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Marine Biogeochemical Sciences for the Sustainability of the West Pacific Biosphere

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Effect of seasonal acidification on $CaCO_3$ cycling in the Yellow Sea

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2018-09-18

Outline

- Background
- Seasonal acidification the Yellow Sea
- Controls of the seasonal acidification and a threshold value of aragonite saturation state between community $CaCO_3$ precipitation and dissolution
- The basin-scale $CaCO_3$ dissolution as indicated by field data of dissolved calcium
- Summary

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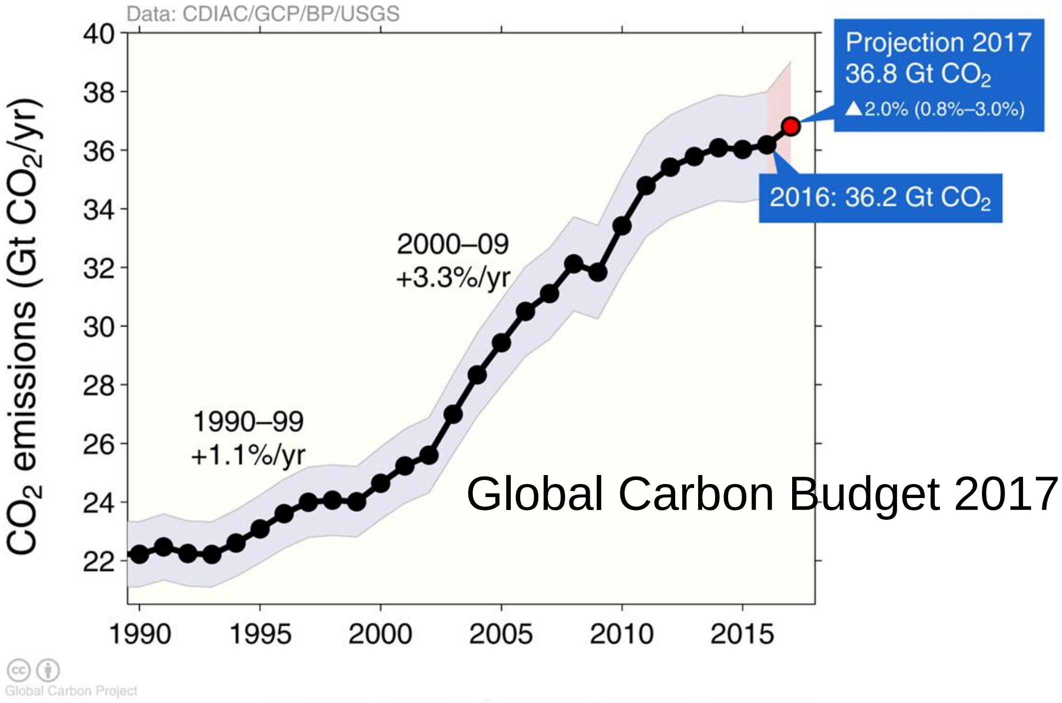
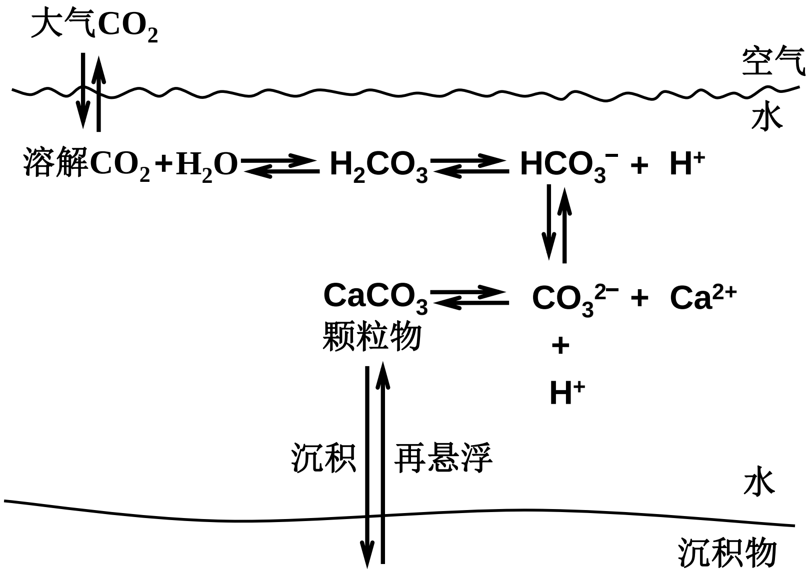
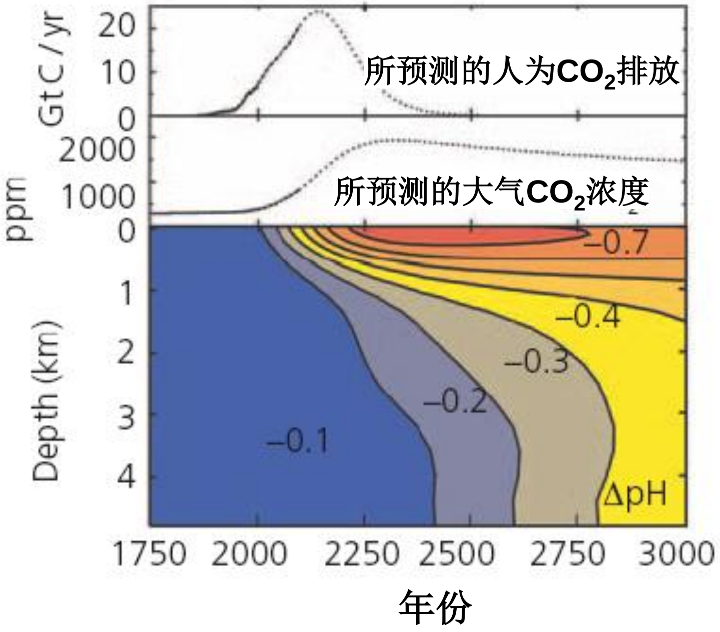
The atmospheric CO_2 rise induces ocean acidification

截止到2011年，海洋吸收了工业革命以来因化石燃料使用和水泥生产导致的人为来源CO_2的41% (IPCC, 2013)，导致海表pH下降0.1单位



Global Carbon Budget 2017

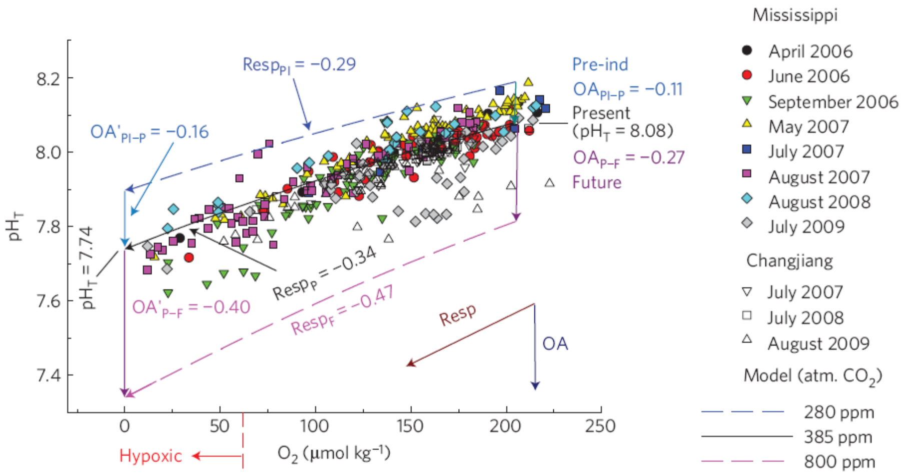




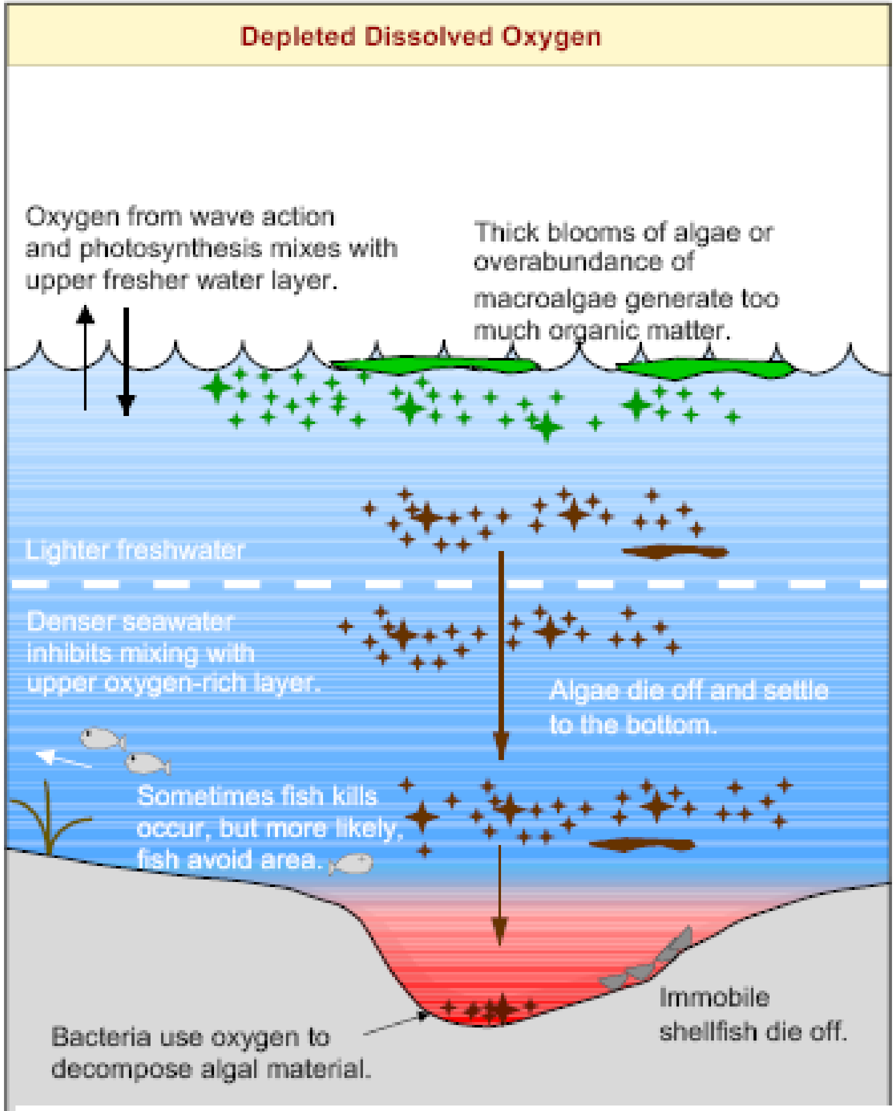
Caldeira and Wickett, 2003, Nature

In coastal oceans, algae blooms and/or marine aquaculture enhance community respiration and subsurface acidification

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

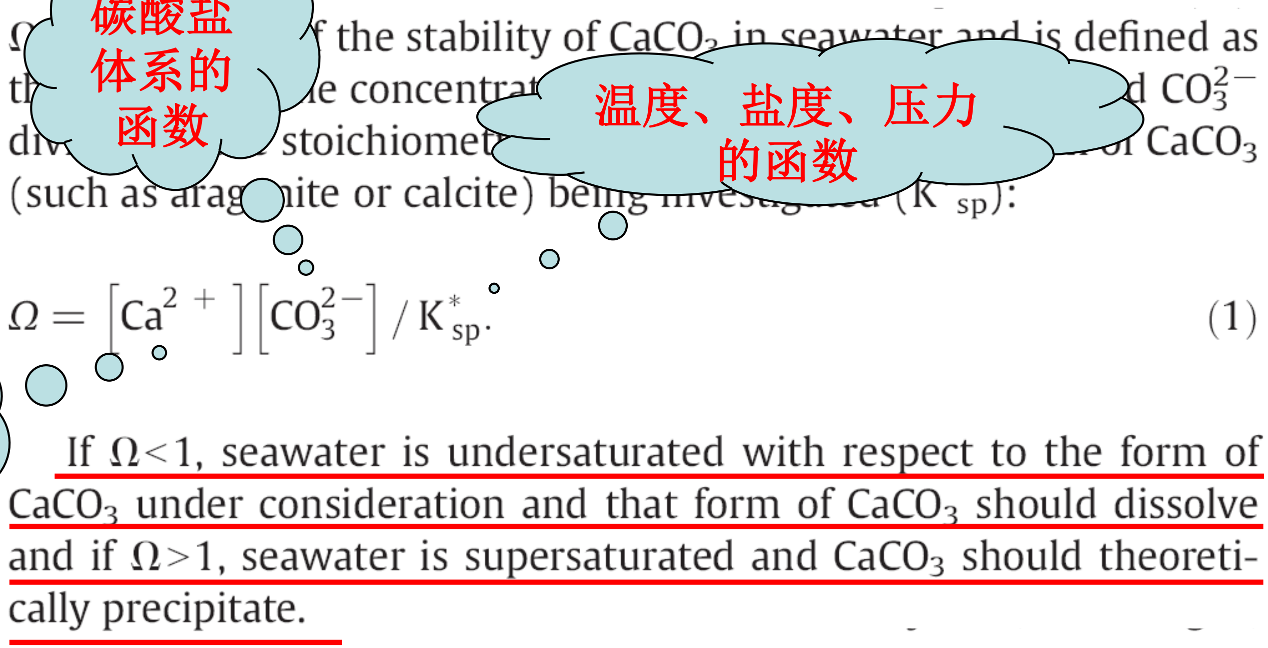


Cai et al., 2011, *Nature Geoscience*



Bricker, S.B., C.G. Clement, D.E. Pirhalla, S.P. Orlando, and D.R.G. Farrow. 1999. **National Estuarine Eutrophication Assessment: Effects of Nutrient Enrichment in the Nation's Estuaries**. NOAA, National Ocean Service, Special Projects Office and the National Centers for Coastal Ocean Science. Silver Spring, MD: 71 pp.

