

Sea-ice CO₂-carbonate chemistry and impact on the underlying water-column

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Senior Scientist and Director of Research

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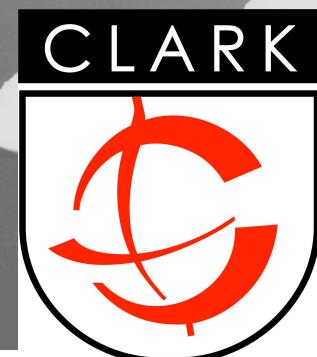
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Also thanks to: Jessica Cross,
Bruno Delille, Soren Rysgaard



Karen Frey photo

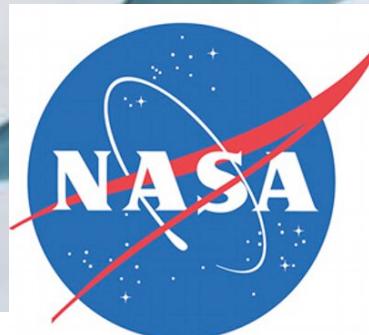


Bates et al, OCB Meeting 2014

Sea-ice CO₂-carbonate chemistry

Outline

- Sea-ice CO₂-carbonate chemistry:
considerations and caveats
- Fall/freeze-up data
- Sea-ice brines
- Sea-ice chemistry
- Melt ponds and interface waters
- Impacts on underlying water column



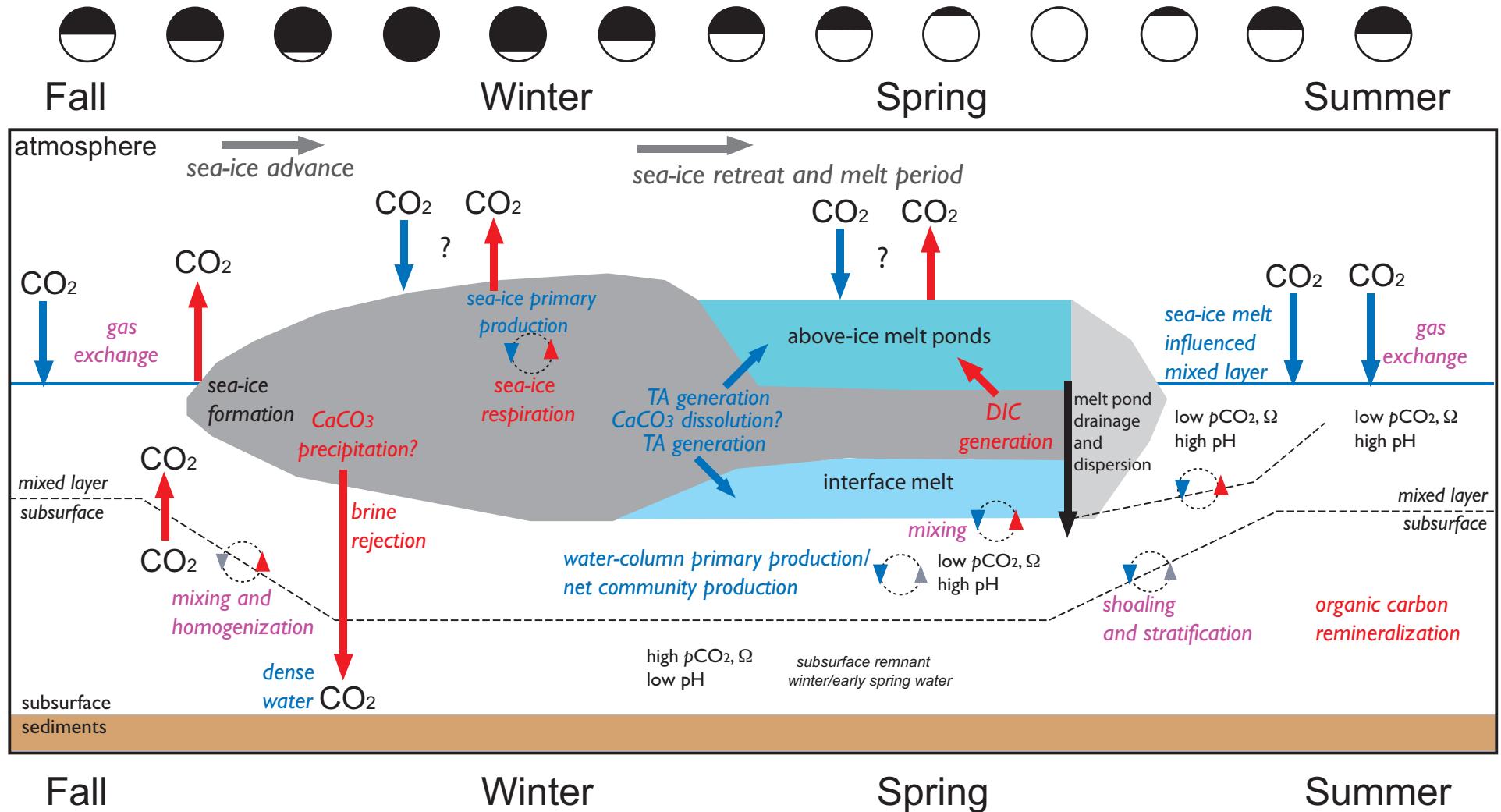
Thanks to
NASA

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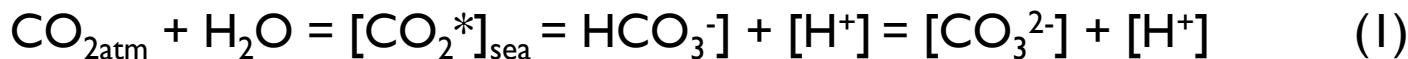
Sea-ice CO_2 -carbonate chemistry

Seasonal changes in generic sea-ice impacted shelf



Sea-ice CO₂-carbonate chemistry

CO₂-carbonate chemistry considerations



Observed or calculated
seawater CO₂-carbonate
chemistry

Dissolved inorganic carbon (DIC)

- DIC = $[\text{HCO}_3^-] + [\text{CO}_3^{2-}] + [\text{CO}_2]$

Total Alkalinity (TA)

