Low pH and carbonate saturation state of aragonite in China Seas: variations and controls

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OUTLINE

• Background of OA
• Coastal acidification and case studies in China;
• Chinese activities at national scale;
The burning of fossil fuels result in increased CO$_2$ in the atmosphere being taken up by the ocean resulting in it becoming more acidic.

Oceans are acidifying fast

Changes in oceanic pH over the last 25 million years
Source after Turley et al. in *Avoiding Dangerous Climate Change* (2006).

![Graph showing ocean acidification](image)


*Oceanic pH is dropping now at a rate and to levels not experienced by marine organisms for over 20 million years.*
Changes in surface oceanic $pCO_2$ (in matm) and pH from time series stations

Source: IPCC, 2007
Ocean Acidification Impacts

- Decrease in pH 0.1 over the last two centuries
- 30% increase in acidity; decrease in carbonate ion of about 16%

These changes in pH and carbonate chemistry may have serious impacts on open ocean and coastal marine ecosystems.

Hall-Spencer, Nature, June 18, 2008
What we know about the ocean chemistry of... *saturation state*

\[ \text{Ca}^{2+} + \text{CO}_3^{2-} \rightarrow \text{CaCO}_3 (s) \]

Calcite, Carbonate, Carbonate

\[ \text{CO}_2 + \text{CO}_3^{2-} + \text{H}_2\text{O} \Leftrightarrow 2\text{HCO}_3^- \]

*Saturation State*

\[ \Omega_{\text{phase}} = \frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{K_{sp,\text{phase}}} \]

\[ \Omega > 1 = \text{precipitation} \]
\[ \Omega = 1 = \text{equilibrium} \]
\[ \Omega < 1 = \text{dissolution} \]

Stein, 2009; Feely 2009

Calcite

Aragonite
marine calcifying organisms may require much higher $\Omega$ for optimal growth

Saturation State

$$\Omega_{phase} = \frac{[Ca^{2+}][CO_3^{2-}]}{K_{sp,phase}}$$

**Fig. 6.** $\Omega_{arag}$ versus calcification rate for coral reef ecosystems (solid symbols) and coral mesocosms (open symbols). Lines are the linear least-squares best fit of the data. References for data are: Kaneohe Bay barrier reef data (black diamonds and solid line), this study; Elat Reef, Red Sea (dark gray squares and solid line) (Silverman et al., 2007a, b); Rukan-sho, Japan (light gray triangles and solid line) (Ohde and van Woesik, 1999); Biosphere 2 (black circles and dashed line) (Langdon et al., 2000, 2003); Kaneohe Bay mesocosm, 2005 (light gray squares and dashed-dot line); Kaneohe Bay mesocosm, 2009 (dark gray triangles and dotted line) (Andersson et al., 2009).
Natural processes that could accelerate the ocean acidification of coastal waters

- Local Oceanography: coastal upwelling
- Metabolism Processes
- Regional Environ. Changes: eutrophication

Stein, 2009; Feely 2009
In the California current system, habitats along the sea floor will become exposed to year-round undersaturation within the next 20 to 30 years.

Natural Processes that can Accelerate the Ocean Acidification of Ocean Water Masses

Biological Remineralization of Organic Matter

\[(CH_2O)_n + O_2 \rightarrow CO_2 + H_2O\]

Can cause hypoxia and pH decrease

Feely 2009
Eutrophication

\[(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}\text{H}_3\text{PO}_4 + 138\text{O}_2 \rightarrow 106\text{CO}_2 + 16\text{HNO}_3 + \text{H}_3\text{PO}_4 + 122\text{H}_2\text{O}\]

The organic matters are remineralized through oxygen-consuming processes below the euphotic depth.

Coastal Acidification and OA induced by $pCO_2$ in atmosphere

Cai et al., 2011, Nature Geoscience
Case Studies of Coastal Acidification in China Seas

Study Area
Coastal acidification in summer bottom oxygen-depleted waters in northwestern-northern Bohai Sea from June to August in 2011

Area map and sampling sites, and the locations of the two scallop-breeding counties of Laoting and Changli are also marked.

Typical vertical profiles of water temperature in the northwest (Bohai Bay) and the north (Liaodong Bay) during the 2 surveys

Source: Zhai et al., 2012. Chin Sci Bull
In August, both the bottom DO and the pH had significantly declined in the northwestern-northern near-shore areas.

Vertical profiles of DO and pH at all sampling sites during the June survey (triangles) and the August survey (gray circles).

Source: Zhai et al., 2012. Chin Sci Bull
Distributions of August bottom DO and pH (at 25°C), and differences in bottom DO (c) and bottom pH (d) between June and August.