Besides pH, we also use seawater aragonite (one type of $CaCO_3$ crystal) saturation state to characterize acidification



Ω … f the stability of $CaCO_3$ in seawater and is defined as
th … e concentrat … d CO_3^{2-}
div … stoichiomet … of $CaCO_3$
(such as arag … nite or calcite) being investigated (K^*_{sp}):

$$\Omega = \left[Ca^{2+}\right]\left[CO_3^{2-}\right] / K^*_{sp}. \qquad (1)$$

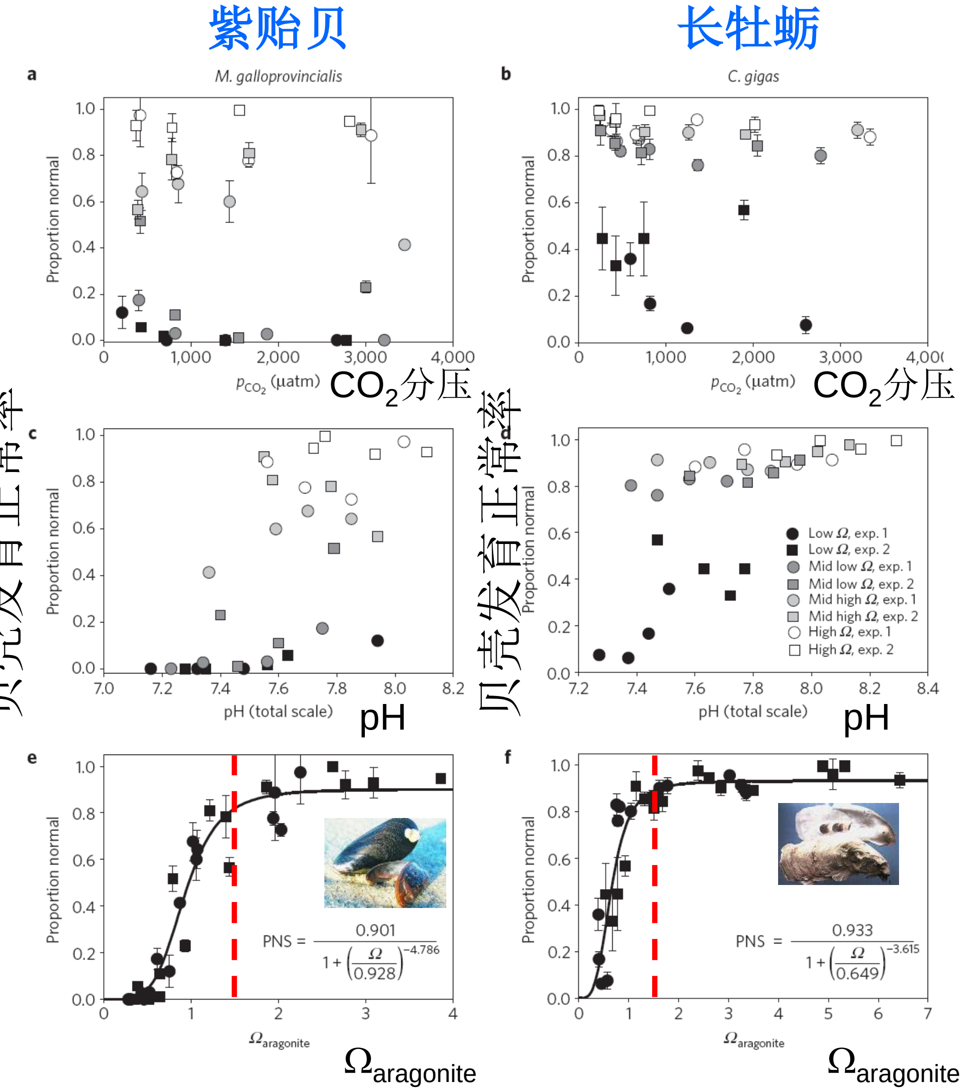
If Ω<1, seawater is undersaturated with respect to the form of $CaCO_3$ under consideration and that form of $CaCO_3$ should dissolve and if Ω>1, seawater is supersaturated and $CaCO_3$ should theoretically precipitate.

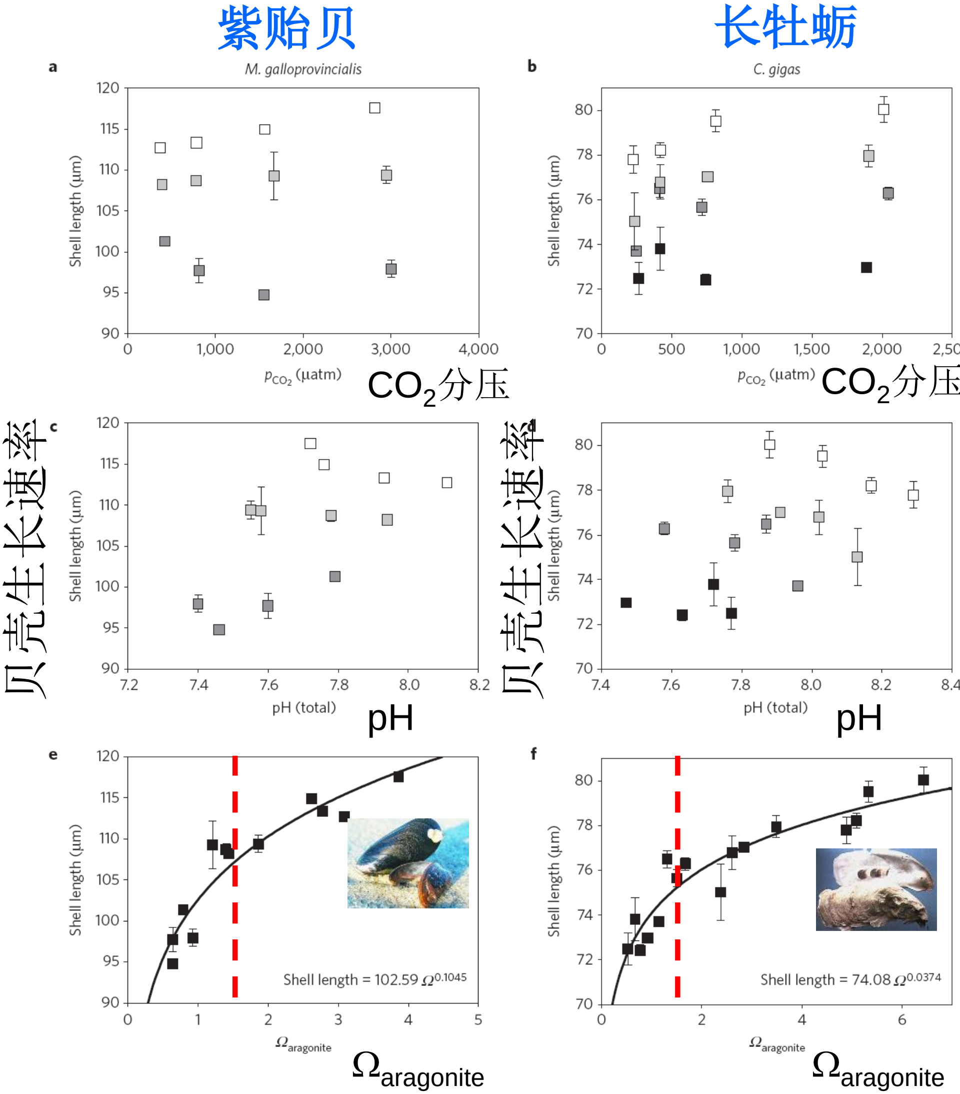
碳酸盐体系的函数

温度、盐度、压力的函数

通常与盐度呈正比例关系

Shell development and growth rate of bivalve larvae in response to carbonate system variables for two species





$\Omega_{aragonite}$ is the key parameter to control shell development and growth rate of shellfish species (Waldbusser et al., 2015, Nature Climate Change).

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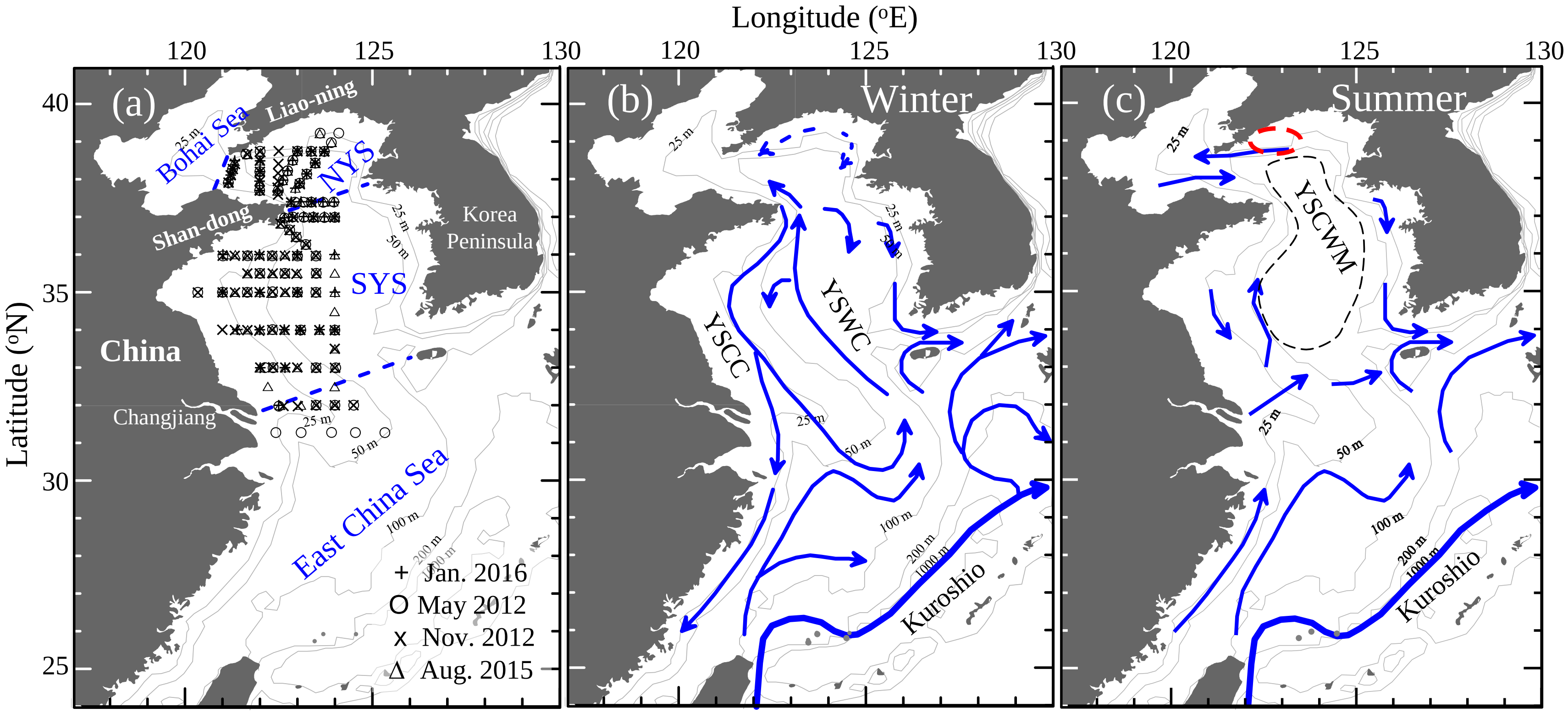
The Yellow Sea