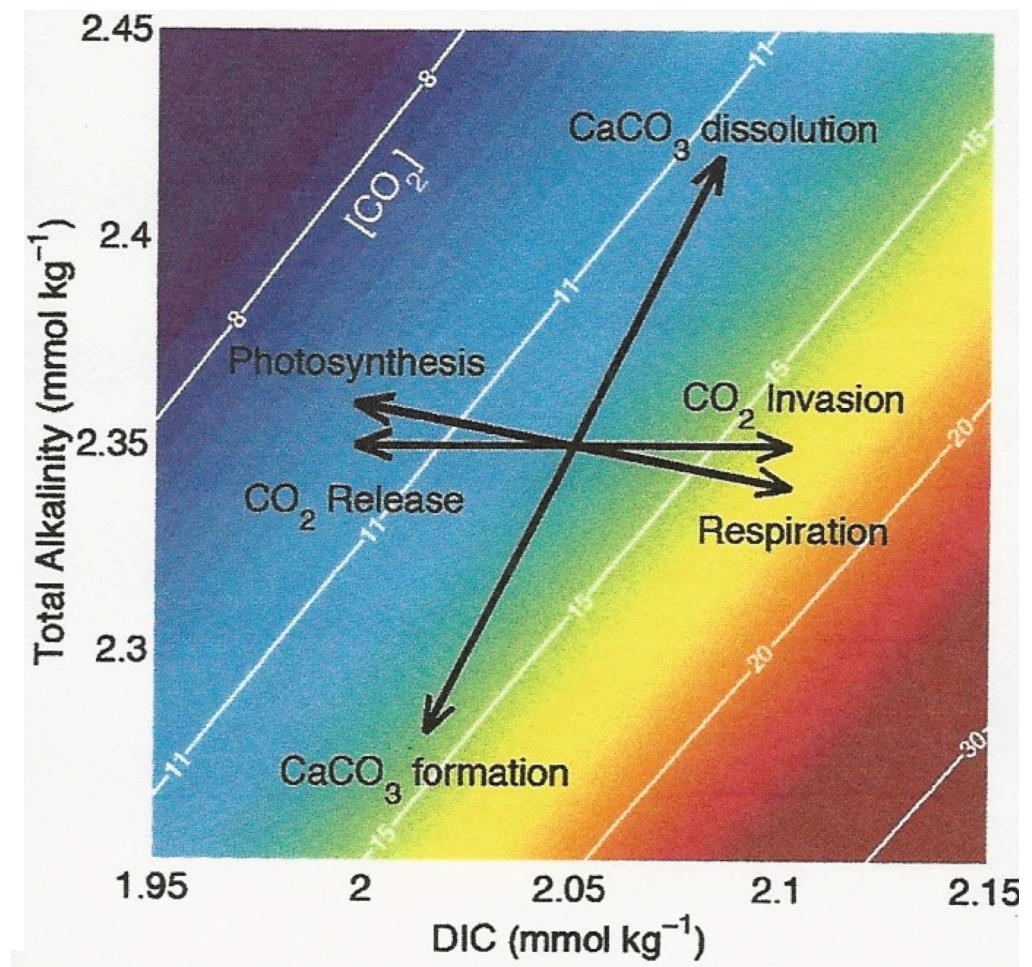
- TA = $[\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B(OH)}^-] + [\text{OH}^-] - [\text{H}^+]$

Partial pressure of CO₂

- $p\text{CO}_2$ or $f\text{CO}_2$

pH

- $-\log_{10} [\text{H}^+]$



Sea-ice CO₂-carbonate chemistry

Caveats associated with sea-ice CO₂ carbonate chemistry

Thermodynamic Issues

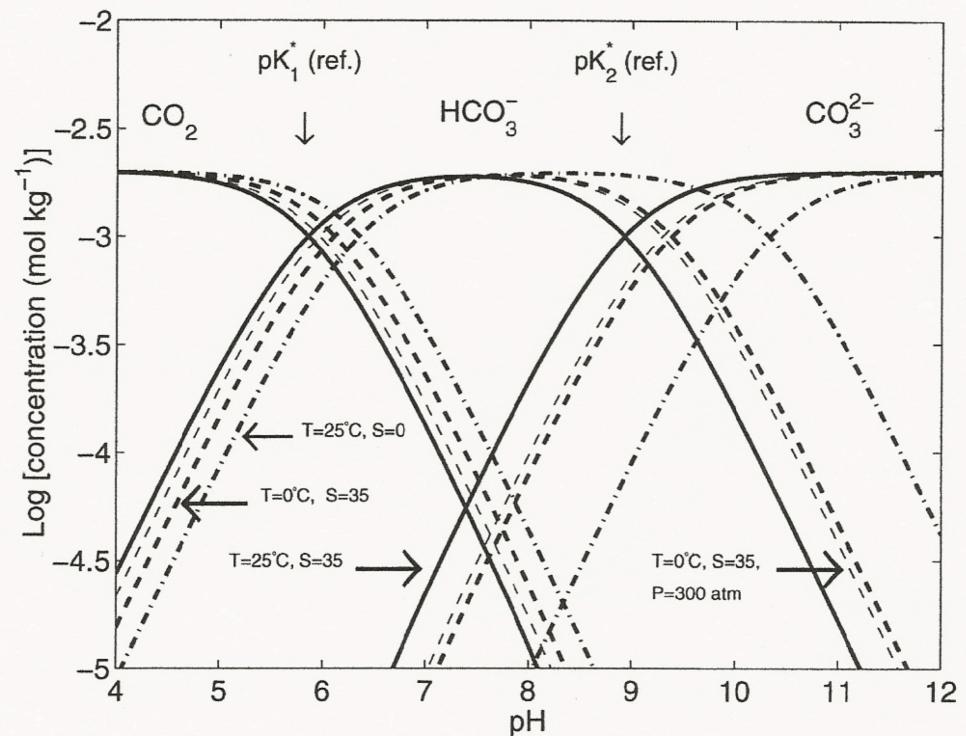
1. Uncertainty with dissociation constants for waters less than 1°C and salinity of 25
2. Low ionic strength of sea-ice meltwaters
3. High ionic strength of sea-ice brines