Source: Zhai et al., 2012. Chin Sci Bull
Based on the significant positive correlation between the bottom DO and pH, we suggest that both the bottom DO depletion and the coastal acidification were induced by remineralization of biogenic particles. These biogenic particles were supplied either by coastal red tides or by near-shore marine aquaculture.

\[
(CH_2O)_{106} (NH_3)_{16} H_3PO_4 + 138O_2 \rightarrow 106CO_2 + 16HNO_3 + H_3PO_4 + 122H_2O
\]

**Relationship between bottom pH and DO in the Bohai Sea in the summer of 2011.**

Source: Zhai et al., 2012. Chin Sci Bull
Seasonal variations of subsurface low pH and carbonate saturation state of aragonite on China side of the North Yellow Sea

pH, carbonate saturation state of aragonite ($\Omega_{\text{arag}}$), and ancillary parameters

Source: Zhai et al., 2013, BGD
Between 2011 and 2012, we investigated carbonate system in the Bohai Sea and the Yellow Sea. Low $\Omega_{\text{arag}}$ values of $<2.0$ were frequently observed in bottom layer water, especially in autumn.

Source: Zhai et al., 2013, BGD
In November 2012, the lowest $\Omega_{\text{arag}}$ of 1.0 were revealed in bottom waters in the central part of the Yellow Sea, which is the trigger value for calcic shells and skeletons to dissolve. On the other hand, very low $\Omega_{\text{arag}}$ values of 1.5-2.0 were also observed in surface waters in the west side of the North Yellow Sea, suggesting the ocean acidification status might have impacted adjacent marine aquaculture zones, which are of major economic importance in North China.

Carbonate saturation state of aragonite ($\Omega_{\text{arag}}$) in surface and bottom waters in the Bohai Sea and Yellow Sea in November 2012
Critically low $\Omega_{\text{arag}}$ values of 1.00 to 1.20 were mainly observed in subsurface waters in a salinity range of 31.50 to 32.50 in autumn, accounting for ~10% of the North Yellow Sea.

Source: Zhai et al., 2013, BGD
Subsurface waters were nearly in equilibrium with air in May and June. From July to October, the fugacity of CO$_2$ (fCO$_2$) of bottom water gradually increased to 697 ± 103 µatm and pH decreased to 7.83 ± 0.07 due to respiration/remineralization processes of primary production induced biogenic particles. In November and January, bottom water fCO$_2$ decreased and pH gradually returned to an air-equilibrated level due to cooling enhanced vertical mixing.

Source: Zhai et al., 2013, BGD
sea surface $p\text{CO}_2$ level at the end of this century

Source: Zhai et al., 2013, BGD
Fig. 8. Depth profiles of (a) pH at 25 °C, and (b) $\Omega_a$ over the East China Sea shelf in spring and summer 2009. Squares and circles denote the data in (SSS < 31) and out (SSS > 31) of the Changjiang plume area, respectively. SSS: sea surface salinity.
Ω in a summer upwelling area in the northern South China Sea

Cao et al., 2011
National Activity

China has begun to pay more attention on OA study recently.

Ministry of Science and Technology (MOST) and National Science Foundation of China (NSFC) have started to support research on OA.

CHOICE-C is a funded 5-year project (from 2009 to 2013) to study high CO$_2$ and OA issues in Chinese marginal seas, a joint project of seven major institutions with funding of 34 million RMB.
NSFC started to fund projects on OA from 2006, and there are several ongoing national-level projects exploring the impacts of OA on calcifying organisms.

Marine taxa covered:
- algae (Corallina pilulifera, Thalassiosira pseudonana, Emiliania huxleyi),
- Copepod (Centropages tenuiremis, Calanus sinicus, Tigriopus japonicas),
- mollusks (Crassostrea gigas, Crassostrea angulata, Pinctada martensii, Haliotis diversicolor).
Does the popular shellfish species in China coasts survive in the acidified surroundings?
Air-Sea CO$_2$ flux operational observing program (Started from 2008)

Seasonal underway mapping cruises were conducted in spring, summer, autumn and winter, covering the Bohai Sea, the Yellow Sea, the East China Sea and the northern South China Sea. Based on observing results in 2011 and 2012, the surveying sea area acts as a weak sink of atmospheric CO$_2$ when integrated annually.
Ocean acidification status

Activity: SOA is planning to start the construction of ocean acidification monitoring system in China.
Questions

• At global level, how to start OA observing including process and impact, especially in developing states;
• To set up **standardize methodology** for OA observing and research, to set up time-series observing stations;
• Ocean Acidification and Coastal Acidification;
• OA impact on the aquaculture;
Mollusk occupy 82% aquaculture production in China
Thanks for your attentions!