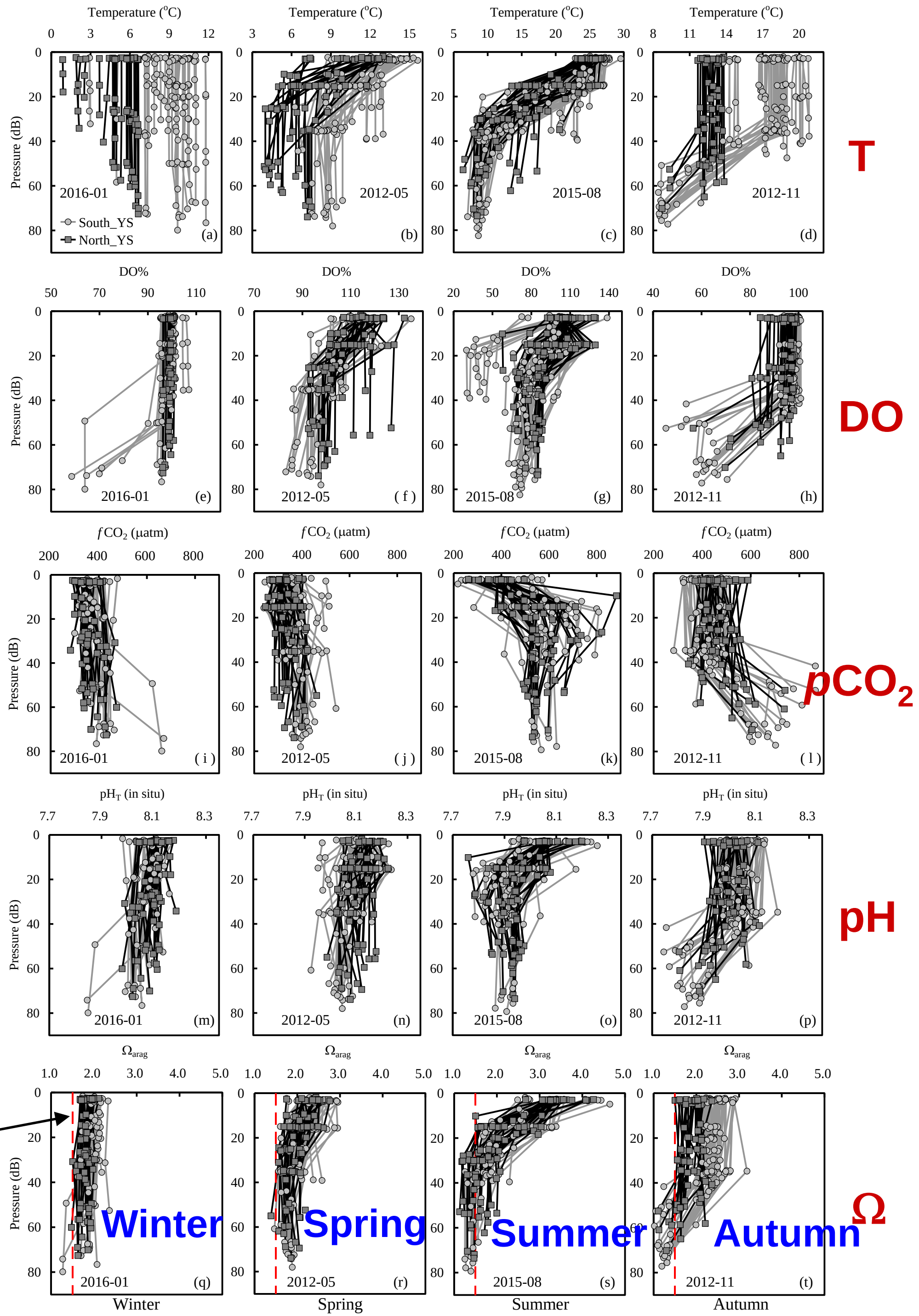
红色虚线椭圆显示辽宁东南海水养殖海域，紧邻黄海冷水团的北侧边缘

Zhai, 2018, China Science Earth Science

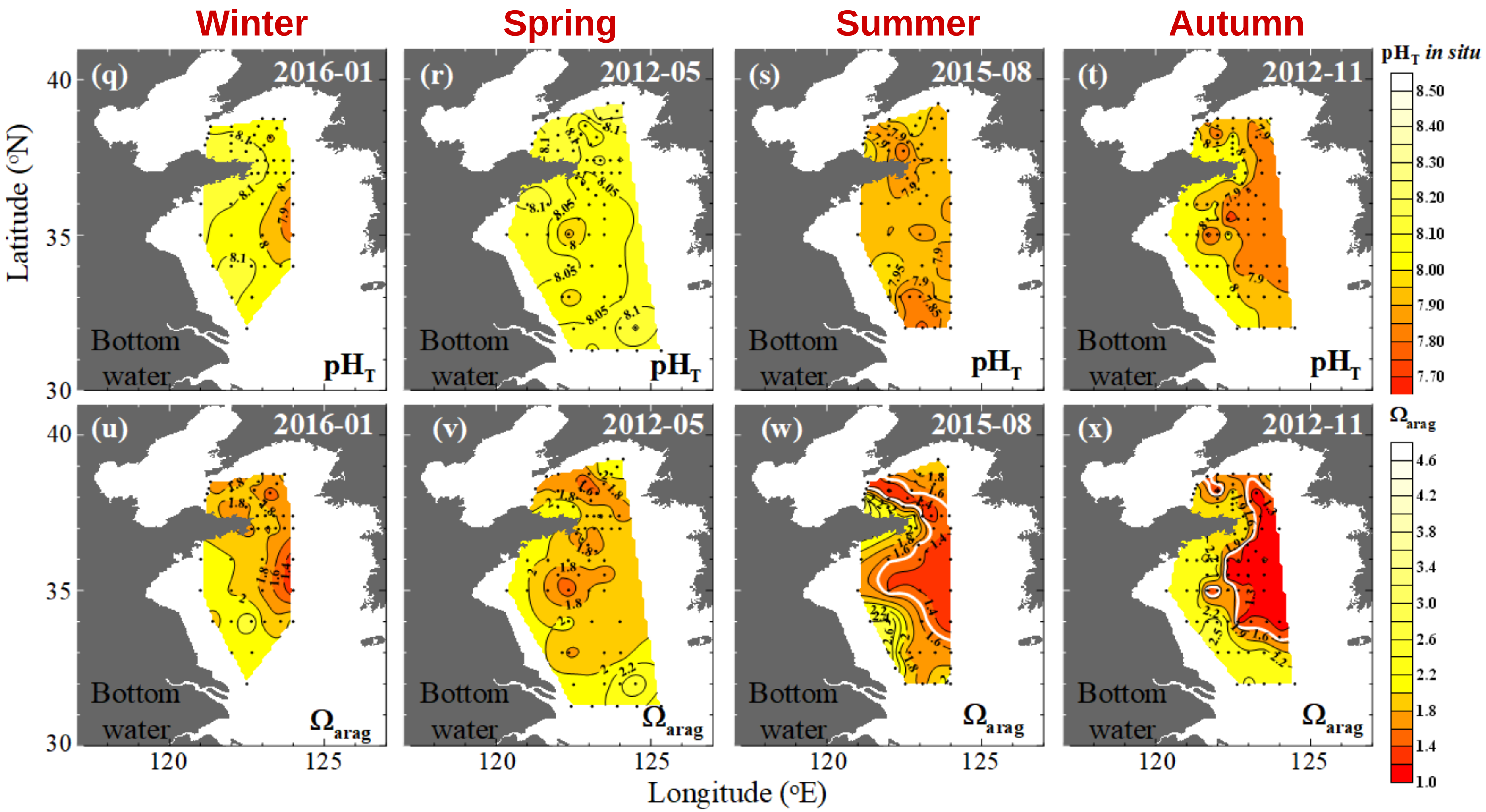
Seasonal variations of vertical profiles

Zhai, 2018, China Science Earth Science

$\Omega_{arag} = 1.5$



Seasonal acidification in bottom waters in the Yellow Sea



Now one third of the Yellow Sea suffer from serious subsurface seawater acidification (with aragonite saturation state of <1.5) during summer and autumn.

Zhai, 2018, China Science Earth Science

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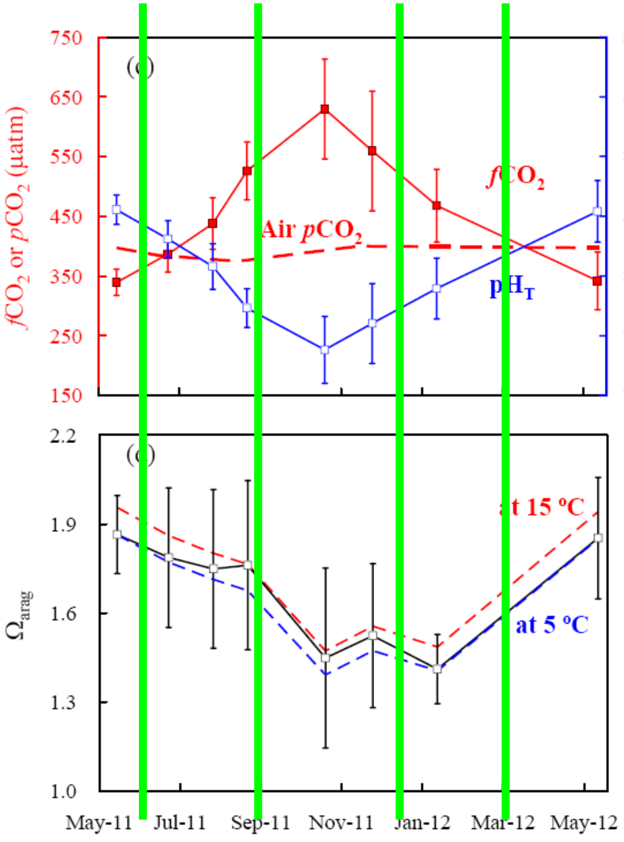
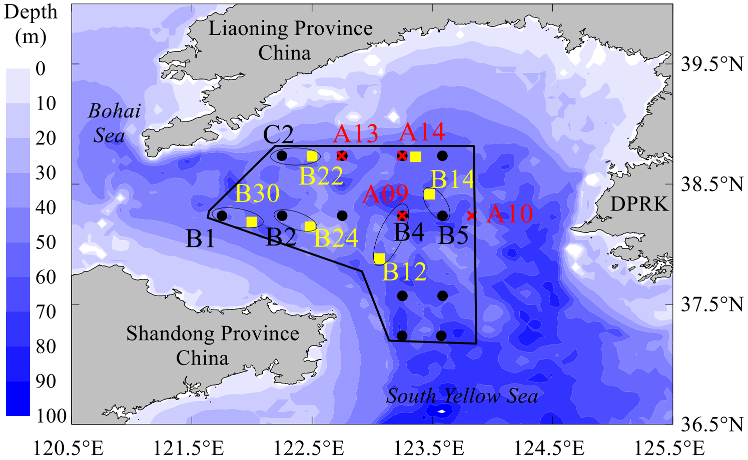
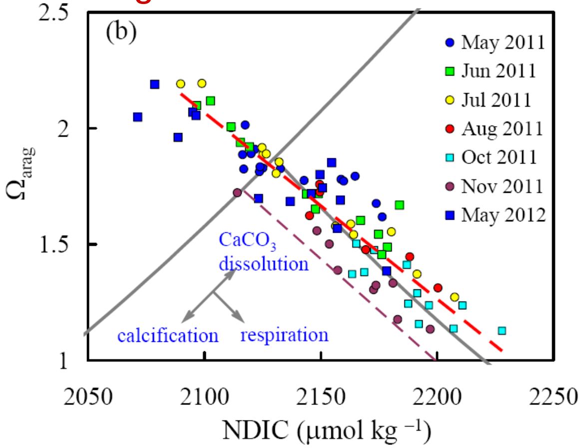
Monthly variations of subsurface CO_2, pH and Ω in the North Yellow Sea, and the biogeochemical controls (Zhai et al., 2014, Biogeosciences)



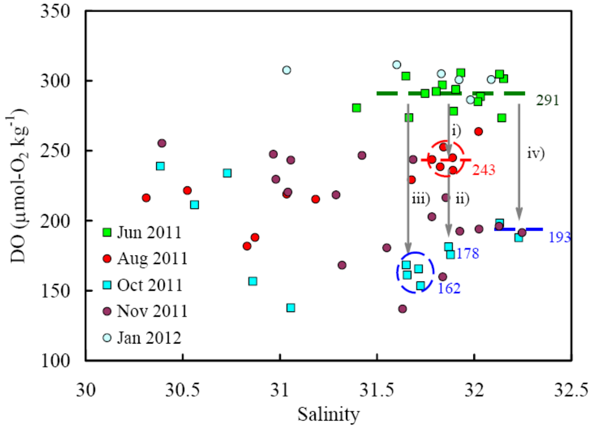
Spring Summer Autumn Winter Spring



Biogeochemical controls of Ω

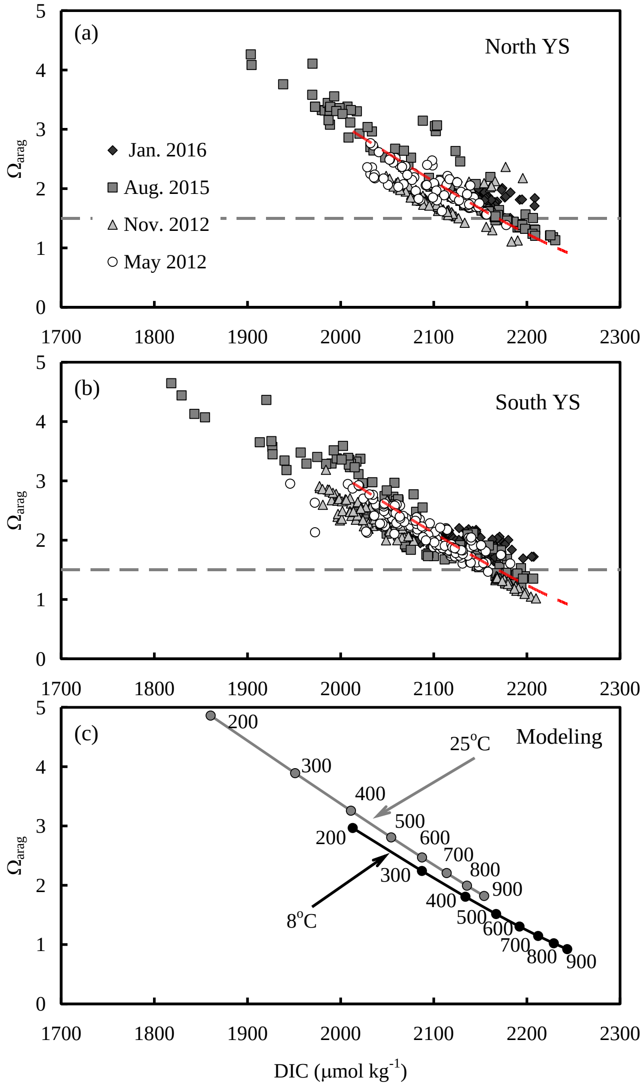


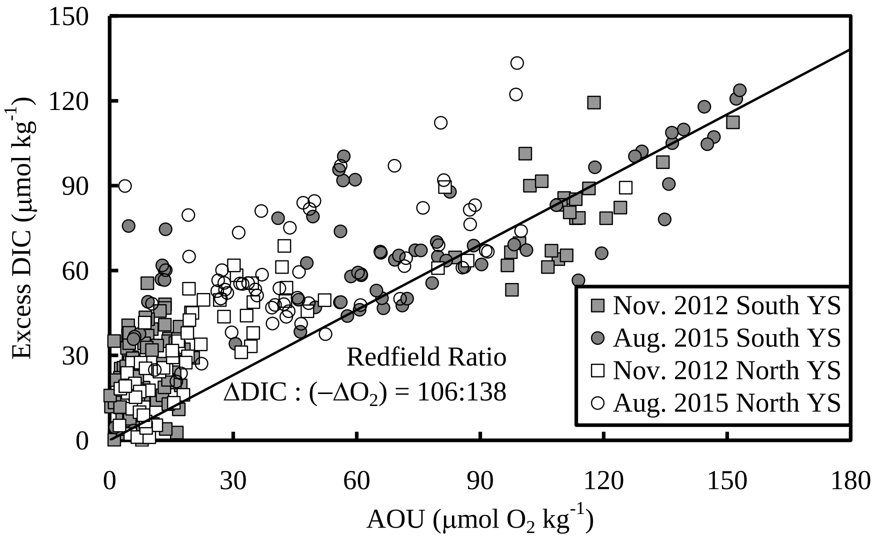
Net community respiration estimate



Bottom-water apparent oxygen depletion rates at deeper stations (water depth > 25 m) are estimated at ~1 µmol O_2 kg^{-1} day^{-1}.

