Aragonite undersaturation in the western Arctic Ocean

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Arctic Ocean

FW, OC, Fe, contaminants etc.

Surrounded by continents
~10 % of global river discharge

Inflow from both
Atlantic and Pacific oceans

Outflow to the North Atlantic
Arctic Ocean

- **AMERICAN RIVERS**
- **Eurasian Rivers**
- **Ice**
- **Sea Ice Melt**
- **PACIFIC INFLOW**
- **ATLANTIC INFLOW**
- **BS (Canada Basin)**
- **LR**
- **FS**

Depth levels:
- 50m
- 500m
- 2000m

**Regions:**
- **North Pacific**
- **Arctic/Nordic**
- **North Atlantic**
Arctic Ocean

Silicate (umol/kg)

excess Phosphate (umol/kg)

2007-2008

excessP=P-1/16N

[Yamamoto-Kawai et al., in prep.]

[Yamamoto-Kawai et al., Nature, 2006]
Arctic Ocean---melting

September summer sea ice extent & age of ice

[1981, 2002]

[Rigor and Wallace, GRL, 2004]
Arctic Ocean---warming

[Steele et al., GRL, 2007]
Recent changes in seawater observed in the western Arctic Ocean

• Aragonite undersaturation: surface & subsurface
  [Yamamoto-Kawai et al., Science, 2009]

• Surface freshening
  [Yamamoto-Kawai et al., JGR, 2009]

• Acceleration of ice/ocean circulation
  [Shimada et al., GRL, 2006; Rainville & Woodgate, GRL, 2009]

• Changes in nutrient distribution and in plankton size
  [McLaughlin & Carmack, subm.; Li et al., Science, 2009]
Aragonite saturation state

**Aragonite** – a form of CaCO$_3$ that is more soluble than calcite and thus is more sensitive to ocean acidification.

**Calcite** – the form of CaCO$_3$ that is less sensitive to acidification.

  *High-Mg calcite* – least stable

**CaCO$_3$ saturation state of seawater = $\Omega$**

**Decease in $\Omega$ --- difficult to maintain CaCO$_3$ shells**

  *$\Omega < 1$ --- risk of dissolution*
Aragonite saturation state

(left) Global mean Atm. pCO₂  
(right) Global mean Ω aragonite Surface water

[Steinacher et al., Biogeosciences, 2009]
Aragonite saturation state

Why is surface Ω low in polar regions?

[CARINA+GLODAP]
Aragonite saturation state

Southern Ocean

- **Cooling** --- low T seawater dissolve more CO$_2$ (high DIC)
- **Upwelling** of DIC enriched deep water (high DIC)

**Example:** Cooling of tropical surface water to -1.8°C

- DIC = 1937 umol/kg
- $\Omega = 3.8$
- S = 34.6
- T = 29 °C
- TA = 2265 µmol/kg
- pCO$_2$ = 390 µatm

- DIC = 2163 umol/kg
- $\Omega = 1.3$
- Coolng
Aragonite saturation state

Southern Ocean

- **Cooling** --- low T seawater dissolve more CO₂ (high DIC)
- **Upwelling** of DIC enriched deep water (high DIC)

\[ \Omega_{\text{aragonite}} \]

\[ \text{DIC [umol/kg]} \]

low \( \Omega = \text{high DIC} \)

[CARINA+GLODAP]
Aragonite saturation state

Arctic Ocean

- Cooling

\[ \Omega \downarrow \quad \text{DIC} \uparrow \]

\[ \Omega_{\text{aragonite}} \]

DIC [umol/kg]

\[ \text{low } \Omega = \text{high DIC} \]

[CARINA+GLODAP]
Aragonite saturation state

**Arctic Ocean**

- Cooling: $\Omega \downarrow$, DIC $\uparrow$
- Freshening: $\Omega \downarrow$, DIC $\downarrow$, TA $\downarrow$

**Surface salinity**

- Pacific or Atlantic water: $> 2000$ umol/kg
- Arctic River: TA$\sim$DIC $\sim 1000$ umol/kg

[PARTNERS 2009]

[PHC3.0, Steele et al., J. Climate, 2001]
Aragonite saturation state

Arctic Ocean

- Cooling
- Freshening
- Low pCO₂

Ω ↓ DIC ↓ Warming
Ω ↓ DIC ↓ More freshwater input
Ω ↑ DIC ↑ Anthropogenic CO₂, Changes in P.P and air-sea gas exchange

pCO₂^sw [µatm]

High primary productivity over shelves
Cooling
Sea ice cover
Aragonite undersaturation – western Arctic Ocean (JOIS)

Ω ar

1997  2005  2006  2007  2008

~1.4

<1.0

Undersaturated!

