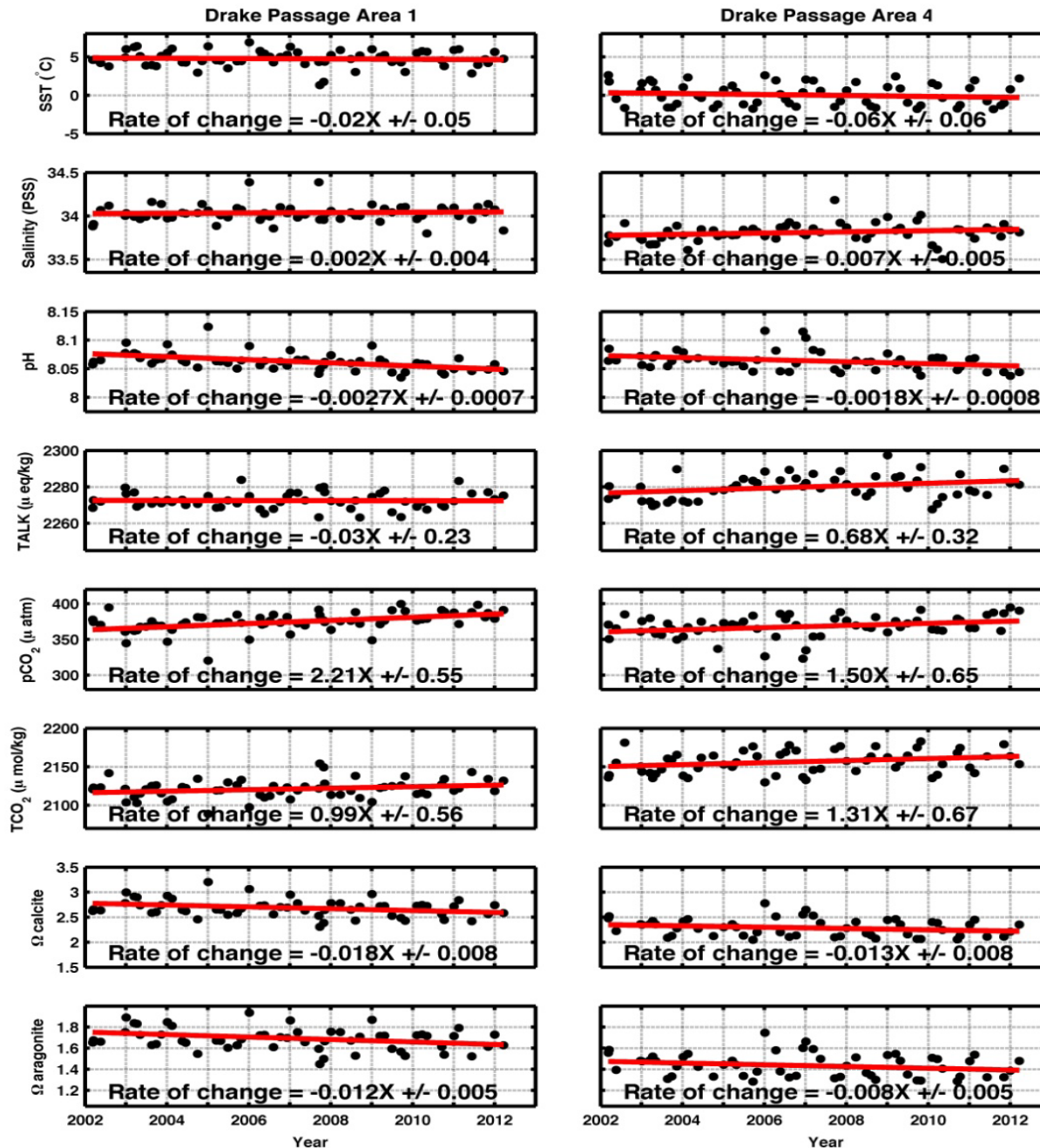


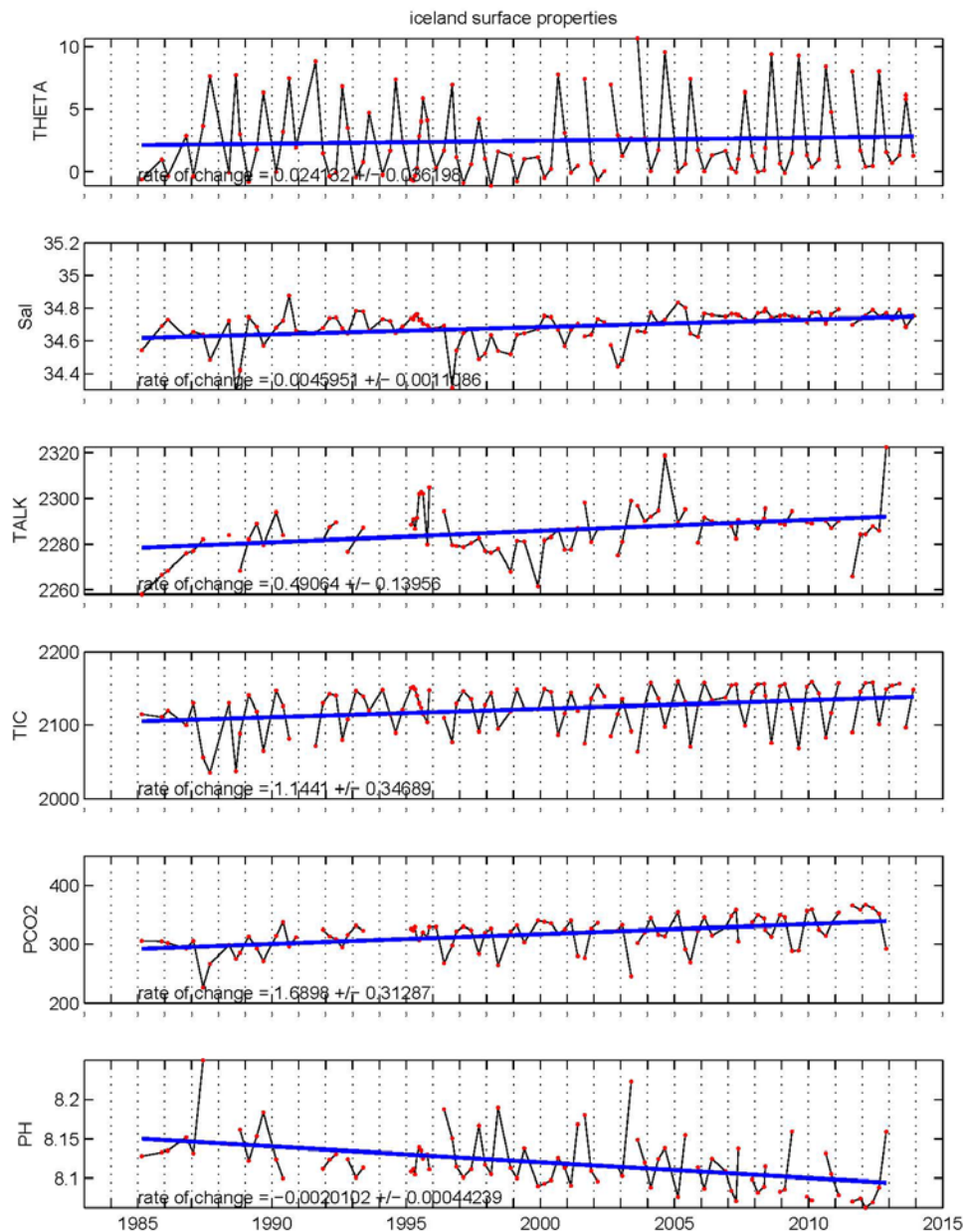
DRAKE PASSAGE TIME-SERIES 2002-2012

Takahashi et al.
Marine Chem.,
2014.

Mean rate of pH
change:

-0.002 pH/yr.
-0.02 pH/decade
(-5% H⁺/decade)
-50% H⁺/century)





**Annual Rate
of change**
0.024 °C
±0.036

Iceland Sea and Vicinity
Time-series, 1985-2013

0.0046 PSS
±0.001

68°N and 12.7°W

0.49 ueq/kg
± 0.14

Olafsson and Takahashi,
(in preparation)