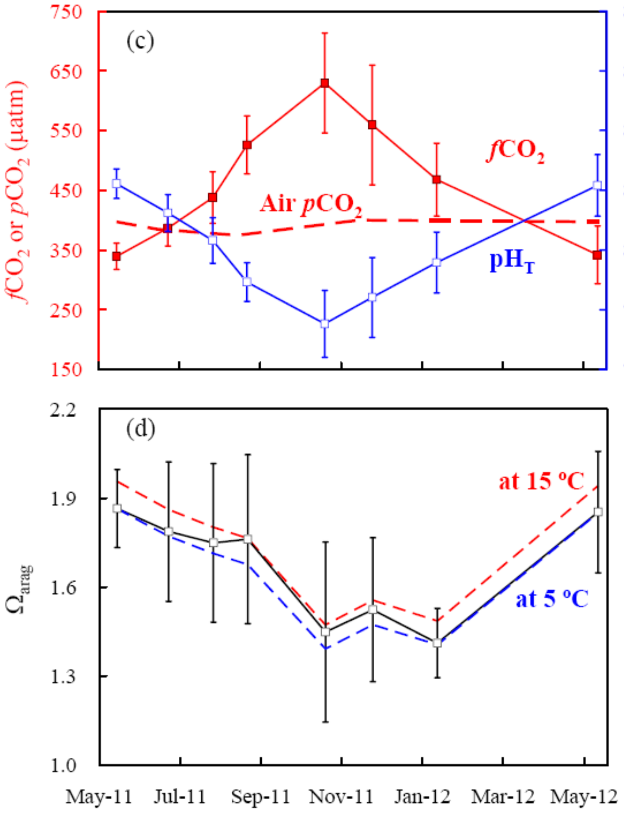
Similar biogeochemical controls in the whole Yellow Sea



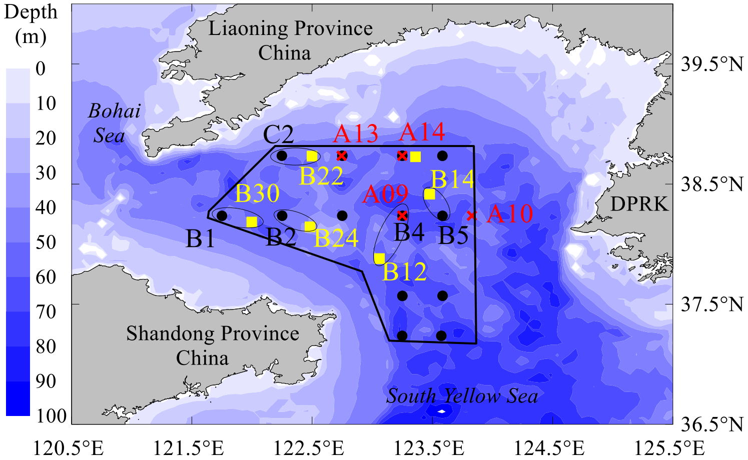


Zhai, 2018, China Science Earth Science

Decomposing monthly declines of subsurface-water pH and aragonite saturation state from spring to autumn in the North Yellow Sea



Zhai et al., 2014, Biogeosciences



原理：

$$(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 138O_2 + 18HCO_3^- \rightarrow 124CO_2 + 16NO_3^- + HPO_4^{2-} + 140H_2O \quad \mathbf{X}$$

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^- \quad \mathbf{Y}$$

$$\Delta DIC = 106X + Y$$

$$\Delta TAlk = -17X + 2Y$$

$$X = (2\Delta DIC - \Delta TAlk)/229$$

$$Y = (17\Delta DIC + 106\Delta TAlk)/229$$

Chen C.-T.A, 1978, Science

Therefore,

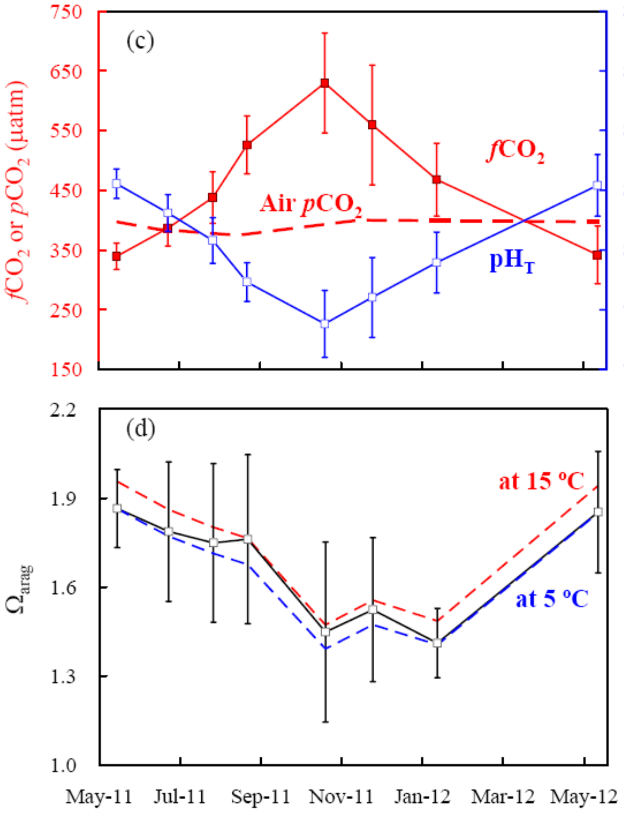
$$\Delta\Omega^{Resp} = (106X/\Delta DIC)\,\Delta\Omega^{\Delta DIC} + (-17X/\Delta TAlk)\,\Delta\Omega^{\Delta TAlk}$$

$$\Delta\Omega^{Diss} = (Y/\Delta DIC)\,\Delta\Omega^{\Delta DIC} + (2Y/\Delta TAlk)\,\Delta\Omega^{\Delta TAlk}$$

$$\Delta\Omega^{Calc} = -\,[(Y/\Delta DIC)\,\Delta\Omega^{\Delta DIC} + (2Y/\Delta TAlk)\,\Delta\Omega^{\Delta TAlk}]$$

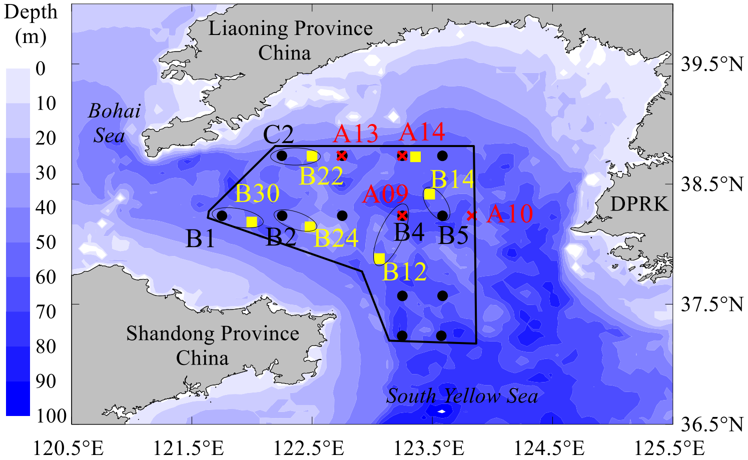
Li and Zhai, 2018, under review (2nd round)

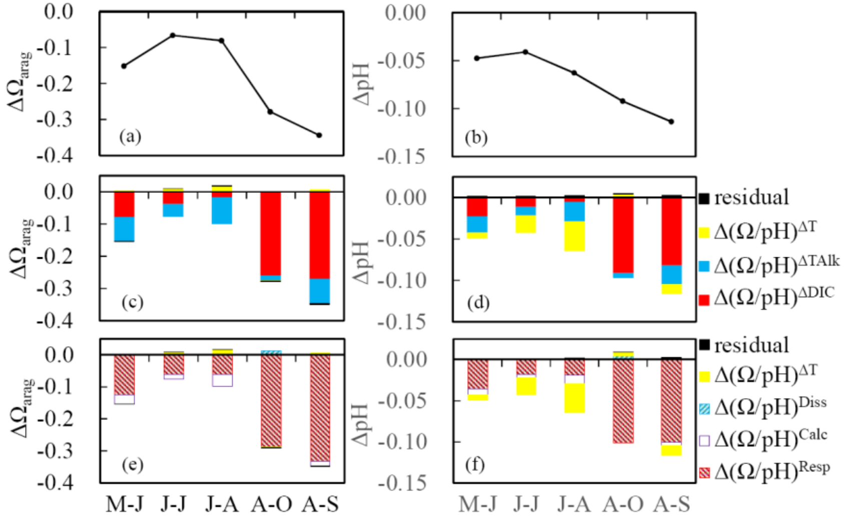
Decomposing monthly declines of subsurface-water pH and aragonite saturation state from spring to autumn in the North Yellow Sea



Zhai et al., 2014, Biogeosciences

结果：





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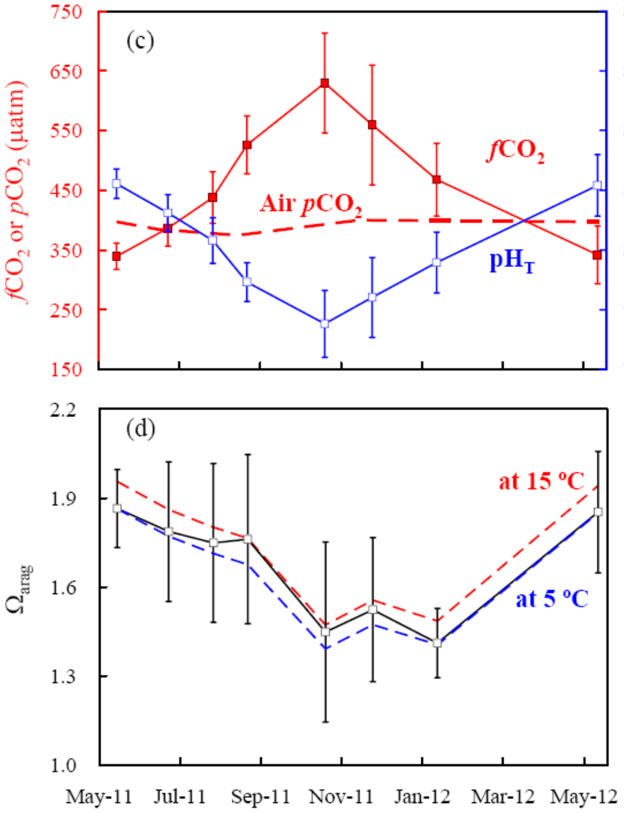
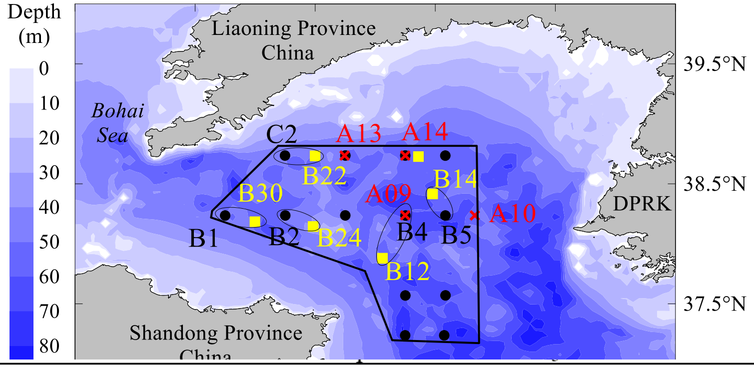
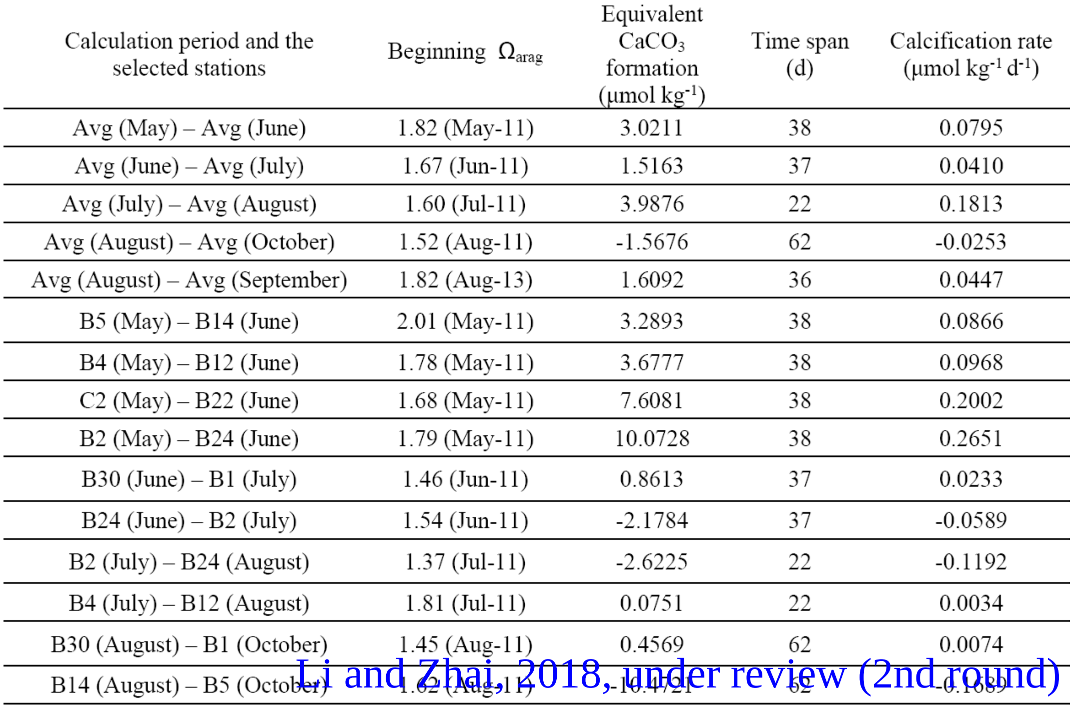