Measurement Issues

4. Higher salinity, open ocean seawater certified reference materials
5. Calibration to low salinity waters

Calculation Issues

6. What is the inaccuracy of computing pCO₂, pH, etc in sea-ice?



Sea-ice CO₂-carbonate chemistry

Caveats associated with sea-ice carbonate chemistry

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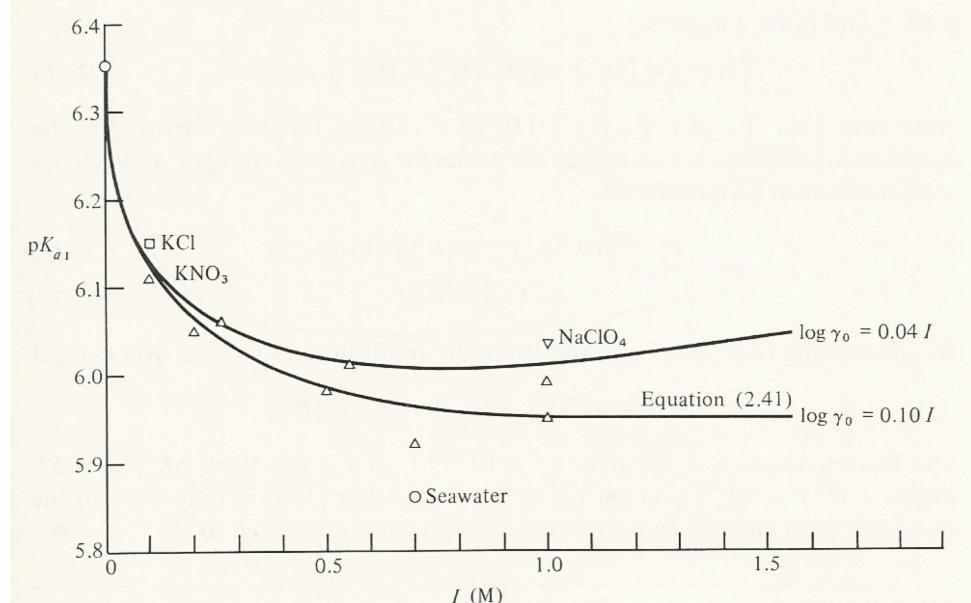


Fig. 2.6. First acidity constant of CO₂, pK_{a1} , as a function of ionic strength. Note that seawater falls well below the data for NaClO₄ and KNO₃ media, and that $b = 0.04$ or $b = 0.10$ give equally good fits to the data for $I \leq 1$ M.

Sea-ice CO₂-carbonate chemistry

$p\text{CO}_2$ observed and calculated comparison

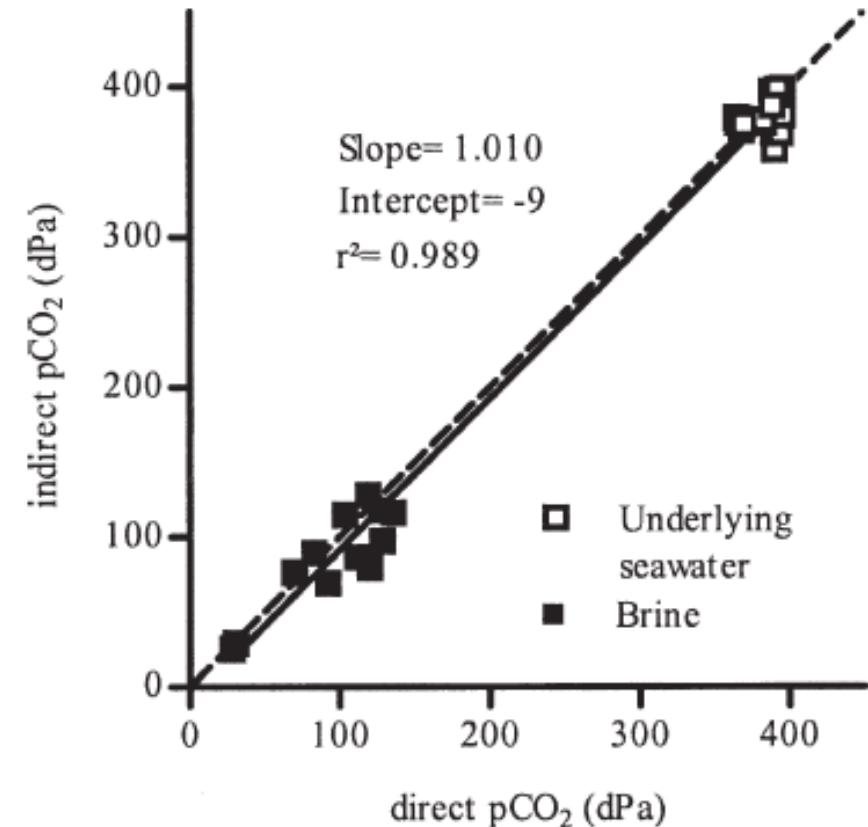
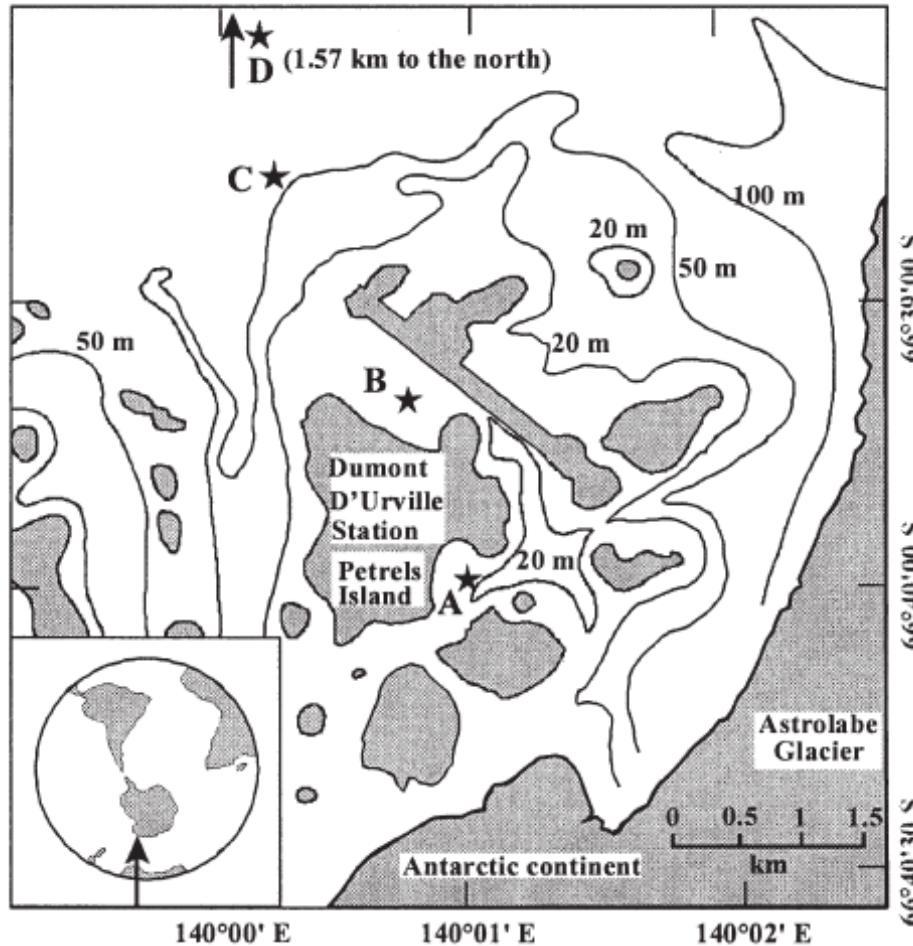