1.14 umol/kg
±0.35

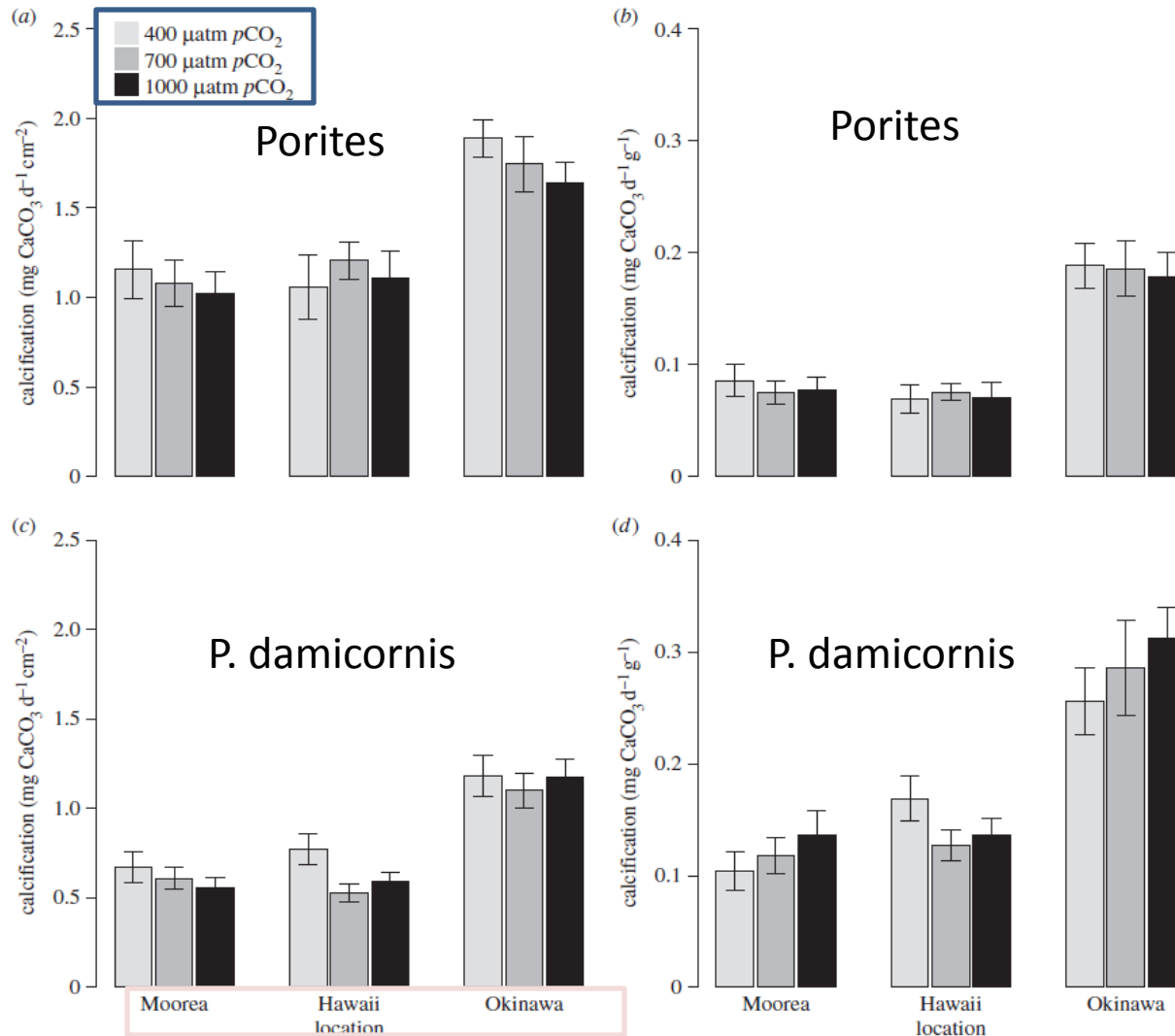
1.69 uatm
±0.31

-0.0020 pH
±0.0004

HOW ARE THE MARINE ECOSYSTEMS AFFECTED BY THE ACIDIFICATION OF WATER?

- 1) Ocean acidification is occurring at a decreasing pH rate of 0.02 pH/decade (5% increase in H^+) or 0.2 pH/century (50% increase in H^+). In comparison, seasonal variability is 0.1 pH (from 8.05 in winter and to 8.15 in summer; 25% in H^+) in the modern oceans.
- 2) Since H^+ is involved in every chemical process in photosynthesis, calcification, and oxidation/degradation of organic compounds, ocean acidification should affect all marine ecosystem.
- 3) Addition of CO_2 to seawater should change H^+ (pH), $(CO_2)_{aq}$, H_2CO_3 , HCO_3^- , $CO_3^{=}$, and the solubility of $CaCO_3$. Photosynthesis may be affected by changes in $(CO_2)_{aq}$, H_2CO_3 , which are most