Zhai et al., 2014, Biogeosciences



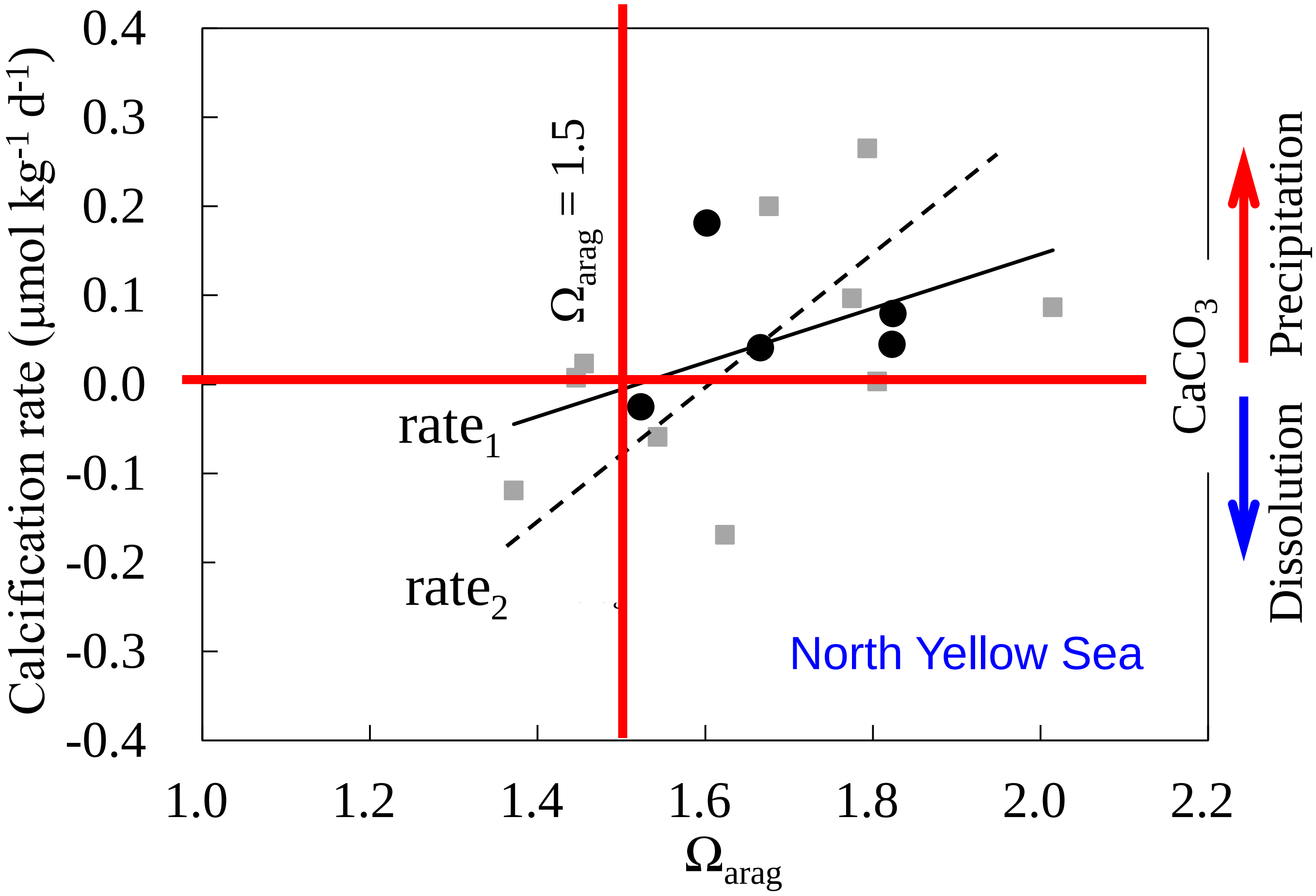
结果:



Calculation period and the selected stations	Beginning Ω_{arag}	Equivalent $CaCO_3$ formation (μmol kg^{-1})	Time span (d)	Calcification rate (μmol kg^{-1} d^{-1})
Avg (May) – Avg (June)	1.82 (May-11)	3.0211	38	0.0795
Avg (June) – Avg (July)	1.67 (Jun-11)	1.5163	37	0.0410
Avg (July) – Avg (August)	1.60 (Jul-11)	3.9876	22	0.1813
Avg (August) – Avg (October)	1.52 (Aug-11)	-1.5676	62	-0.0253
Avg (August) – Avg (September)	1.82 (Aug-13)	1.6092	36	0.0447
B5 (May) – B14 (June)	2.01 (May-11)	3.2893	38	0.0866
B4 (May) – B12 (June)	1.78 (May-11)	3.6777	38	0.0968
C2 (May) – B22 (June)	1.68 (May-11)	7.6081	38	0.2002
B2 (May) – B24 (June)	1.79 (May-11)	10.0728	38	0.2651
B30 (June) – B1 (July)	1.46 (Jun-11)	0.8613	37	0.0233
B24 (June) – B2 (July)	1.54 (Jun-11)	-2.1784	37	-0.0589
B2 (July) – B24 (August)	1.37 (Jul-11)	-2.6225	22	-0.1192
B4 (July) – B12 (August)	1.81 (Jul-11)	0.0751	22	0.0034
B30 (August) – B1 (October)	1.45 (Aug-11)	0.4569	62	0.0074
B14 (August) – B5 (October)	1.62 (Aug-11)	-10.4721	62	-0.1689

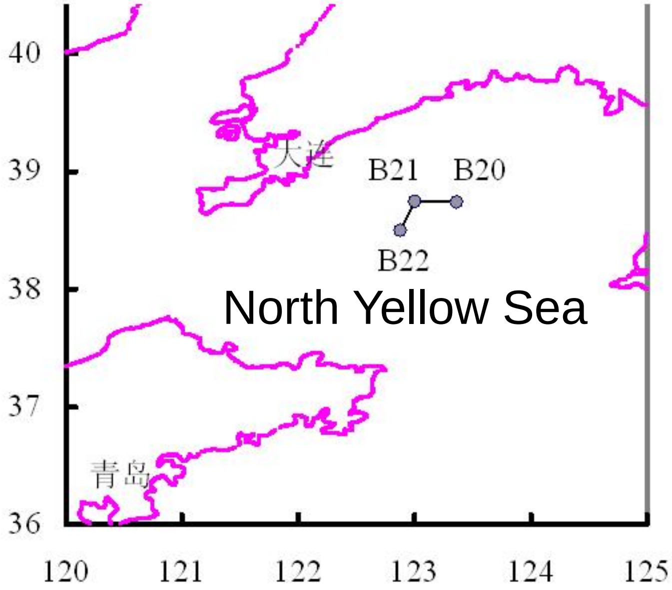
Li and Zhai, 2018, under review (2nd round)

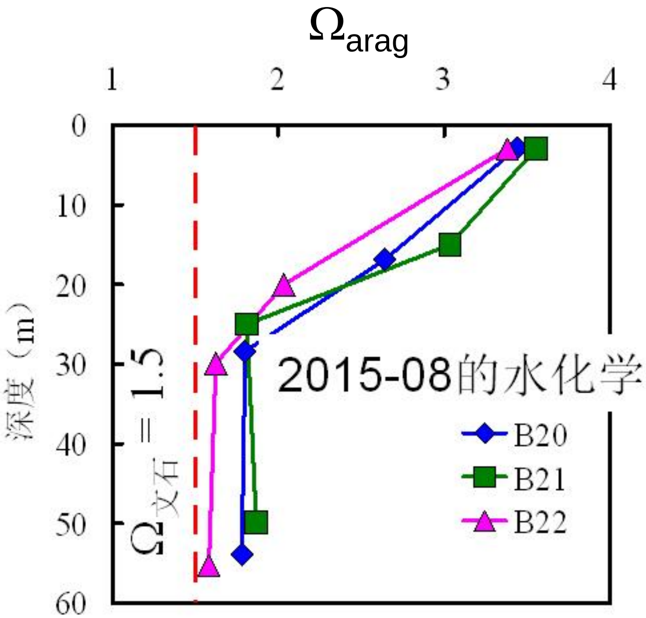
A threshold value of aragonite saturation state between community $CaCO_3$ precipitation and dissolution



Li and Zhai, 2018, under review (2nd round)

国家自然科学基金委共享航次的北黄海底栖生物拖网2018-08





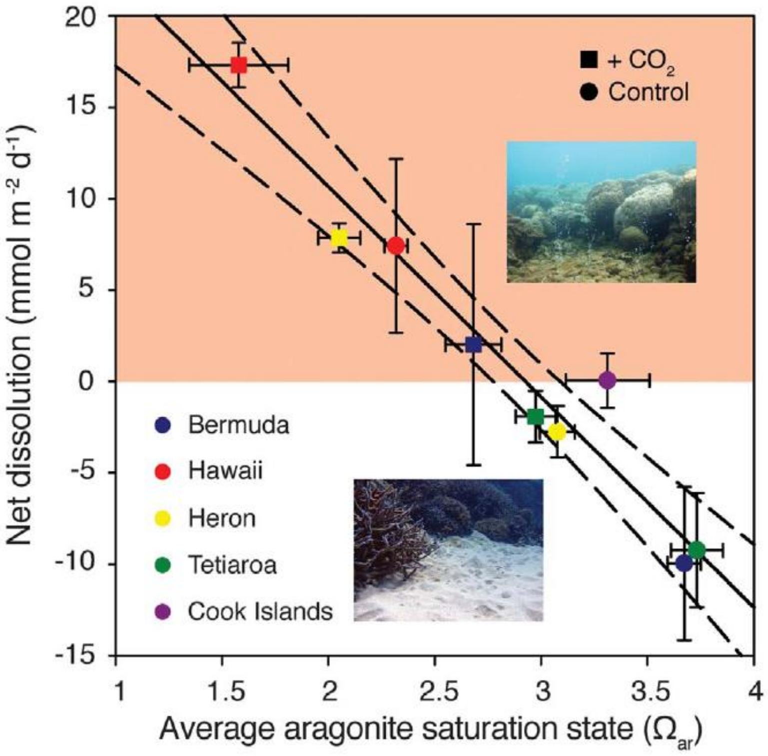
2015-08的水化学数据

扇贝

海葵寄居在扇贝壳上

The North Yellow Sea result is much different from the coral reefs

Fig. 1. Average $CaCO_3$ permeable sediment dissolution rates for each set of control (circles) and high pCO_2 (squares) treatments for each of the five reefs as a function of seawater average aragonite saturation state (Ω_{ar}) (r^2 = 0.94, $P < 0.0001$, $n = 9$; $y = -11.51x + 33.683$). No high-pCO_2 treatments were available for the Cook Islands. Error bars represent standard error. The sediments transition from net precipitating to net dissolving at a seawater Ω_{ar} value of ~2.92 ± 0.16 (±95% confidence interval). Data are in table S5. [Top photo by K. Fabricius, Australian Institute of Marine Science, and bottom photo by A. Andersson, Scripps Institution of Oceanography]



The Ω_{arag} threshold of net calcification rate reaching zero is **2.9-3.0** in coral reef systems.