Δ -0.4/10yrs
ALOHA -0.08/10yrs

Pteropods

Calcification rate is highly correlated to the aragonite saturation state

[Comeau et al., PLoSOne, 2010]

Further cooling?
Further freshening?
Increase in pCO₂?

[Yamamoto-Kawai et al., Science, 2009]
Aragonite undersaturation – western Arctic Ocean

Further cooling? NO!
Further freshening? NO!
Increase in pCO₂? NO!
Aragonite undersaturation – western Arctic Ocean

Further cooling? NO!
Further freshening? NO!
Increase in pCO$_2$? YES!

1997

2008
Aragonite undersaturation – western Arctic Ocean

\[ pCO_2^{SW} \Delta +60 \mu atm \quad 1997 \rightarrow 2008 \]

not enough 1. Anthropogenic CO₂

atm pCO₂ increase 1997→2008 \( \Delta 15 \) ppm

not likely 2. Decrease in P.P. at the surface

P.P. increased due to longer growing season [Arrigo et al., GRL, 2008]
mean Chl.a did not change in 0-150 m layer [Li et al., Science, 2009]

! 3. Enhanced air-sea gas exchange

Less ice cover !
Aragonite undersaturation – western Arctic Ocean

\[ pCO_2^{SW} \Delta +60 \mu \text{atm} \ 1997 \rightarrow 2008 \]

Can this explain the decrease in \( \Omega \) for by 0.4?

\[ pCO_2^{SW} +60 \mu \text{atm} \]

T, S, TA = constant

\[ pCO_2^{SW} +60 \mu \text{atm} \]

\[ \Omega \ ar \]
Aragonite undersaturation – western Arctic Ocean

Further cooling? NO!
Further freshening? YES!
Increase in pCO₂? YES!

River or ice melt?
SSS

from H$_2$O$_{18}$O
(freshwater tracer)

Sea ice meltwater

Meteoric water
(=River water)

[Yamamoto-Kawai et al., JGR, 2009+]
Aragonite undersaturation – western Arctic Ocean

[Graph showing the relationship between sea ice meltwater (%) and Ω ar with a correlation coefficient of r = -0.87.]

[Yamamoto-Kawai et al., Science, 2009]
Aragonite undersaturation – western Arctic Ocean

+ 60 µatm pCO$_2$
+ 10% sea ice meltwater

Can these explain the decrease in Ω$_{ar}$ by 0.4?

- Dilute S & TA with 10% SIM
  pCO$_2$ = pCO$_2^{1997}$ + 60 µatm

Δ -0.4!
Aragonite undersaturation – western Arctic Ocean

Melting of sea ice decreased surface $\Omega$ in the western Arctic

Enhanced air-sea gas exchange

Dilution by sea ice melt

[Yamamoto-Kawai et al., Science, 2009]
Subsurface Aragonite undersaturation

cooling
remineralization
on shallow shelves

Ω ar

PWW
low T, high nutrients, high DIC

⇒ low Ω
Subsurface Aragonite undersaturation

DIC ant = 40 µmol/kg (0m) ~ 30 µmol/kg (500m) [Tanhua et al., JGR, 2009]

DIC bio = ~70 µmol/kg ---from AOU and N* [Sabine et al., GBC, 2002]
Subsurface Aragonite undersaturation

More frequent upwelling of corrosive PWW in recent years

[Williams and Yamamoto-Kawai, in prep.]
melting of sea ice enhances upwelling of corrosive subsurface water

[Carmack & Chapman, GRL, 2003]
Upwelling is also enhanced by accelerated motion of upper ocean.

More mobile ice → more upwelling at shelf break

[Yang, JGR, 2009]
**On the shelf**

**Up-welling of subsurface water**

Aragonite undersaturated

→ Negative impacts on Benthos

**Silicate (umol/kg)**

Nutrient enriched

→ Positive impacts on P.P.
On the shelf ≠ In the Basin

Up-welling

Down-welling

accumulate surface freshwater → decrease Ω

thicker surface layer increased stratification deeper nutricline
Deepening of nutricline

[McLaughlin & Carmack, subm.]
Deepening of Chl.a maximum depth

[McLaughlin & Carmack, subm.]
Melting of more sea ice and/or less ice formation

\[ \downarrow \]

Increased atm-ocean coupling:
- increased ice drift velocities
- increased Ekman pumping

\[ \rightarrow \]

thicker surface layer
- increased stratification
deeper nutricline

nutricline and chlorophyll maximum have deepened

\[ \downarrow \]

- Light limitation may play a greater role now in P.P.