readily used for photosynthesis. The solubility of $CaCO_3$ depends upon the product (Ca^{++}) ($CO_3^{=}$): $CaCO_3$ (shells) = $Ca^{++} + CO_3^{=}$. Corals and calcareous algae in reef community as well as macro and planktonic calcifiers (coccolithophores and foraminifera) may be affected.
- 4) Because of complexity in biology and confusions in chemical control of biological experiments, the results of studies are often controversial. Some reefs are thriving (e.g. Truck Is. in Pacific), while others (Florida keys) are negatively affected. Reported pH effects are often conflicting. How so??

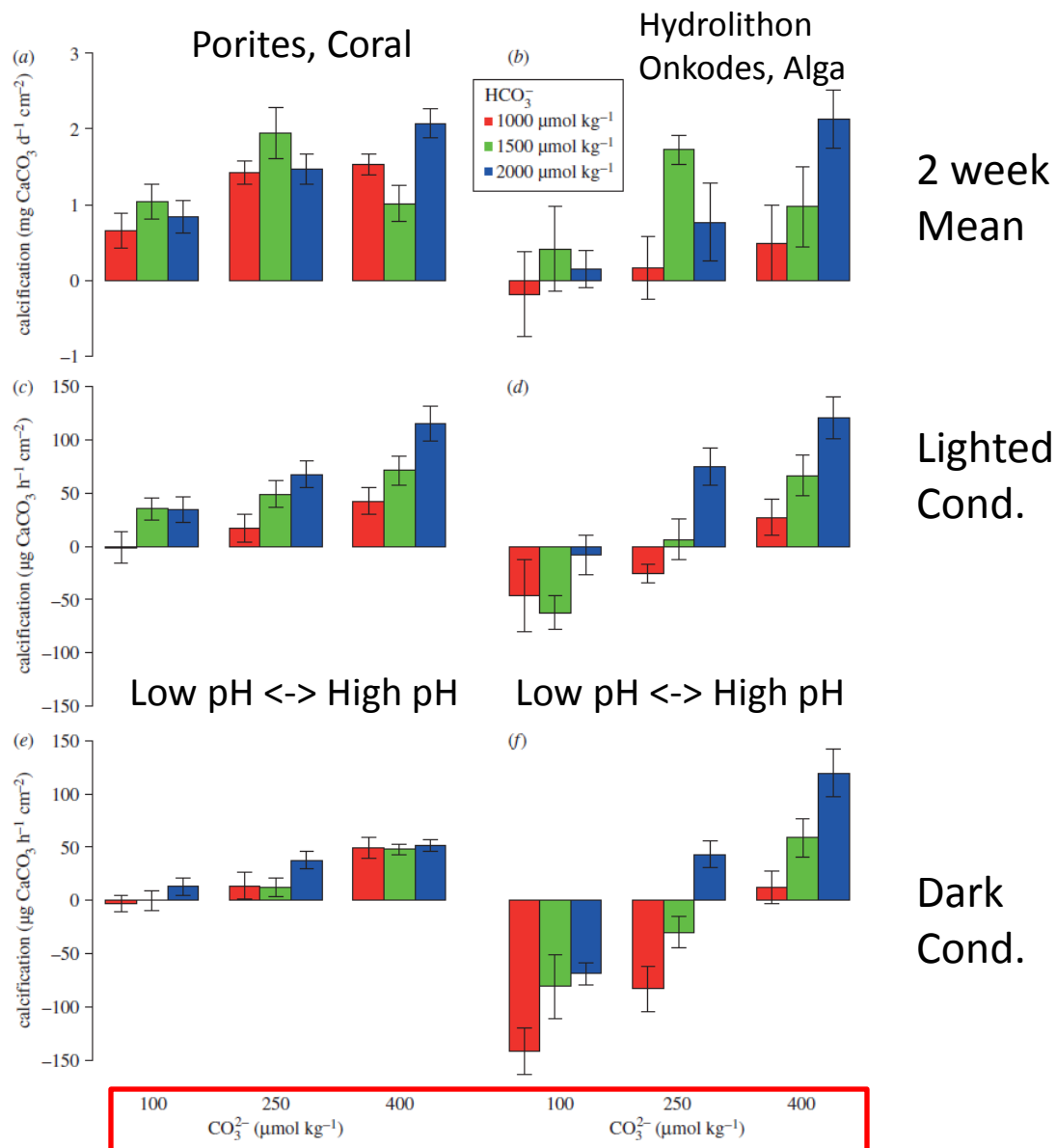
RESPONSE OF CORALS TO ACIDIFICATION (Three Pacific reef samples)



Comeau et al. (2014). Pacific-wide contrast highlights resistance of reef calcifiers to ocean acidification. Proc. Roy. Soc. B 281, 2014.1339.