Eyre et al., Science 359, 908–911 (2018)

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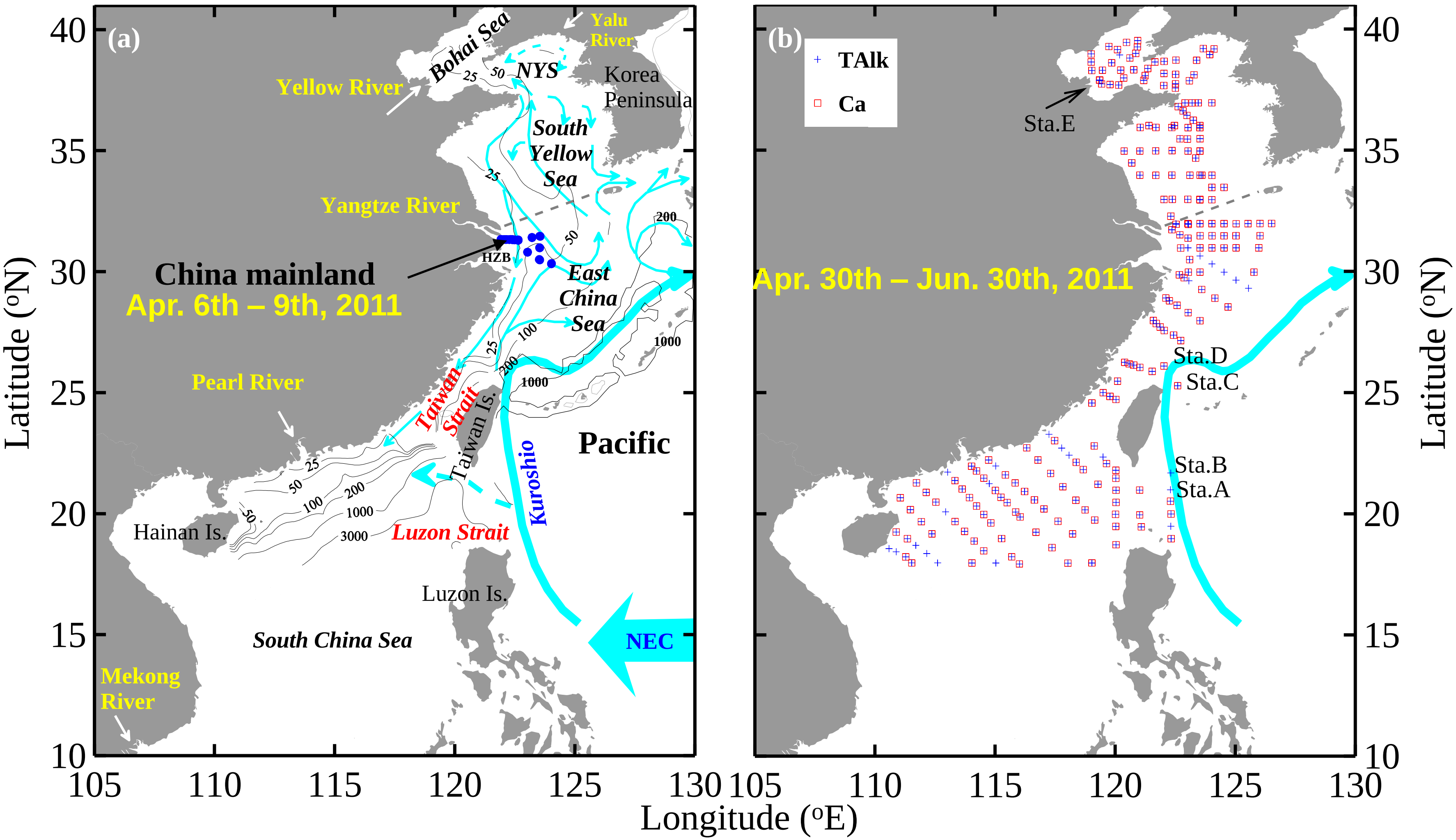
Sampling from late spring to early summer in 2011 in China Seas

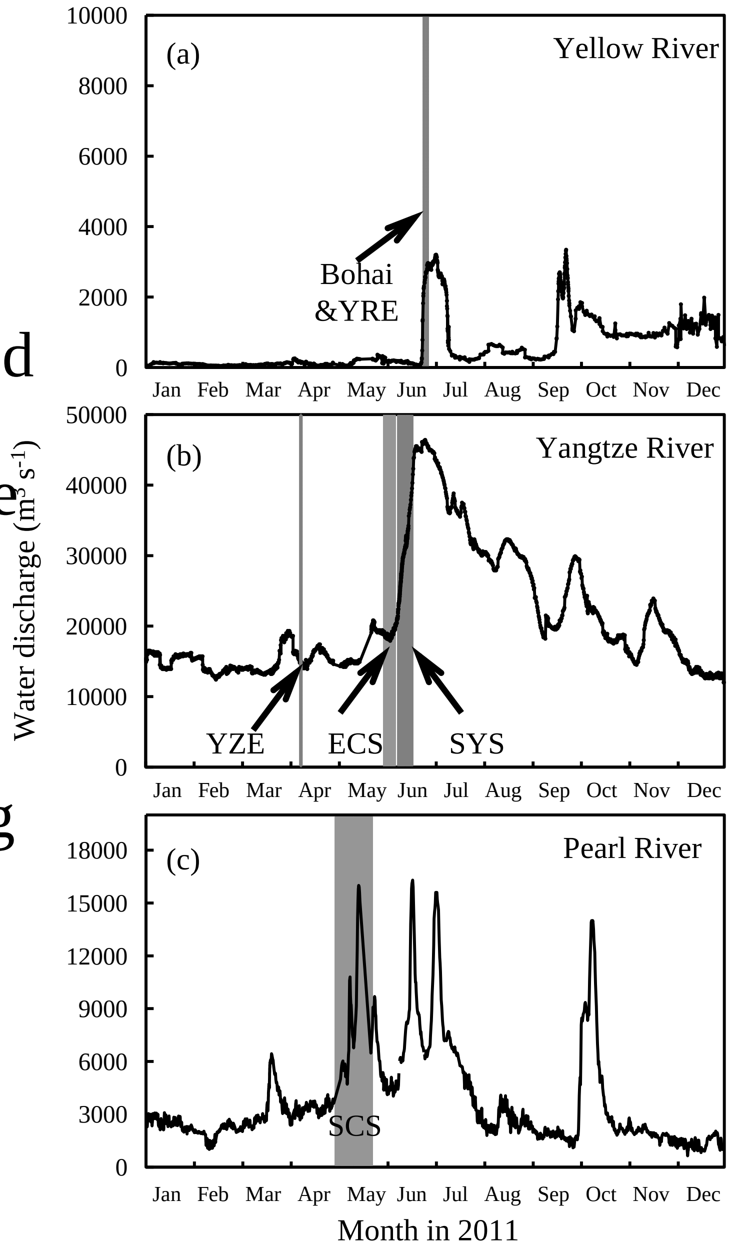


Apr. 6th – 9th, 2011

Apr. 30th – Jun. 30th, 2011

Hydrological background of the cruises

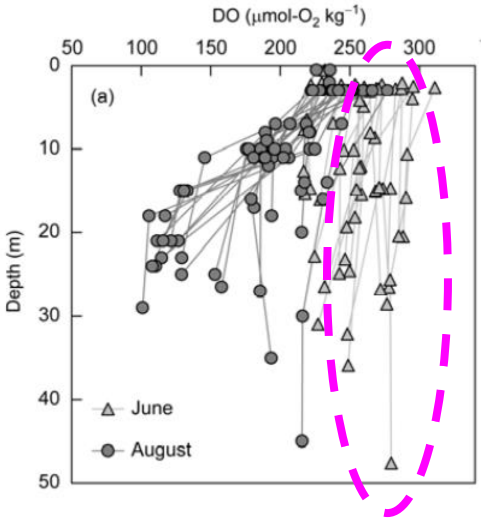
- In the South China Sea, the survey was conducted shortly before and during the first flood in 2011
- In the East China Sea, both of the estuarine cruise and the shelf cruise were conducted before the first flood in 2011
- In the Yellow Sea, we conducted the survey during the summer flood of the Yangtze River in 2011
- In the Bohai Sea and the Yellow River Estuary, the field survey was conducted shortly before and during the summer flood of the lower Yellow River in 2011
- Basically a transitional period between dry/cold and wet/warm seasons



Biogeochemical position of the major survey on an annual basis

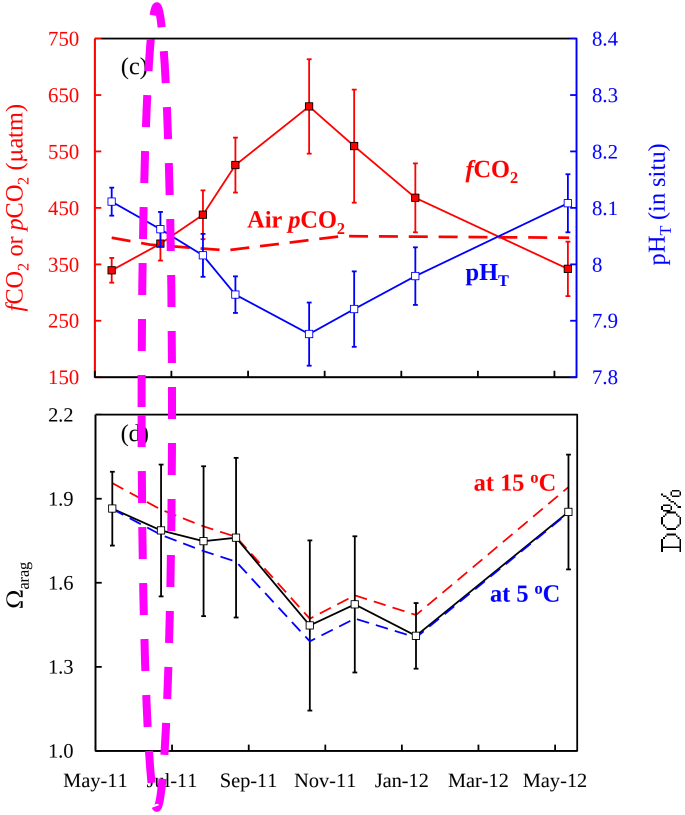
At the beginning stage of yearly stratification in the Bohai, Yellow and East China Seas.

Bohai Sea



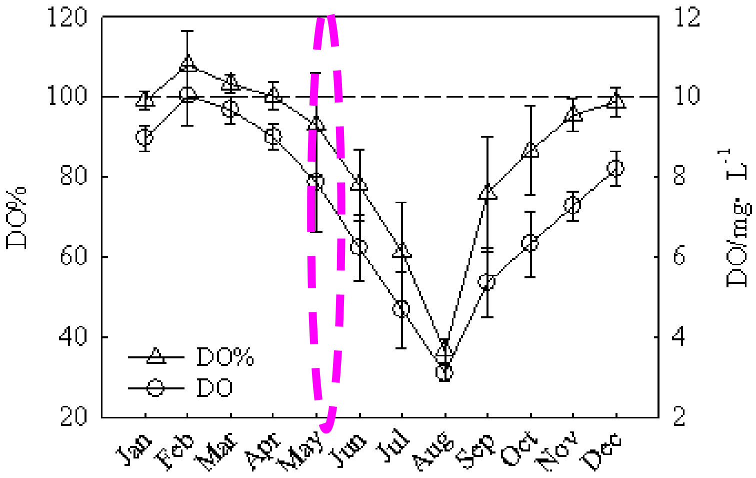
Zhai et al., 2012, Chinese Science Bulletin