Fig. 2. Comparison of direct partial pressure of CO₂ ($p\text{CO}_2$) measurements and $p\text{CO}_2$ computed from pH and total alkalinity measurements (indirect $p\text{CO}_2$) carried out during the ISPOL cruise in the western Weddell Sea between Nov 2005 and Jan 2006. Open and filled squares correspond to underlying water and brine, respectively, while solid and dashed lines correspond to linear regression and 1 : 1 lines, respectively.

Physical and Biological Processes in Sea-Ice

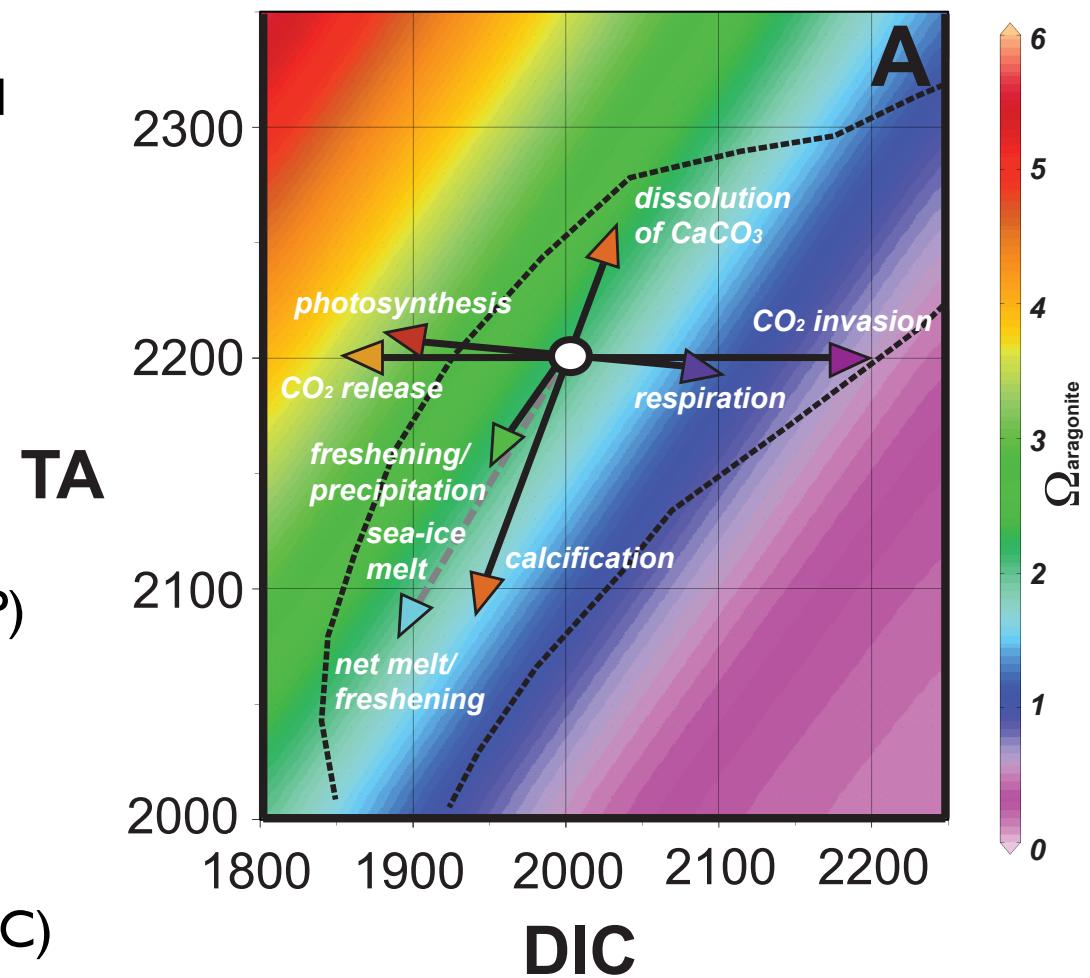
Primary drivers of sea-ice CO₂

Physical Processes

1. Brine rejection
2. Sea-ice gas exchange with air and seawater (after ice formation)
3. Precipitation/oblation
4. Sea-ice melting (end of season)

Biological/biogeochemical processes

5. Primary production
6. Respiration
- Net Ecosystem Metabolism (NEP)
7. CaCO₃ formation (e.g., Ikaite formation)
8. CaCO₃ dissolution
- Net Ecosystem Calcification (NEC)