[McLaughlin & Carmack, subm.]
Surface S

Nitrate

2004 2005 2006 2007 2008

Salinity (psu)

Temperature (°C)

Nitrate (mmol m$^{-3}$)

2004 2005 2006 2007 2008

Picophytoplankton
(<2 μm)

Nanophytoplankton
(2-20 μm)

2004 2005 2006 2007 2008

Nitrate

2004 2005 2006 2007 2008

[Ni et al., Science, 2009]
Summary
Summary

**Basin**
- Surface freshening
- Increased pCO$_2$
- Aragonite undersaturation in surface water

**Shelf**
- Enhanced Upwelling of corrosive acidified water onto the shelf bottom
- Supply of nutrients

**Ice**
- Melting of sea ice

**Deepening**
- Nutricline
- Chl.a max

**Regolith**
- Supply of nutrients
Concluding remarks

Winter observations

: Sensor, automatic seawater sampler, AUV

Shelf-basin feedback

:—high PP on shelf—high nutrients/low omega PWW-
upwelling onto shelf—high PP on shelf—

Coastal erosion, methane seeps, permafrost thawing

Changes are happening right now!
& likely continue until multi-year ice disappears (~2030?)
: monitoring of the changing Arctic for future
prediction/adaptation in the Arctic and other oceans
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Shelf edge & summer sea ice cover
Aragonite saturation state – western Arctic Ocean

+ 60 μatm pCO₂
+ 10% sea ice meltwater

1997 + 10%SIM
Δ -0.2

1997 + 60 μatm
Δ -0.2

1997 + 60 μatm + 10%SIM
Δ -0.4

Ω ar

2008
Upwelling-enhanced P.P. → lower omega → upwelling
Surface tropical seawaters are generally supersaturated with respect to the carbonate minerals (e.g. calcite, aragonite, and high-magnesium calcites) from which marine organisms construct their shells and frameworks. At deeper water depths, seawater becomes undersaturated and these minerals begin to dissolve, imparting an important control (amongst other factors) on the distribution of coral reefs. We refer to the degree to which seawater is saturated with respect to these minerals as 'saturation state' and denote it using the Greek term $\Omega$ (omega).
Ocean Acidification

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

\[ \text{H}^+ + \text{CO}_3^{2-} \leftrightarrow \text{HCO}_3^- \]

CaCO$_3$ saturation state

\[ \Omega = \frac{[\text{Ca}^{2+}]_{sw} [\text{CO}_3^{2-}]_{sw}}{[\text{Ca}^{2+}]_{sat} [\text{CO}_3^{2-}]_{sat}} = \text{Ksp}^* \]

[Steinacher et al., Biogeosciences, 2009]
Clams (Mercenaria mercenaria)

Arg>>HMgC

Memo

aragonite (corals, mussels)
high-magnesium calcite (sea urchins)

pCO2 sensor---U of Montana Mike DeGrandpre

Pacific inflow の水温・塩分の経年変化は？

底層のpHが下がると、リンが溶出しやすくなる？
脱窒が変化しないなら、大西洋へのPの供給が増える→海洋への窒素供給が増える→CO2が下がる？→負のフィードバック

CARINA (CARbon dioxide IN the Atlantic Ocean)

Polar science center Hydrographic Climatology (PHC)

Omega計算のパラメータ選択＆ODVのパラメータをメモすること！

High-Mg calcite について勉強 北極では？
Bering shelfのココリスブルームは97、98、00に大きくて、あとは小さい。Murata 2006によると、Calcification-photosynthesis で、正味18 µatm程度の p CO2引き下げ。

2007 のBering inflowは水温高い & Flux多い—Wind, Pacific-Arctic pressure head [Woodgate et al., 2010]
2004年以前と以降では以降の方が熱Flux多い(Year&temperature) [Mizobata et al., 2010]

Southern CB, surface T was also high in 2008 but low in 2009 (but 1 month later)

Li のデータは何メーターのもの？150m以浅と150m以深
種類はどう変わったの？減ったナノは珪藻？増えたのは？

Arctic deep water residence time ~400 yrs
炭酸カルシウムは塩分高い方が溶けやすい。
Canada Basin Argonite saturation horizon

- Pre-industrial
- 2005
- 2050

[Anderson et al., DSR, 2010]
[Yamamoto-Kawai et al., 2009b+]
sea surface salinity

pCO2

[Yamamoto-Kawai et al., 2009b+]
Alkalinity
Sea ice meltwater [ml/ml]

Meteoric (River) water [ml/ml]

[Yamamoto-Kawai et al., 2009a+]
Sea Surface Alkalinity [umol/kg]

Sea Surface DIC [umol/kg]

[CARINA+GLODAP]
2003-2005