Moorea, Equatorial Pacific;
Hawaii, N. Central tropical Pacific;
Okinawa, W. Sub-tropical Pacific

figure 2. Calcification of the corals massive *Porites* spp. and *P. damicornis* maintained in three pCO₂ levels (400, 700 and 1000 μatm) in Moorea, Okinawa and Hawaii, respectively. The first row represents: (a) the area-normalized calcification and (b) the biomass-normalized calcification of massive *Porites* spp. The second row shows: (c) the area-normalized calcification and (d) the biomass-normalized calcification of *P. damicornis*. The bars correspond to the mean calcification and the vertical error bars show the s.e. in the measurement of calcification (n = 12).



Comeau et al., (2012). Coral reef calcifiers buffer their response to ocean acidification using both bicarbonate and carbonate. Proc. Roy. Soc. B, 280: 2012.2374.

Figure 2. Calcification rates of *Porites rus* (left column) and *Hydrolithon onkodes* (right column) as a function of $[\text{CO}_3^{2-}]$ and $[\text{HCO}_3^-]$. (a,b) Net calcification measured by buoyant weight over two, two-week incubations; (c,d) net calcification in the light measured by the alkalinity anomaly technique; and (e,f) calcification in the dark measured by the alkalinity anomaly technique. Each group of bars corresponds to three $[\text{CO}_3^{2-}]$ (approx. 100, 250 and 400 $\mu\text{mol kg}^{-1}$); colours of bars are dependent on $[\text{HCO}_3^-]$ (red approx. 1000, green approx. 1500, and blue approx. 2200 $\mu\text{mol kg}^{-1}$). All values are mean \pm s.e.m. ($n = 12$ for buoyant weight and $n = 4$ for the light and dark calcification).

CALCIFICATION PROCESSES IN CORALS

Azooxanthellate cold-water corals (NON-REEF FORMERS)

M. McCulloch et al. / *Geochimica et Cosmochimica Acta* 87 (2012) 21–34

23

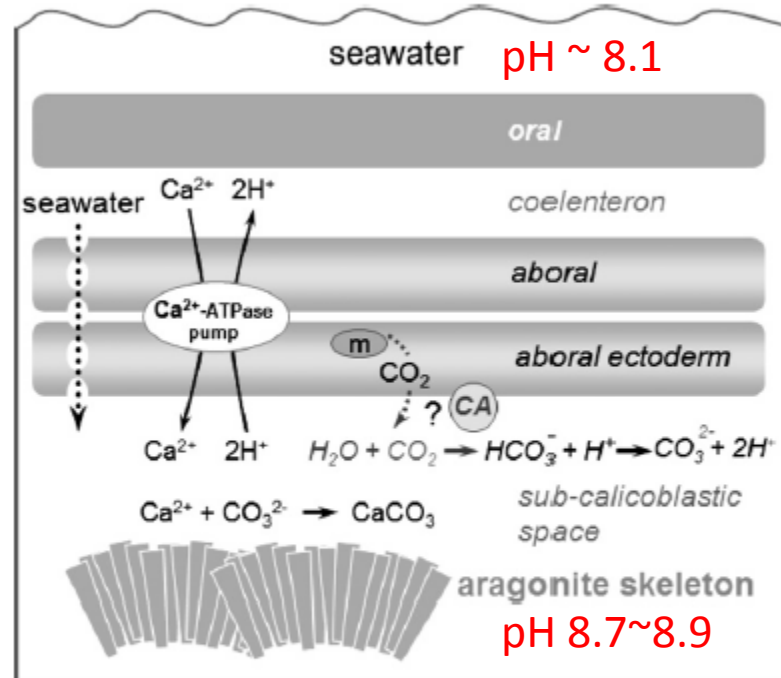


Fig. 1. Schematic of the calcification process in azooxanthellate cold-water corals (modified from Allemand et al., 2004). Removal of protons from the calcification site occurs primarily via Ca^{2+} -ATPase exchangers that pump 2H^+ ions from the calcifying medium into the coelenteron in exchange for each Ca^{2+} ions. The carbonic anhydrases (CA) catalyse the forward reactions converting seawater derived HCO_3^- into CO_3^{2-} ions (Moya et al., 2008), the latter being essential for calcification. Due to the greater pH_c in azooxanthellate corals (see discussion), it is likely that diffusion of CO_2 into the sub-calicoblastic space is minimal and thus the DIC of the calcifying fluid is similar to that in seawater (Erez, 2003).