Bottom water variation
North Yellow Sea



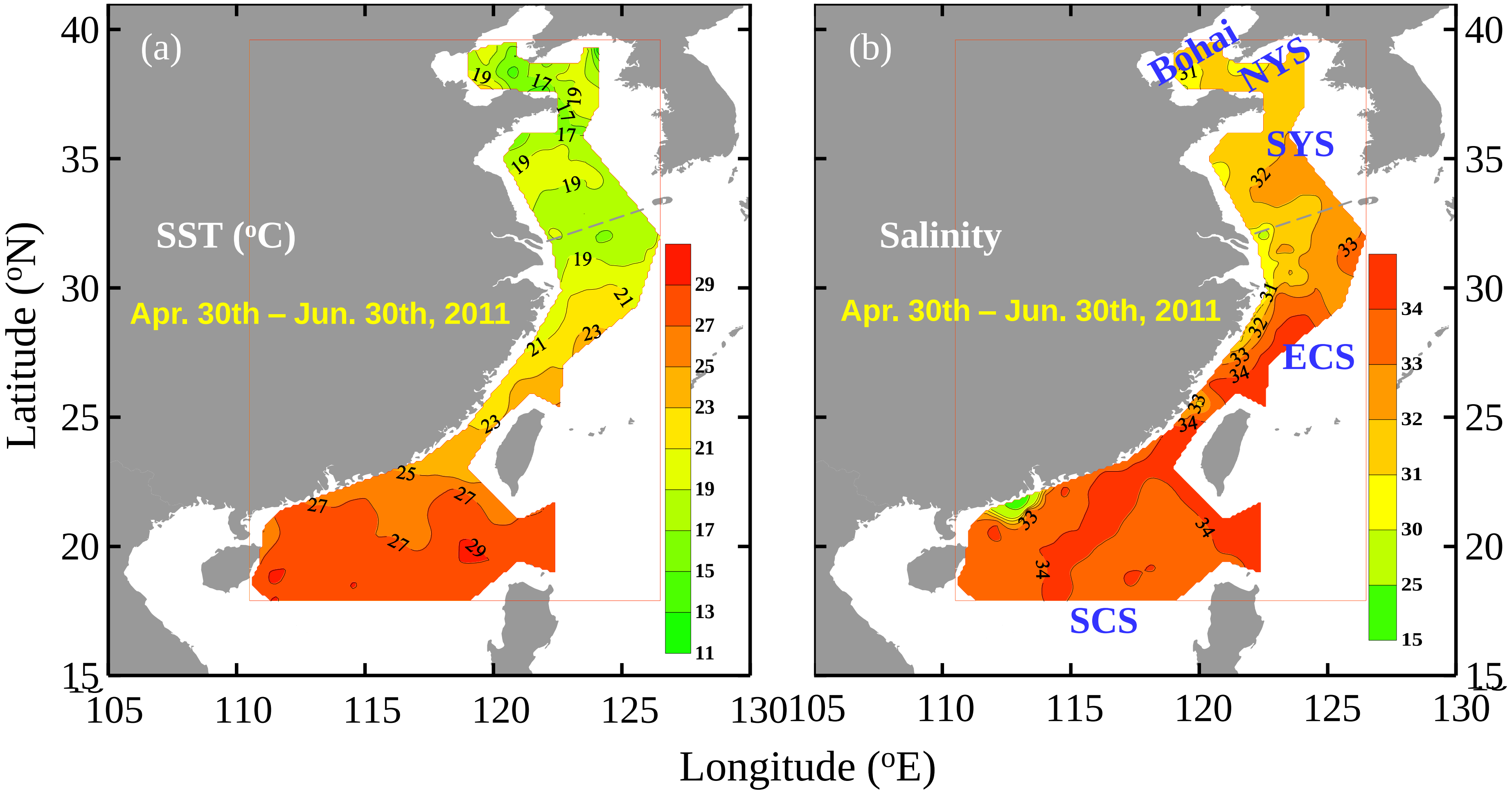
Zhai et al., 2014, Biogeosciences

Bottom water variation
East China Sea off the Yangtze River Estuary

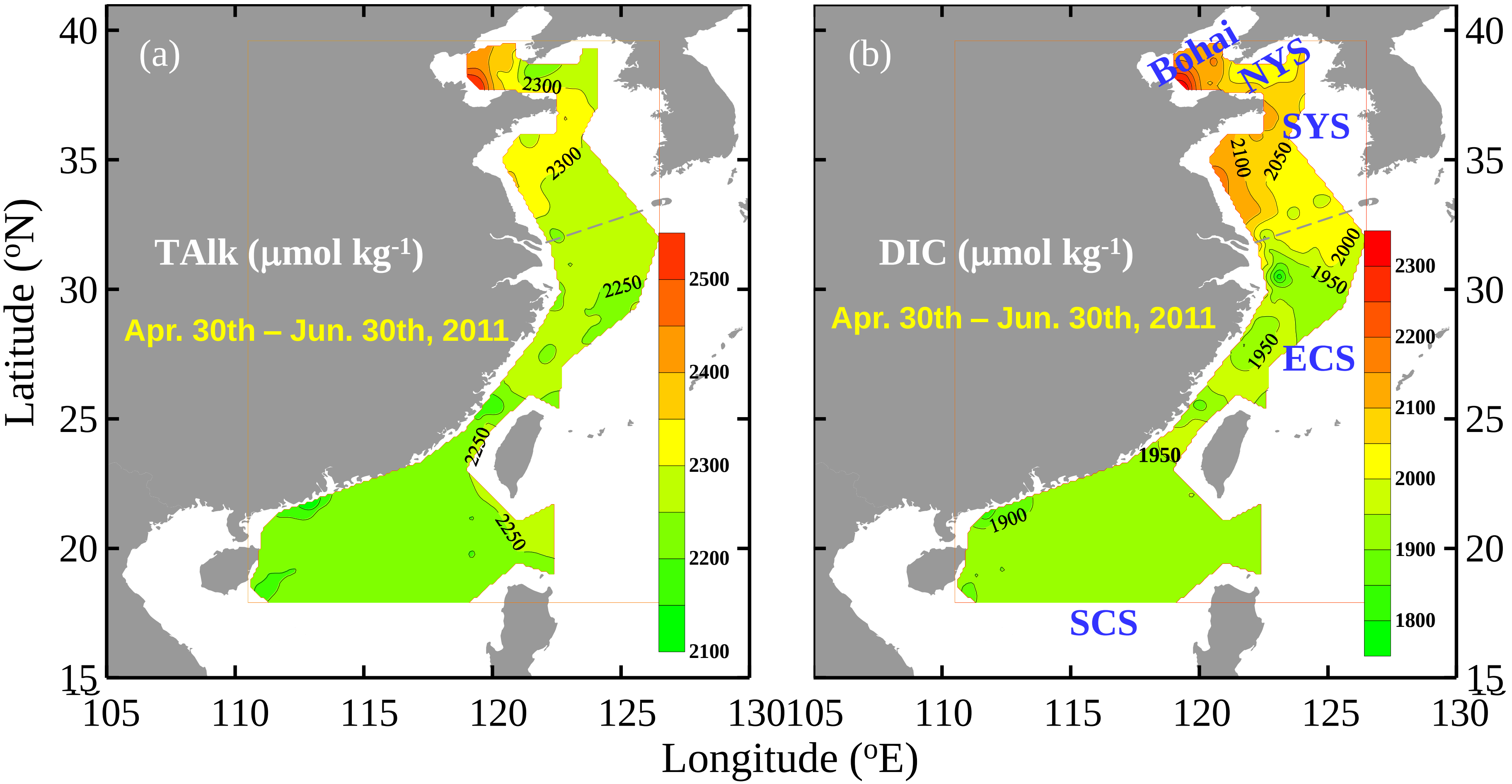


Wang et al., 2012

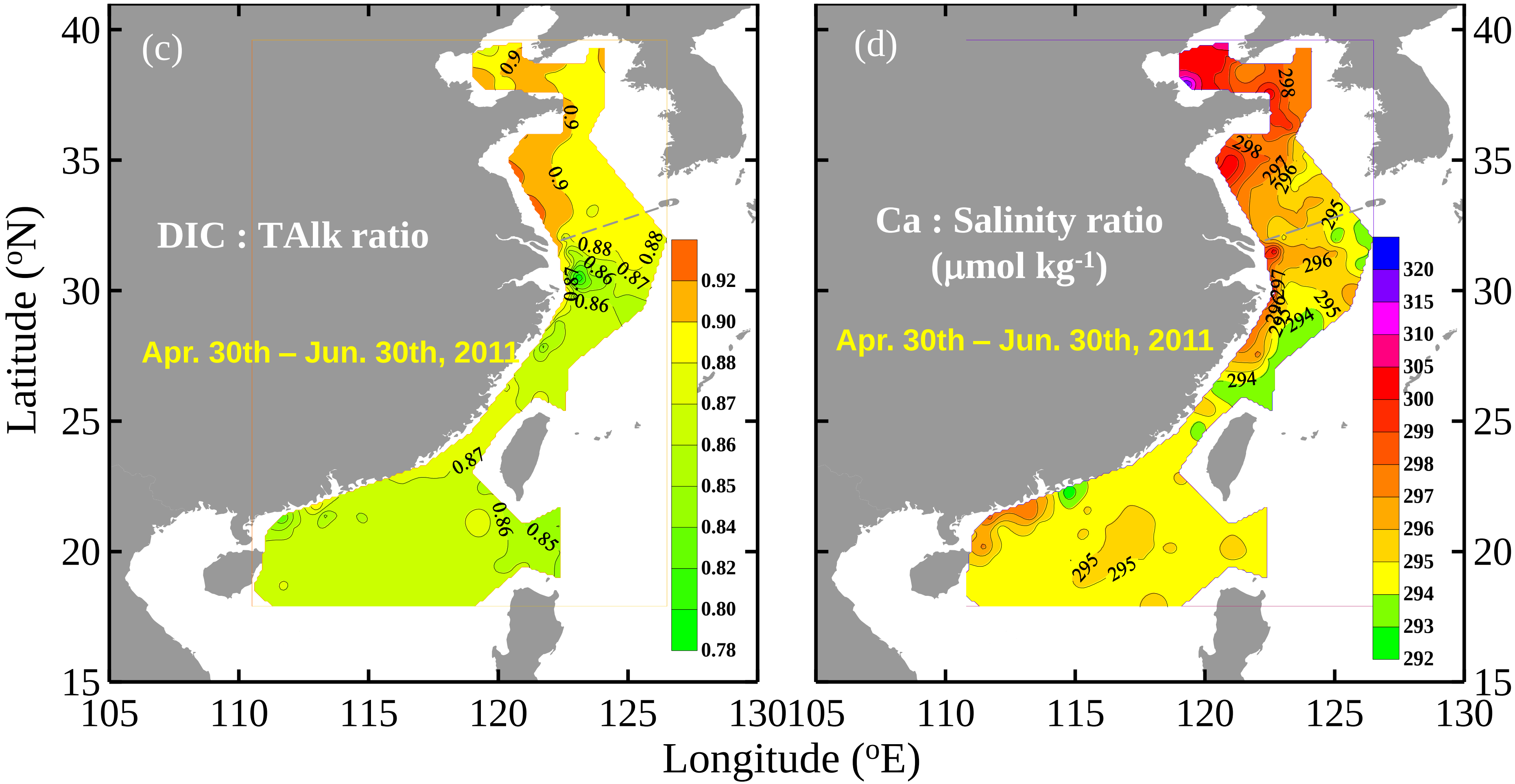
Sea surface temperature and salinity



Sea surface alkalinity and dissolved inorganic carbon

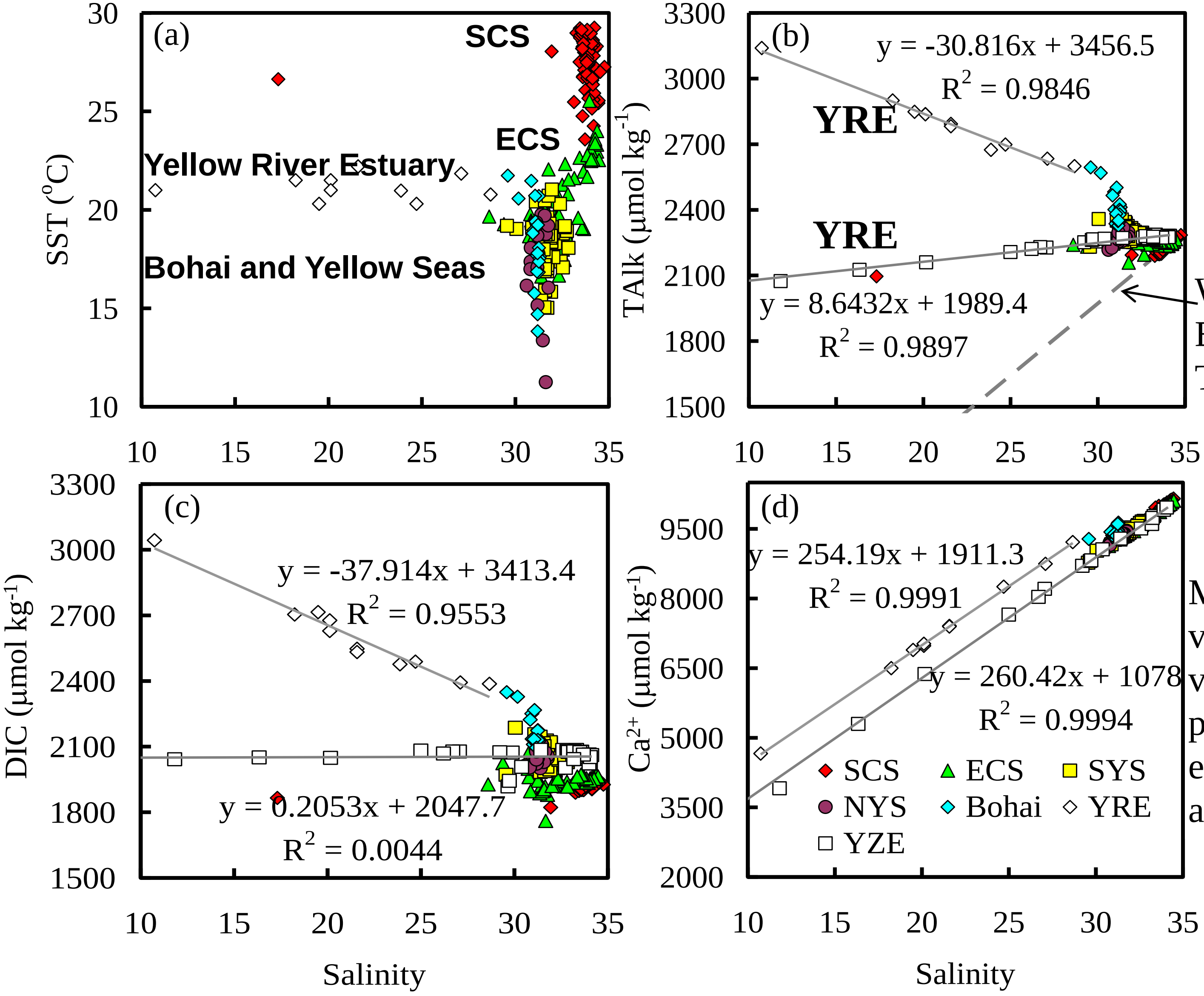


Sea surface dissolved calcium : salinity ratios



- According to Millero (1979), the oceanic mean of sea surface Ca:salinity ratio is 293.8 μmol kg^{-1}.