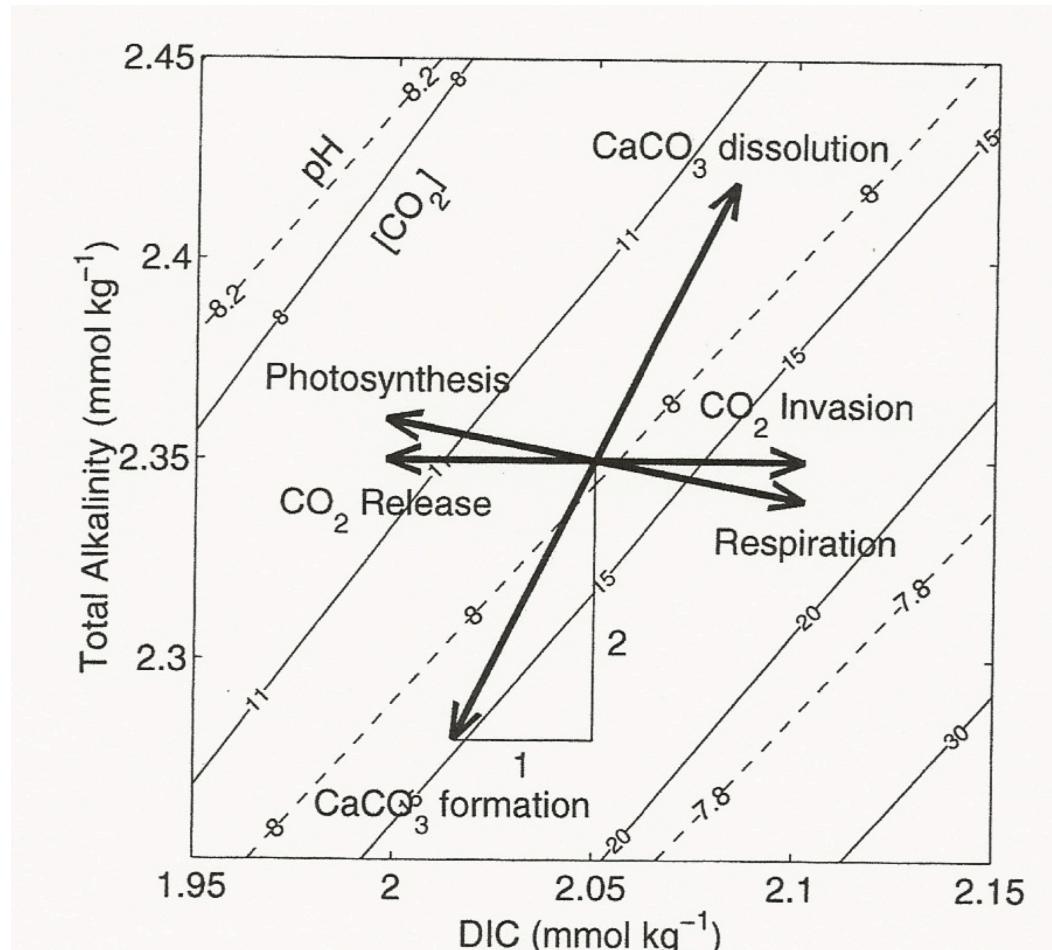
Physical and Biological Processes in Sea-Ice

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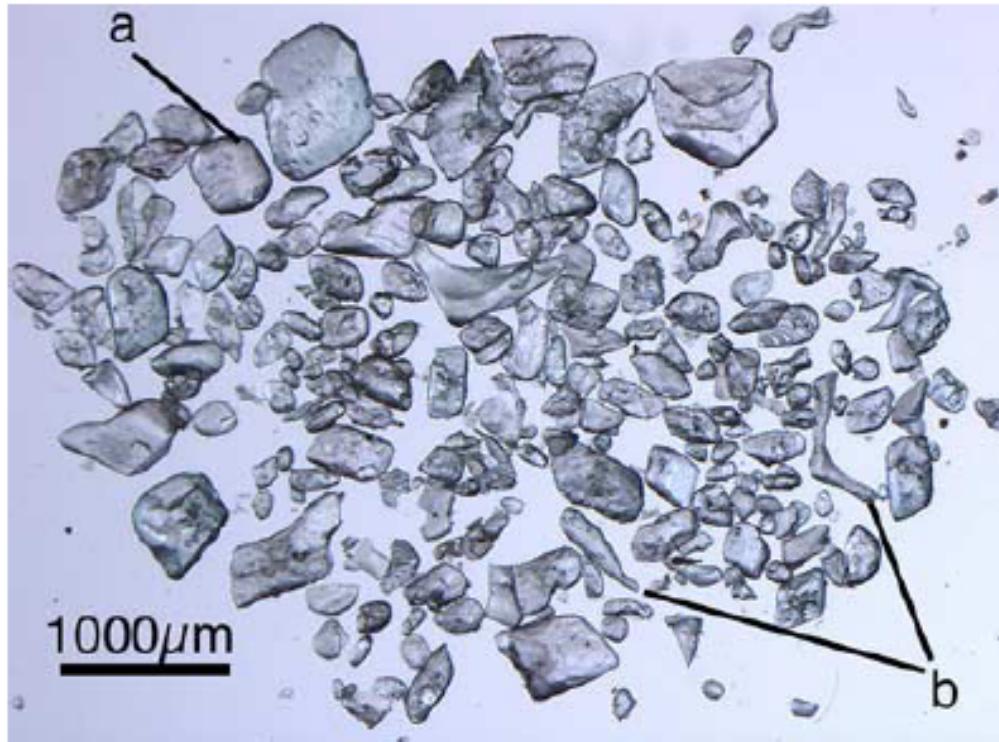
$$\text{NEM} = \text{NEP} + \text{NEP}$$