BORON ISOTOPES AND pH

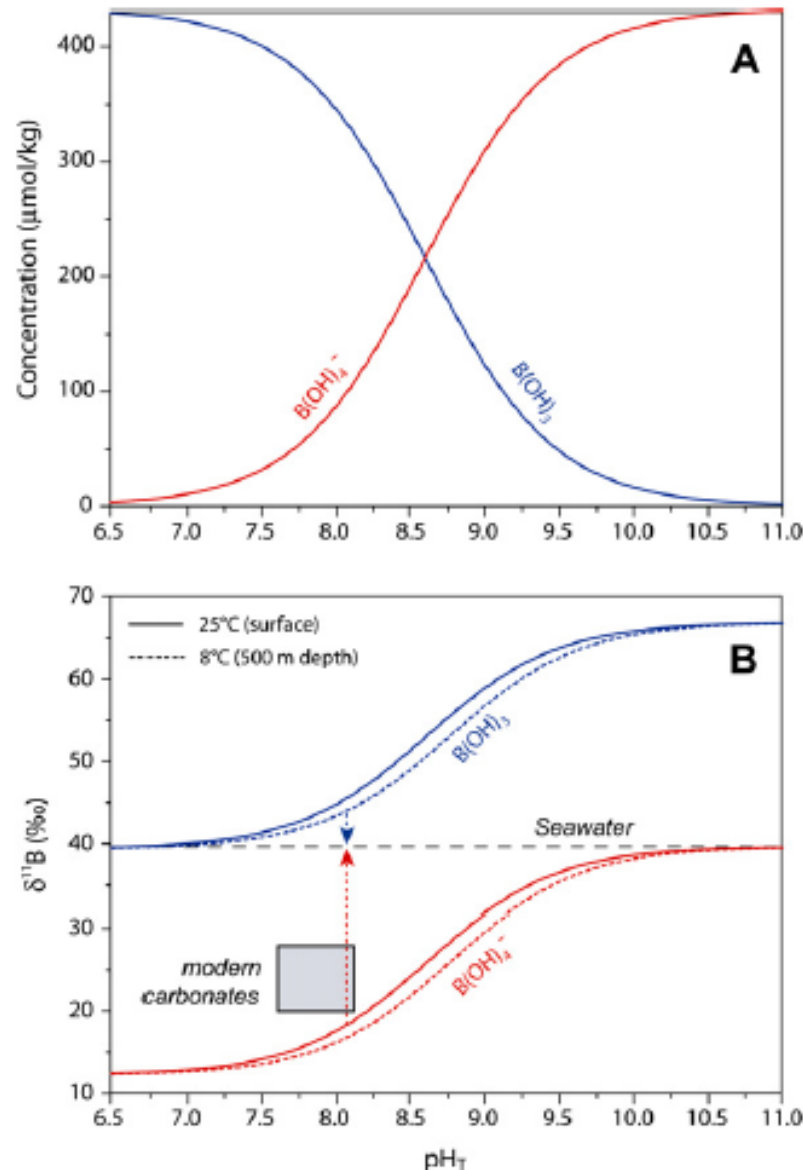


Fig. 2. (A) Boron speciation in seawater as a function of seawater pH_T (Total scale). (B) Boron isotope fractionation of ~27‰ between the boric and borate species (Klochko et al., 2006). Calcifiers appear to take up the borate ion [B(OH)₄⁻] exclusively and thus generally lie on or near the red borate curve. The blue and red arrows show the relative contribution of each species to the overall seawater δ¹¹B composition of 39.6‰. Grey box shows the typical δ¹¹B compositions of marine carbonates, which generally lie above the borate curve. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Isotope fractionation =

$$\frac{[^{11}\text{B}/^{10}\text{B}]_{\text{B(OH)}_3}}{[^{11}\text{B}/^{10}\text{B}]_{\text{B(OH)}_4^-}}$$

This ratio varies with pH.

McCulloch et al., (2012). Resilience of cold-water scleractinian corals to ocean acidification. *Geochim et Cosmochimica Acta*, 87, 21-34.

SUMMARY OF RESPONSE OF CALCIFIERS TO OCEAN ACIDIFICATION

The site or “chamber” of calcification is not exposed directly to the ambient seawater, and is protected from the seawater. Symbiotic photosynthesis consumes CO₂ and helps to reduce the acidity of chamber water. The ions needed for shell construction as well as the nutrients for symbiotic algae in corals and others are transported into the calcification chamber through membranes. The waste products (including H⁺ ions) are disposed through layers of membranes.

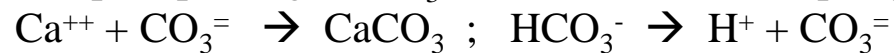
The size and structure of calcification chamber and the membranes protecting it vary from species to species. Hence, the response to seawater acidification depends on species. In some species or during larval stage of some species, the calcification site is directly exposed to the seawater. Hence, the growth is sensitively affected by the seawater pH or degree of CaCO₃ saturation.

Because of the complexity in the biological processes as well as the chemistry of seawater, the effects of ocean acidification on marine life have begun clearer only recently via collaborations among biologists, chemists, oceanographers and meteorologists. Here is an example!

Growth Stages of Pacific Oysters

George Waldbusser et al. (2013). A developmental and energetic basis linking larval oyster shell Formation to acidification sensitivity. *Geophysical Research Letters*, Vol. 40, 2171-2176.

The first shell (periostracum) forms on bare larva in 6~10 hours after the fertilization. After 24~48 hours, full protective calcified shell is formed: 90% of the body weight as CaCO_3 . Energy is needed for precipitating CaCO_3 , and H^+ ions must be pumped out:



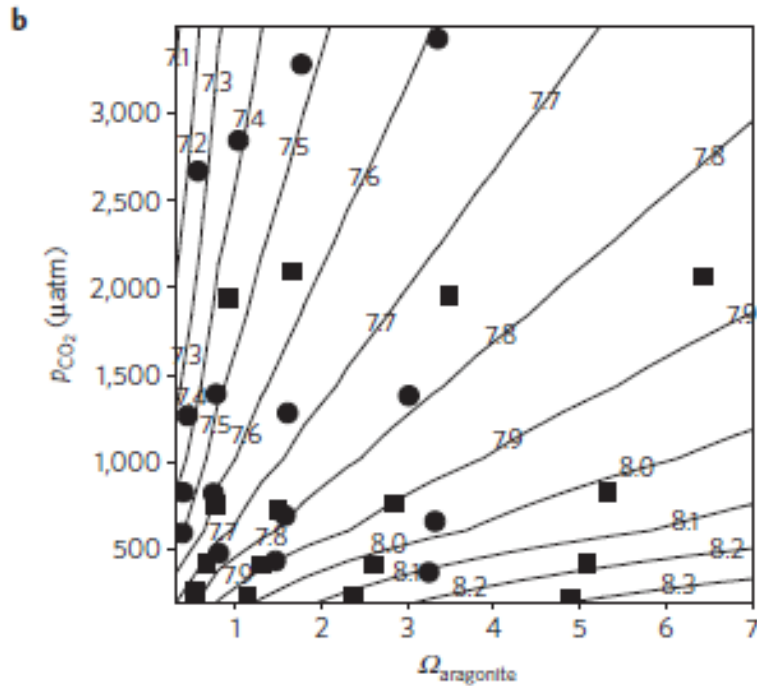
Before the protective shell is formed, larvae are exposed directly to the surrounding seawater. Due to the lack of ability to isolate calcifying fluid from surrounding water, the growth is affected by the chemistry of seawater. Lower degree of saturation of CaCO_3 in seawater due to ocean acidification should cause an increase in the energy cost for calcification, and hence lowers energy available for the metamorphosis and results in greater failure of larvae.

Slow transition of energy source from endogenous (egg) to exogenous food sources occurs. Food supply is another important factor for the survival of larvae.

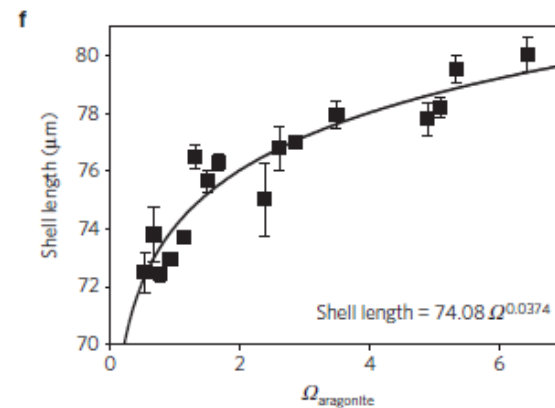
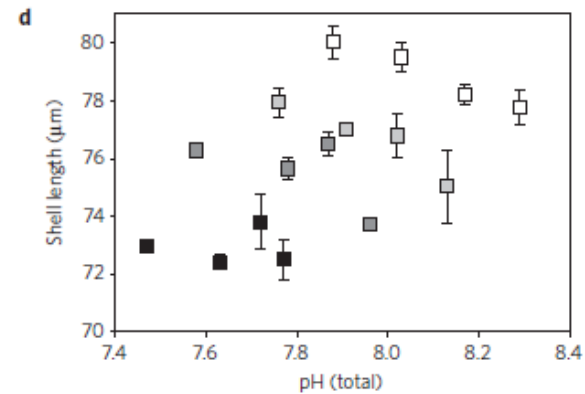
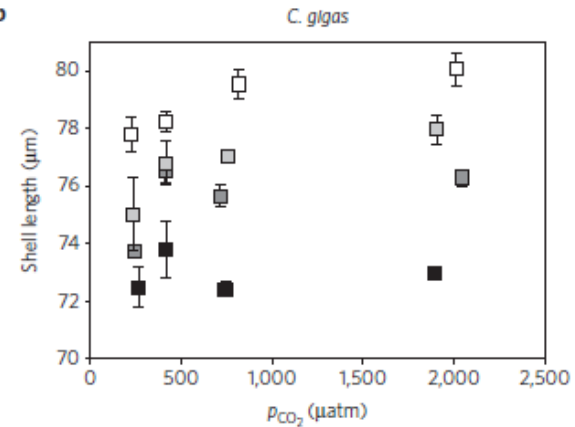
The importance of the early larval stage to favorable fish population was first pointed out by the Norwegian biologist Johan Hjort (1914). His concept has been the guiding principle for fish management for 100 years. His concept applies to the effect of acidification on oysters.

CARBONATE CHEMISTRY EXPERIMENTS WITH OYSTER LARVA ^b

Waldbusser, G., Hales, B. et al. (2014). Saturation-state sensitivity of marine bivalve larvae to ocean acidification. Nature Climate Change, December 15, 2014. doi:10.1038/NCLIMATE2479.



Carbonate chemistry variables are $p\text{CO}_2$, H_2CO_3 , HCO_3^- , CO_3^{2-} , H^+ (pH), Ω