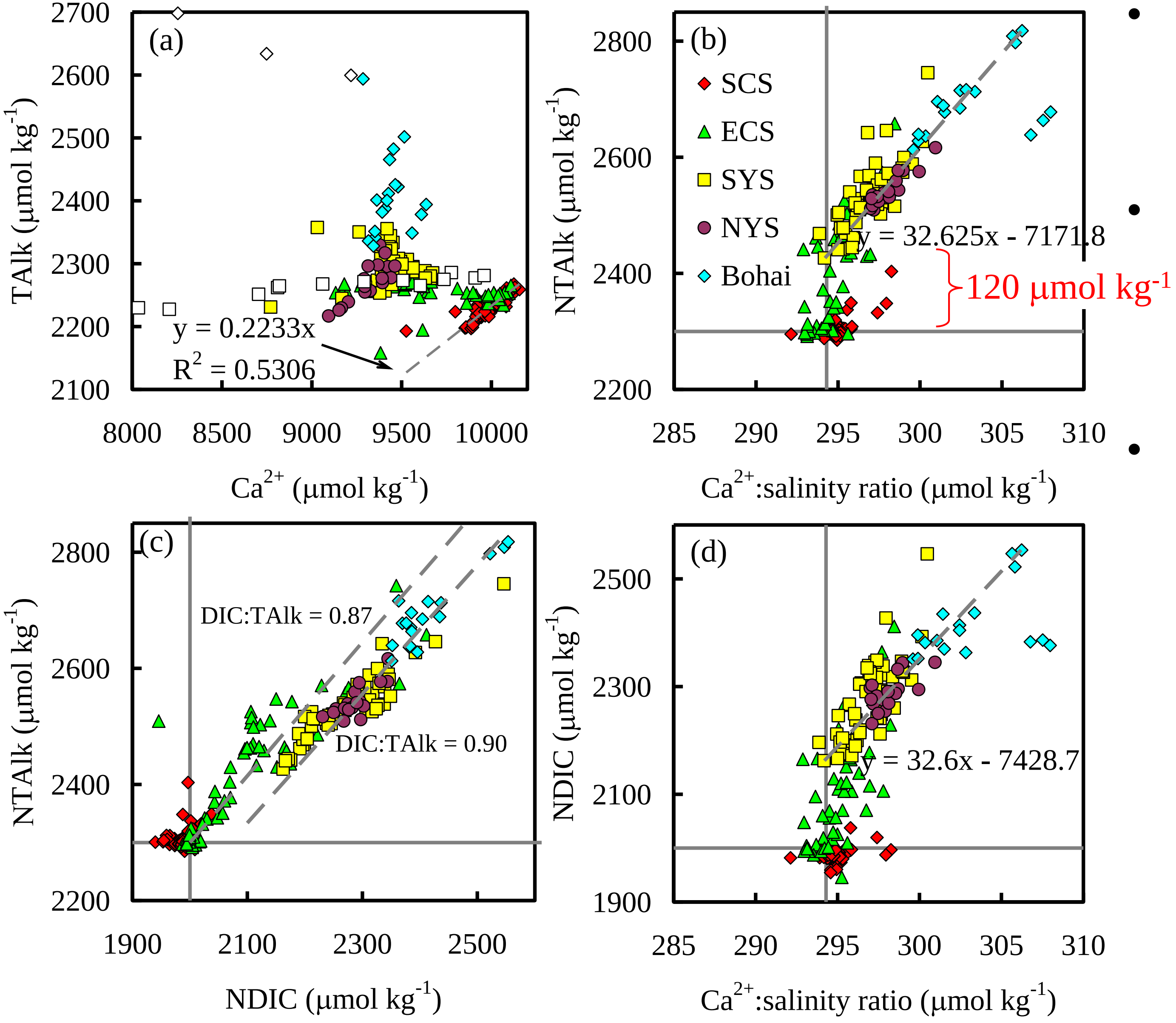
Sea surface T, TAlk, DIC and dissolved calcium as functions of salinity



Water mixing between ECS and rain waters TAlk = 2300/35*S

Mostly sea surface Ca versus salinity shows a very tight direct proportion relationship, except for those estuarine areas.

Surface water mixing behaviors in China Seas

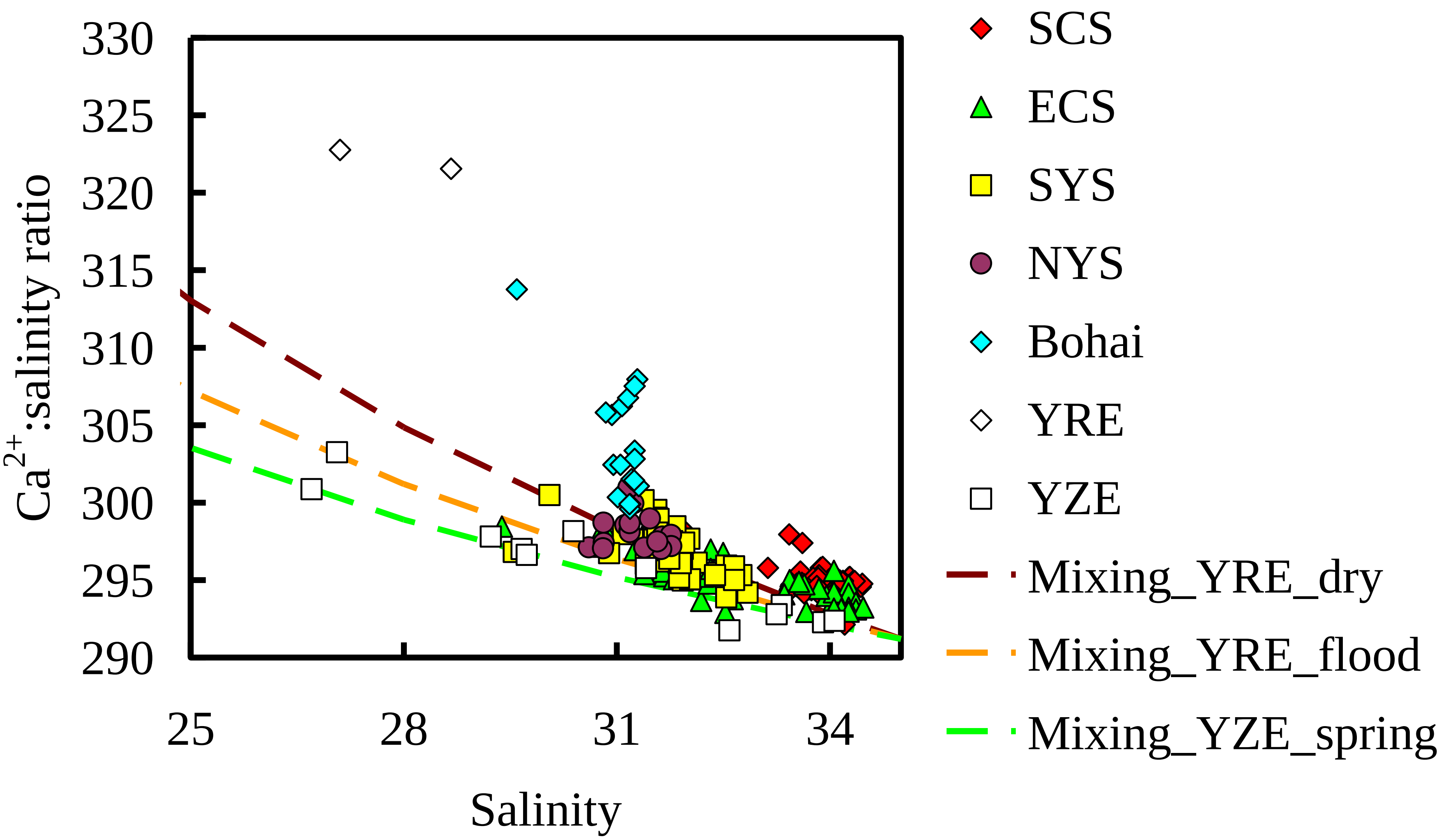


- Many water sources, including estuarine dilution waters

- The SCS shows water mixing similar to adjacent open ocean

- In Bohai and Yellow Seas, water mixing is much different from open ocean. A “background” addition of TAlk of ~110 mmol/kg (=120/35*32) is identified, which is likely from sediment processes.

Terrestrial inputs account for only a part of the high Ca : salinity ratios in Bohai and Yellow Seas



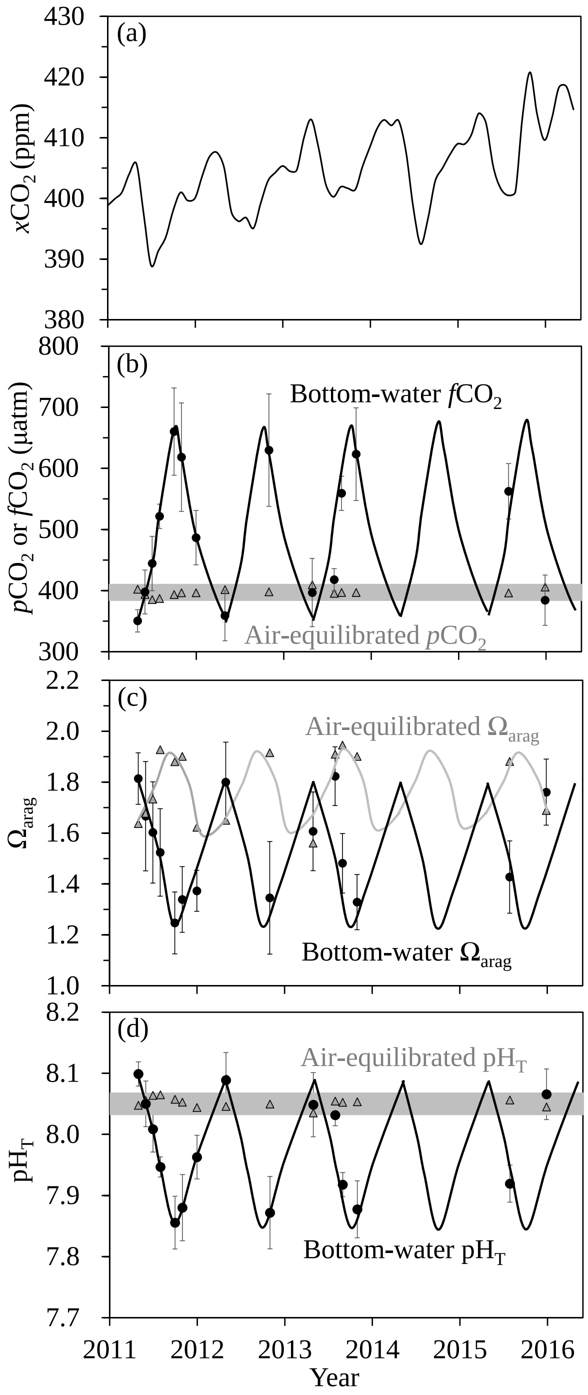
Summary

- Based on field surveys of carbonate system during 2011-2016, we found one third of the Yellow Sea suffer from serious subsurface seawater acidification (with aragonite saturation state of <1.5) during summer and autumn.
- The seasonal subsurface acidification mostly results from the community respiration induced CO_2 accumulation in the cold water mass of the Yellow Sea.
- Based on a parallel study conducted in the North Yellow Sea, we found community calcification rate is related to the aragonite saturation state values, while the aragonite saturation state of ~1.5 serves as a threshold value between community $CaCO_3$ precipitation and dissolution.
- Field data showed higher Ca : Salinity ratios than all those possible river-Kuroshio mixing lines in the Bohai and Yellow Seas, suggesting a basin-scale net $CaCO_3$ dissolution.

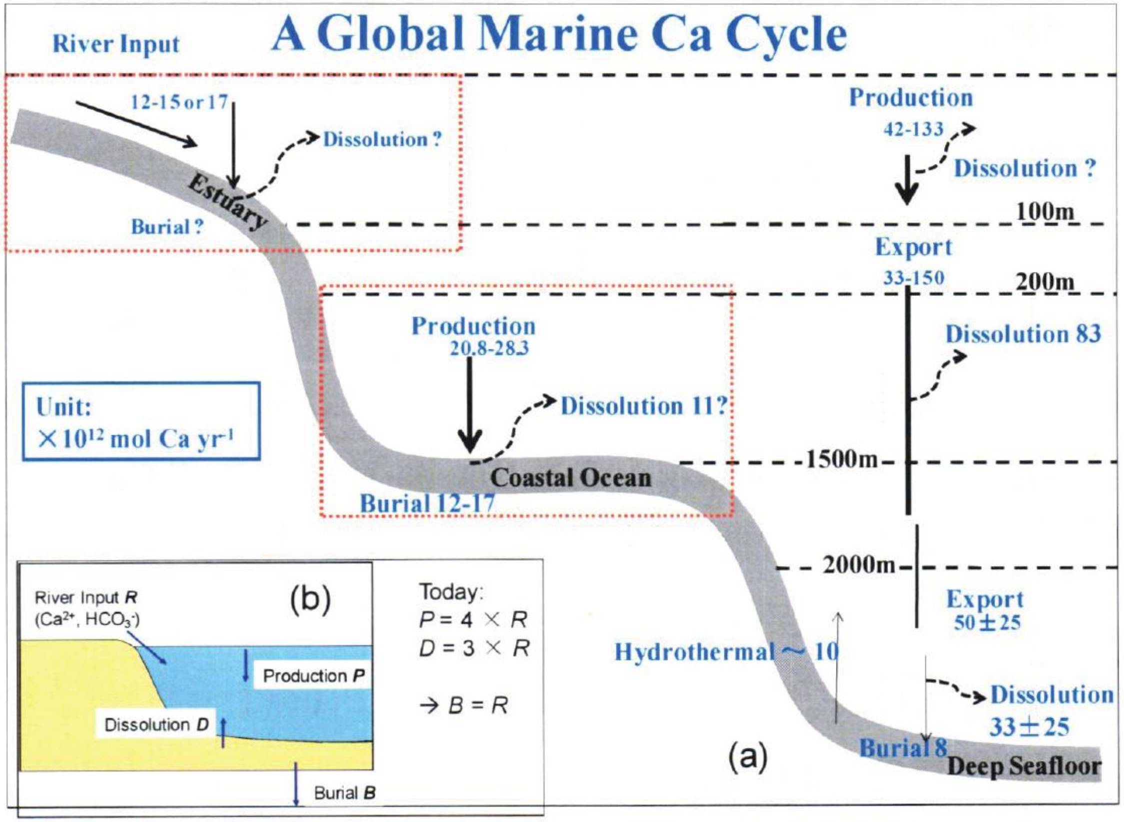
Thank you for the attention.

正在开展的工作：黄海碳化学的潜在年代际变化

- 2017-09 NSFC
- 2017-10 黄海所
- 2017-12 NSFC
- 2018-04 NSFC
- 2018-05 黄海所
- 2018-07 NSFC
- 2018-08 黄海所
- 2018-10 黄海所
- 2018-11 NSFC



对海水钙的物质收支有一定启示



河流输入通量取自Milliman(1993)和Feely et al.(2004)，陆架边缘海生产和沉积通量取自Iglesias-Rodriguez et al.(2002)，陆架边缘海溶解通量取自Anderson et al.(2003)，热液输入取自de Villiers(1998)，其余数据均取自Berelson et al.(2007)

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