Physical and Biological Processes in Sea-Ice

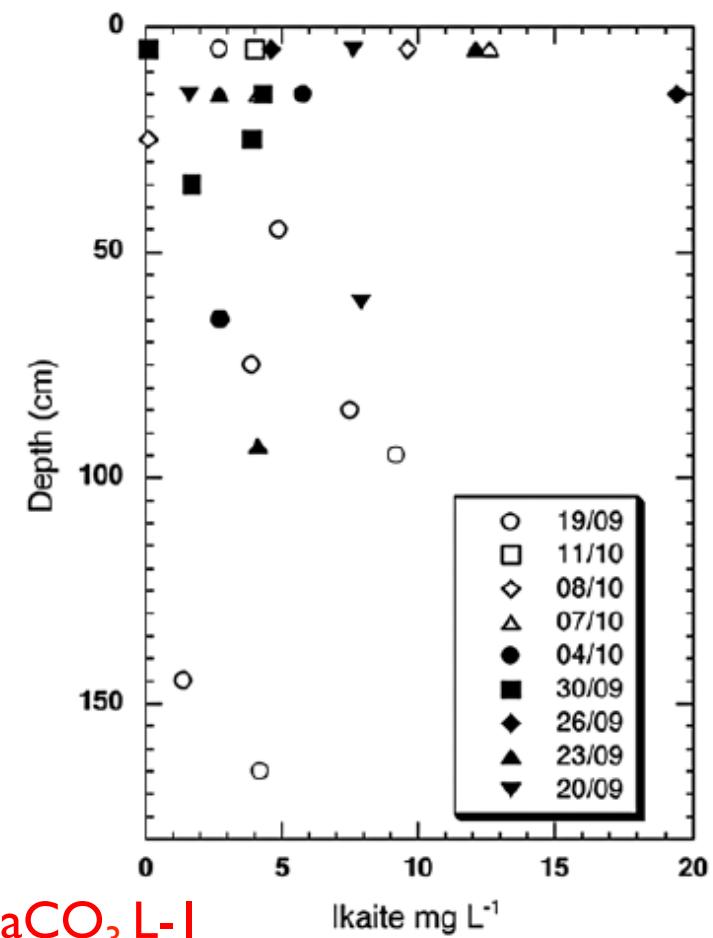
Ikaite formation

Formation of CaCO_3

e.g., Killawee et al., 1998; Tisone et al., 2002; Papadimitriou et al., 2004; Dieckmann et al., 2008; Thomas et al., 2013



~0.5 to 19 mg CaCO_3 L⁻¹



Dieckmann et al., 2008

Bates et al, OCB Meeting 2014

Physical and Biological Processes in Sea-Ice

CaCO_3 formation

Formation of CaCO_3

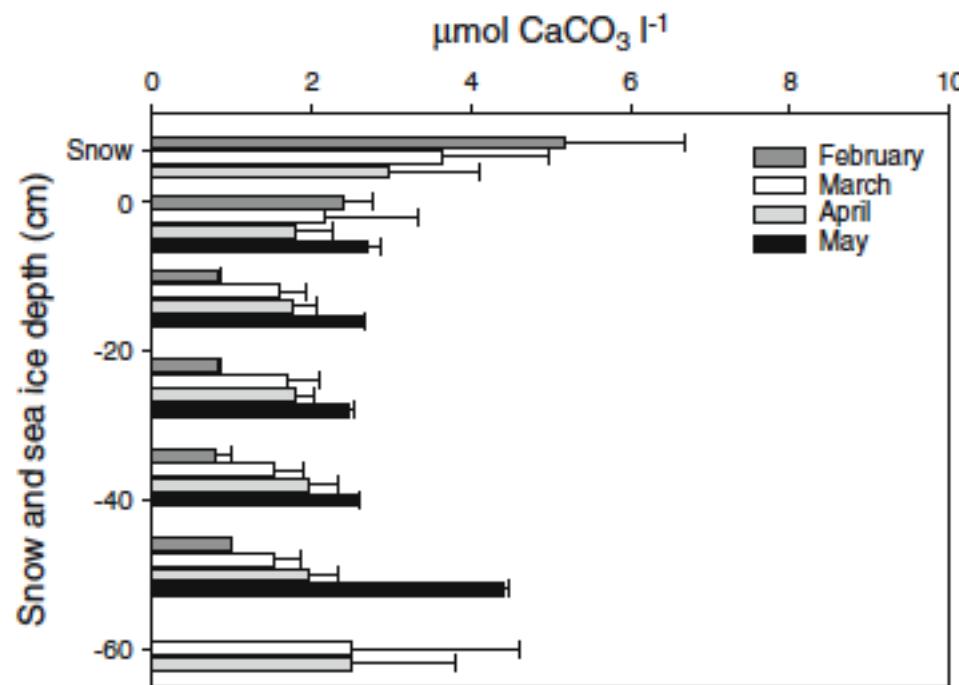


Fig. 5 Temporal development of the CaCO_3 concentration [$\mu\text{mol CaCO}_3 \text{ L}^{-1}$] in bulk sea ice and snow in February, March, April, and May 2010

~0.1 to 0.8 mg $\text{CaCO}_3 \text{ L}^{-1}$

Sogaard et al., 2013

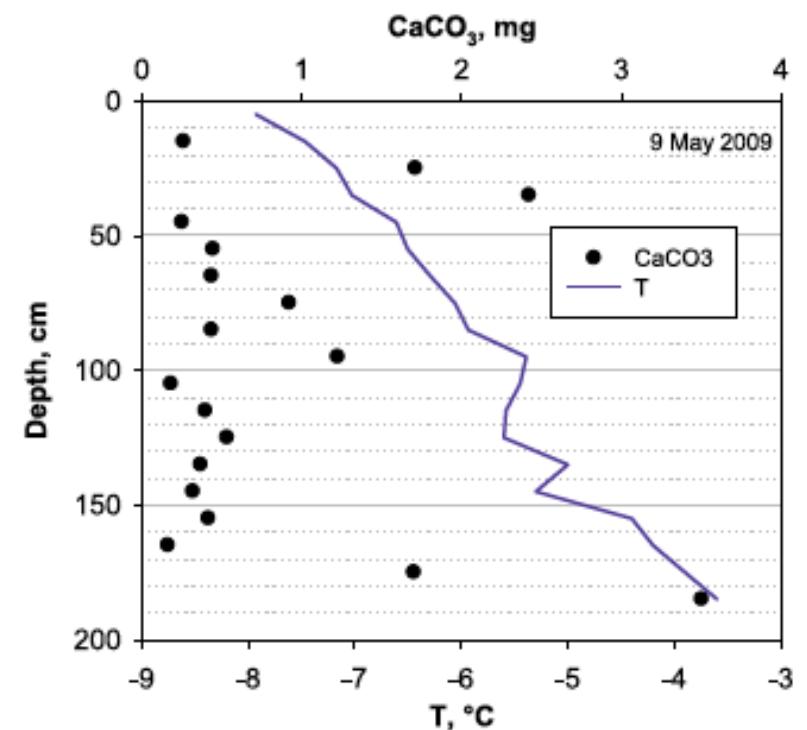


Figure 8. Calcium carbonate and in situ temperature from an ice core collected on 9 May 2009 and stored at -20°C for 5 years.