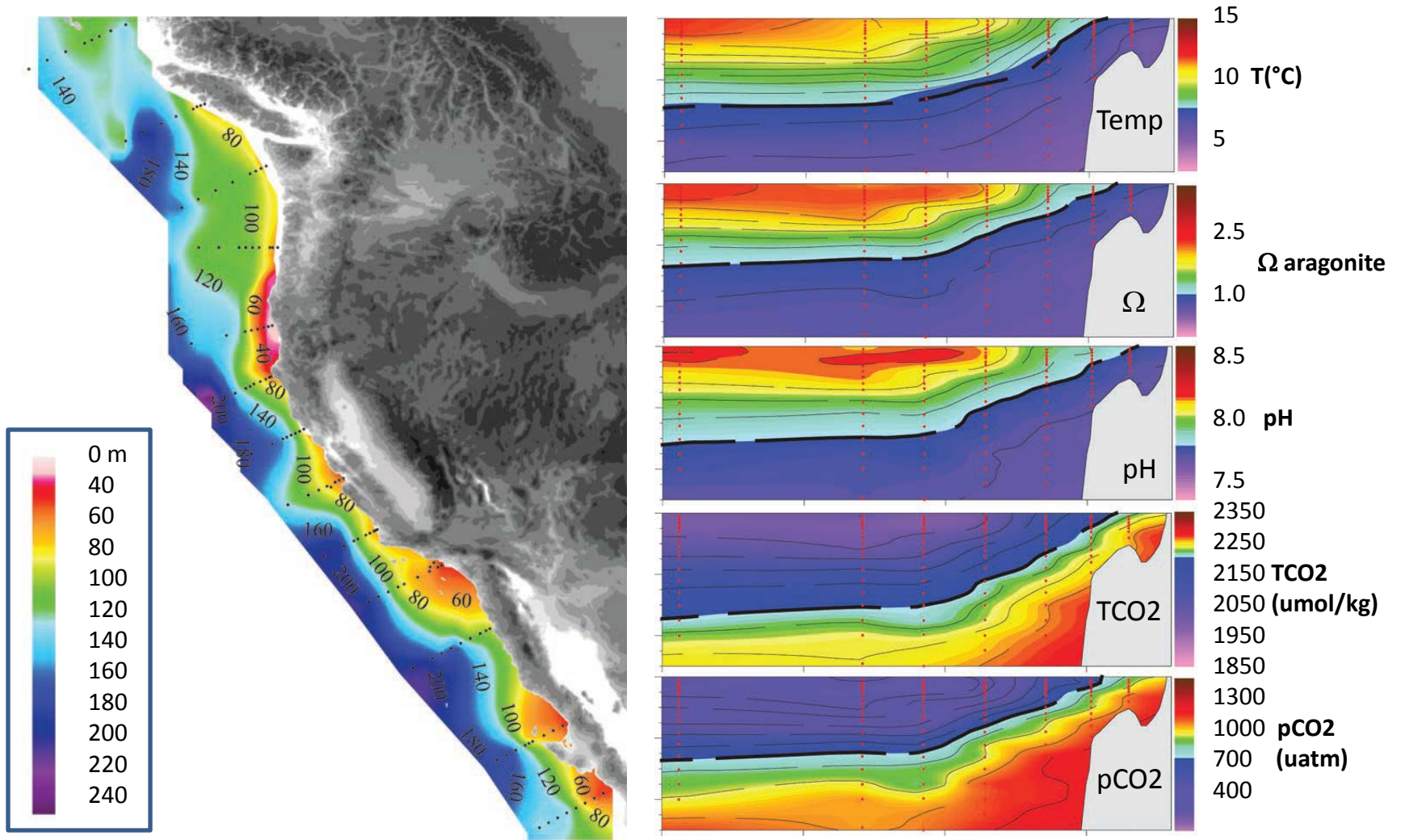


Open
High Ω

Gray
Medium Ω

Filled
Low Ω

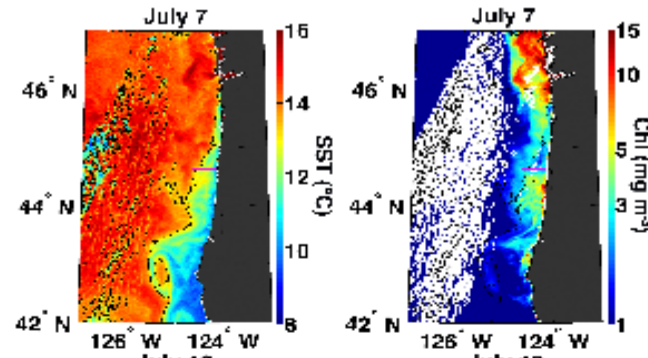
Oregon-California Coast during Upwelling of Deep Waters (Feely et al., Science, vol. 320, 2008)



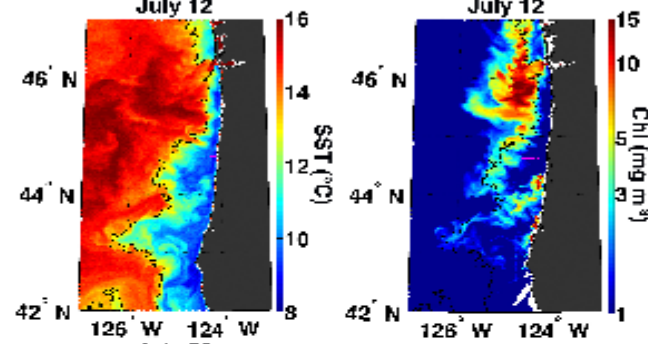
Depth of the waters undersaturated
With aragonite in meters.

OREGON COAST UPWELLING JULY, 2008

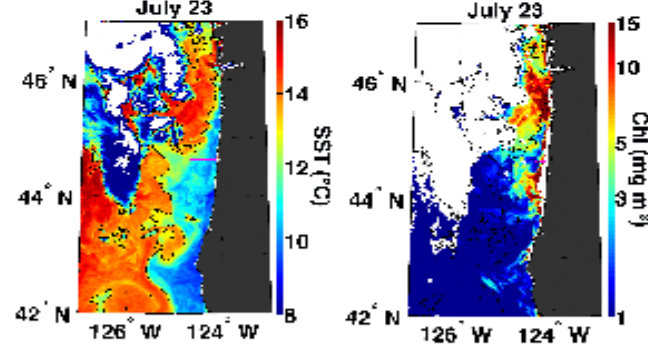
Wind
to
South



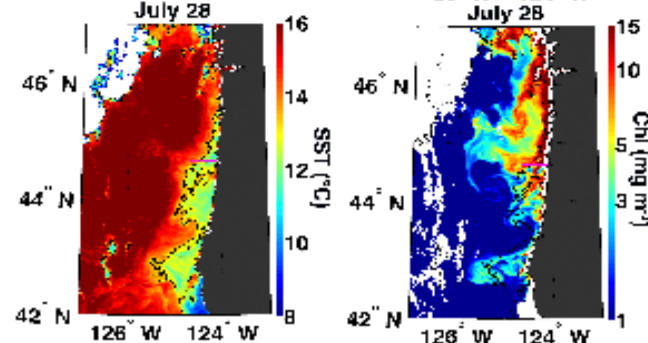
Wind
to
South



Wind
to
South



Wind
to
North



Upwelling of deep waters started on July 8, driven by the southward winds.

