Ocean Acidification and Its Effects on Marine Life

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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 CaCO₃ 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)

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

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:**

\[
\text{CaSiO}_3 + \text{CO}_2 = \text{CaCO}_3 + \text{SiO}_2 \\
\text{Rocks} \hspace{1cm} \text{Air} \hspace{1cm} \text{Calcifiers} \hspace{1cm} \text{Quartz/Diatoms} \\
\text{(Corals and plankton)}
\]

**Regulations of H\(^+\) ions in ocean:**

From land

\[
\text{CaSiO}_3 + \text{H}_2\text{O} = \text{Ca}^{++} + 2 \text{OH}^- + \text{SiO}_2 \ldots \text{make ocean more alkaline}
\]

From the air

\[
\text{CO}_2 + \text{H}_2\text{O} = \text{HCO}_3^- + \text{H}^+ \ldots \ldots \text{make ocean more acidic}
\]

In the sea:

Photosynthesis

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

Calcification

\[
\text{Ca}^{++} + \text{CO}_2 + \text{H}_2\text{O} = \text{CaCO}_3 \text{ (corals)} + 2 \text{H}^+
\]

Growth of calcifiers makes seawater more acidic,

Dissolution of lime stones neutralizes acidic waters.
DEFINITION OF pH AND OMEGA

\[ pH = \log \frac{1}{(H^+)} = - \log (H^+), \text{ and } Kw = (H^+) (OH^-) = 1 \times 10^{-14} \]

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

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

Soda drinks, pH \sim 4,

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

Alkaline waters, pH > 7

Human blood and seawater, pH \sim 8,

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

Degree of Saturation of CaCO\(_3\) in seawater:

Solubility product of CaCO\(_3\) (Ksp) = [Ca\(^{++}\)] [CO\(_3^{−}\)]\text{ at saturation}

\[ \Omega = \frac{[Ca^{++}]_{sw} \cdot [CO_3^{−}]_{sw}}{Ksp} \]

\( \Omega = 1, \text{ saturated} \)

\( \Omega > 1, \text{ favors precipitation or formation of CaCO}_3 \)

\( \Omega < 1, \text{ dissolution of CaCO}_3. \)
Time Trends Observed at the Bermuda Time Series (BATS) and Hawaii Ocean Time-series (HOT) Stations

**BATS**
- \( pCO_2 = +1.78 \text{ uatm/yr} \), \( pH = -0.0018 /\text{yr} \)
- \( TA = +0.47 \text{ ueq/kg/yr} \), \( TCO_2 = +1.55 \text{ umol/kg/yr} \)

**HOT**
- \( pCO_2 = +1.89 \text{ uatm/yr} \), \( pH = -0.0018 /\text{yr} \)
- \( TA = +0.95 \text{ ueq/kg/yr} \), \( TCO_2 = +1.75 \text{ umol/kg/yr} \)

\( H^+ \) concentrations in surface ocean increase at a rate of 4.5% per decade or about 50% per century.
Mean rate of pH change:
-0.002 pH/yr.
-0.02 pH/decade
(-5% H⁺/decade)
-50% H⁺/century)
Iceland Sea and Vicinity
Time-series, 1985-2013
68°N and 12.7°W
Olafsson and Takahashi, (in preparation)

**Annual Rate of change**

0.024 °C
±0.036

0.0046 PSS
±0.001

0.49 ueq/kg
±0.14

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\(_2\)CO\(_3\), HCO\(_3^-\), CO\(_3^{2-}\), and the solubility of CaCO\(_3\). Photosynthesis may be affected by changes in (CO\(_2\))\(_{aq}\), H\(_2\)CO\(_3\), which are most readily used for photosynthesis. The solubility of CaCO\(_3\) depends upon the product (Ca\(^{++}\)) (CO\(_3^{2-}\)): CaCO\(_3\) (shells) = Ca\(^{++}\) + CO\(_3^{2-}\). 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)


Moorea, Equatorial Pacific; Hawaii, N. Central tropical Pacific; Okinawa, W. Subtropical Pacific
Acidification effect on Corals and Alga

Porites, Coral

Hydrolithon Onkodes, Alga

2 week Mean

Lighted Cond.

Low pH $\leftrightarrow$ High pH

Low pH $\leftrightarrow$ High pH

Dark Cond.

CALCIFICATION PROCESSES IN CORALS

Azooxanthellate cold-water corals (NON-REEF FORMERS)

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\(^{2+}\) ion. 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\(_{eq}\) 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).
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.

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!
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:

$$\text{Ca}^{++} + \text{CO}_3^- \rightarrow \text{CaCO}_3$$

$$\text{HCO}_3^- \rightarrow \text{H}^+ + \text{CO}_3^-$$

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 variables are pCO$_2$, H$_2$CO$_3$, HCO$_3^-$, CO$_3^{2-}$, H$^+$ (pH), 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.
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.

\[ \Omega = \left( Ca^{++} \right) \left( CO_3^{-} \right) / K_{sp} \]

and

Ksp is called Solubility product

\[ = \left( Ca^{++} \right) \left( CO_3^{-} \right) \text{ at saturation} \]