~0.2 to 2.5 mg $\text{CaCO}_3 \text{ L}^{-1}$

Miller et al., 2011b

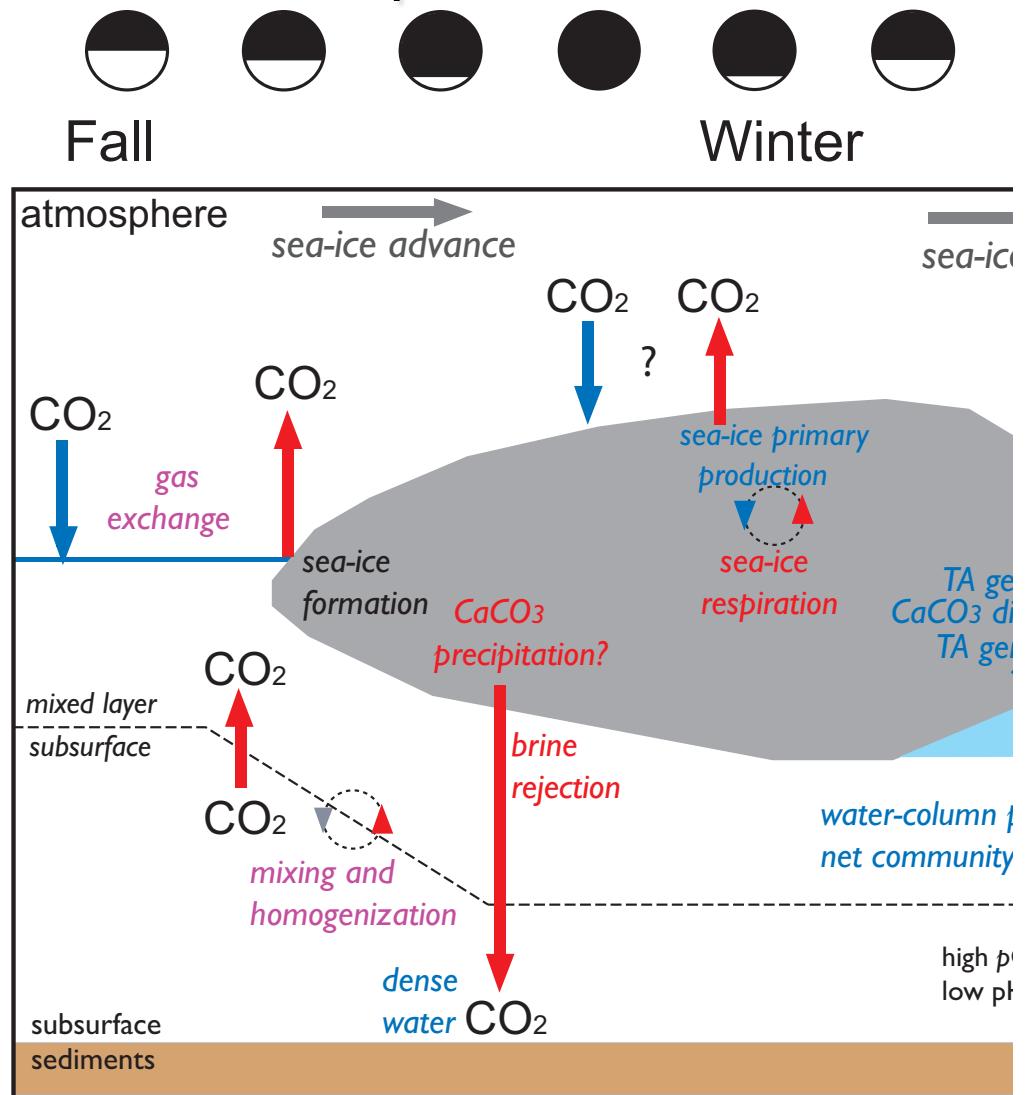
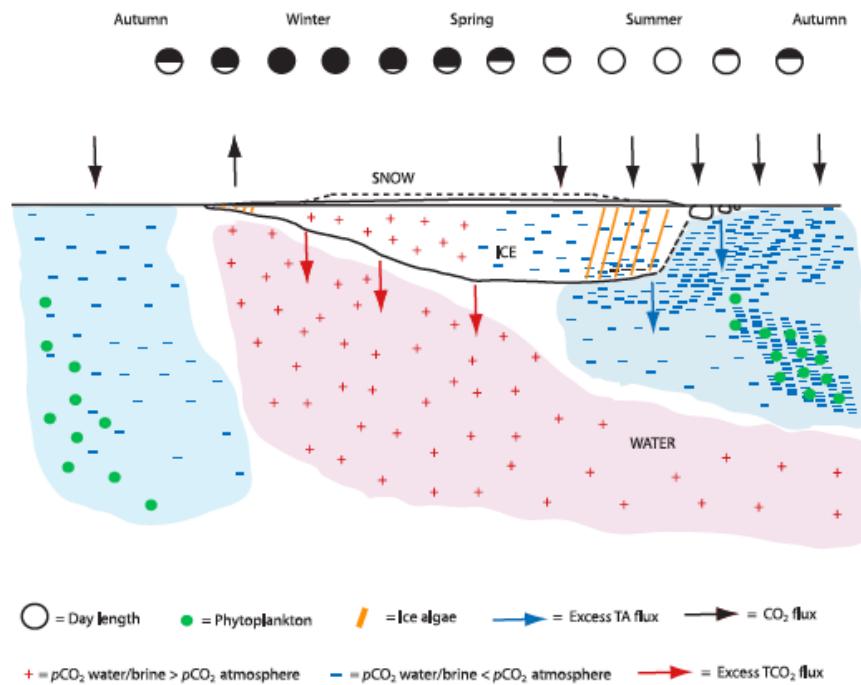
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Sea-ice CO₂-carbonate chemistry