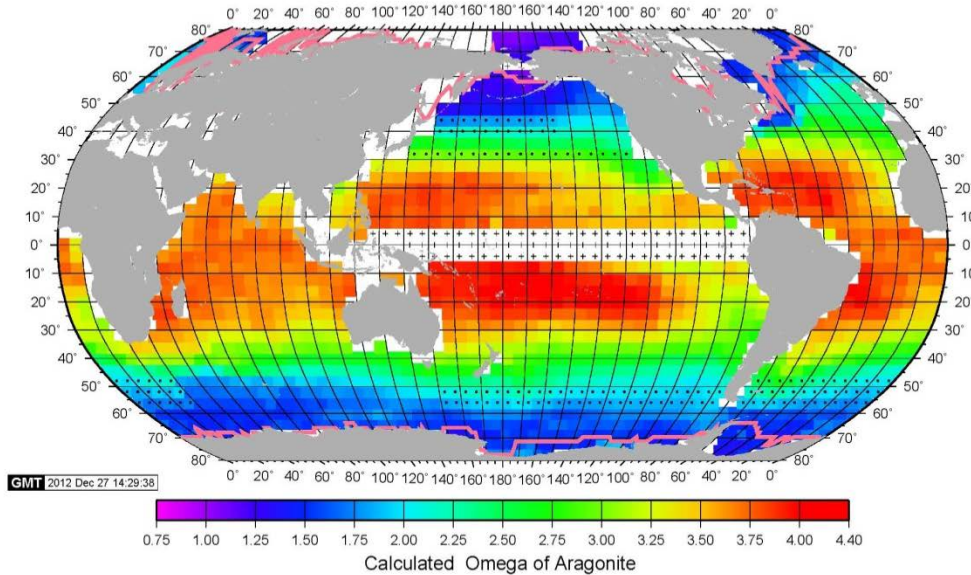
The upwelled waters are colder (blue) and are rich in nutrients and respired CO₂ (hence more acidic).

Before the plankton were in full blooms, the wind direction changed to northward on July 26, and the upwelled waters were covered up by the warm (red) waters. The failed plankton blooms caused the waters in oyster hatcheries to be more acidic causing oyster death.

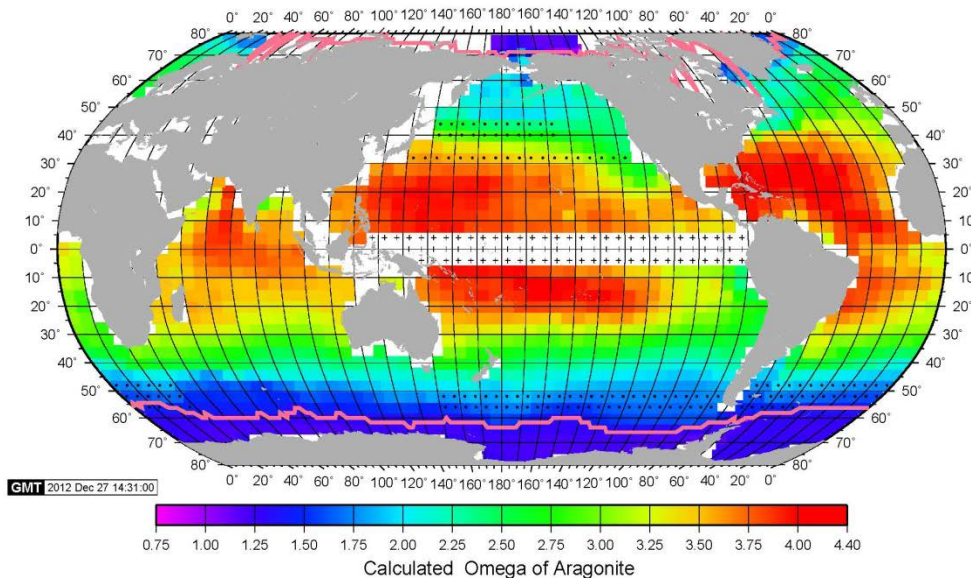
CONCLUSIONS

- 1) The ocean water acidification is attributed primarily to the up-take of CO₂ from the air.
- 2) The response of marine ecosystems vary depending upon the physiology of different organisms. As the result of interdisciplinary studies involving biological/chemical/physical science, the mechanisms of responses are becoming clearer. The Oregon coast case is presented as an example for recent advancement.
- 3) Production of future leaders in health management of our marine, land and air environment relies heavily on the education at the high school and college levels.

A) February, 2005



B) August, 2005



Climatological Mean Distribution of the Degree of Saturation of CaCO₃ (aragonite) Takahashi et al. (2013)

Many corals are made of mineral aragonite (CaCO₃). Surface ocean water is commonly supersaturated with respect to this mineral, and hence provide favorable environment for coral growths.

The degree of saturation is expressed in the OMEGA scale: $\Omega = 1$ is at saturation, $\Omega > 1$ is supersaturation, and $\Omega < 1$ is undersaturation (or dissolution).

Today's surface ocean waters are supersaturated with CaCO₃ (aragonite) up to 440 %. Only a small portion of the Arctic Ocean is undersaturated with aragonite.

$$\Omega = \frac{(\text{Ca}^{++}) (\text{CO}_3^{=})}{K_{sp}}$$

and

K_{sp} is called Solubility product

$$= (\text{Ca}^{++}) (\text{CO}_3^{=}) \text{ at saturation}$$