Sea-ice formation/freeze-up

Physical Processes

I. Brine rejection



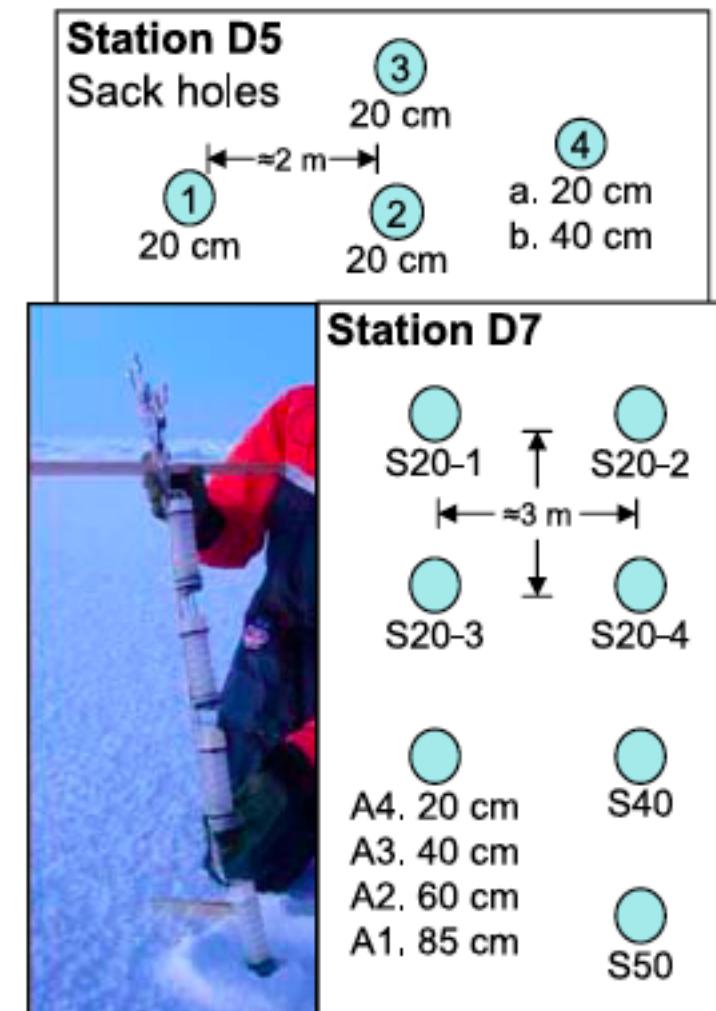
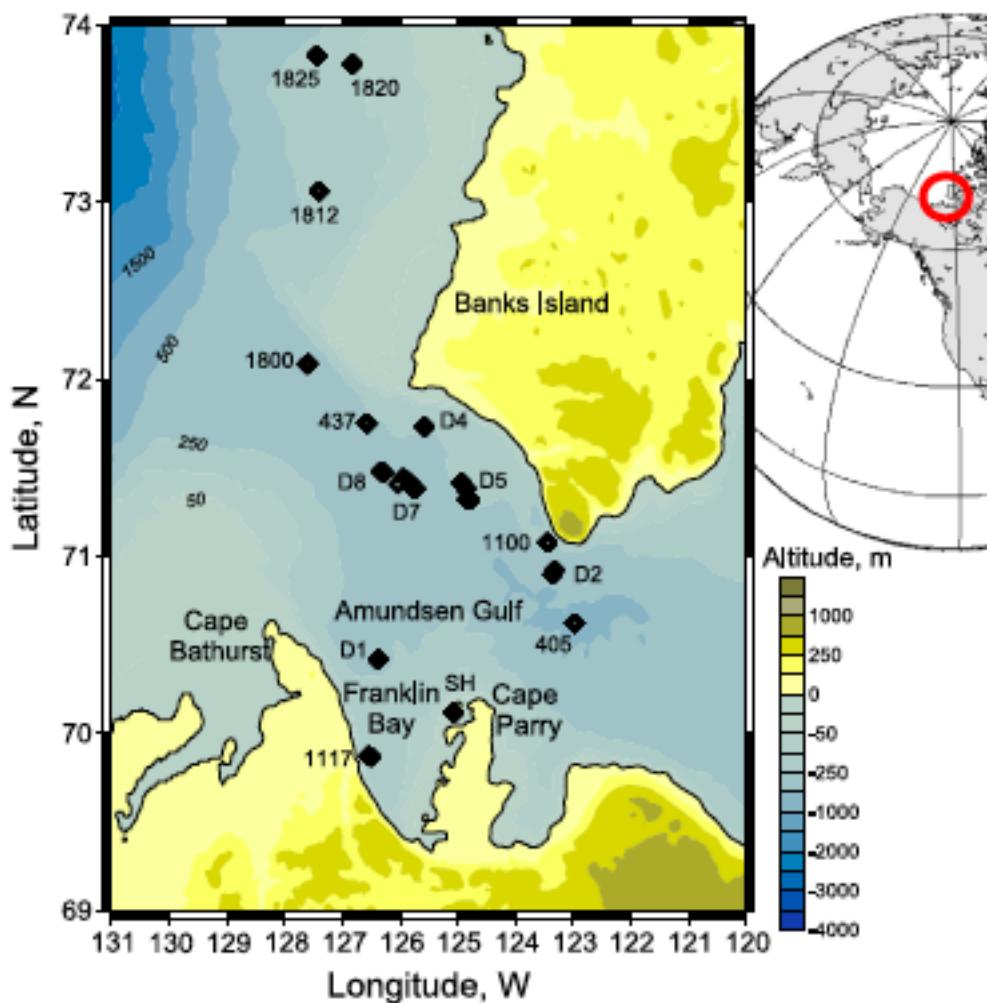
Rysgaard et al., 2007; Bates et al., 2014

Bates et al, OCB Meeting 2014

Sea-ice CO_2 -carbonate chemistry

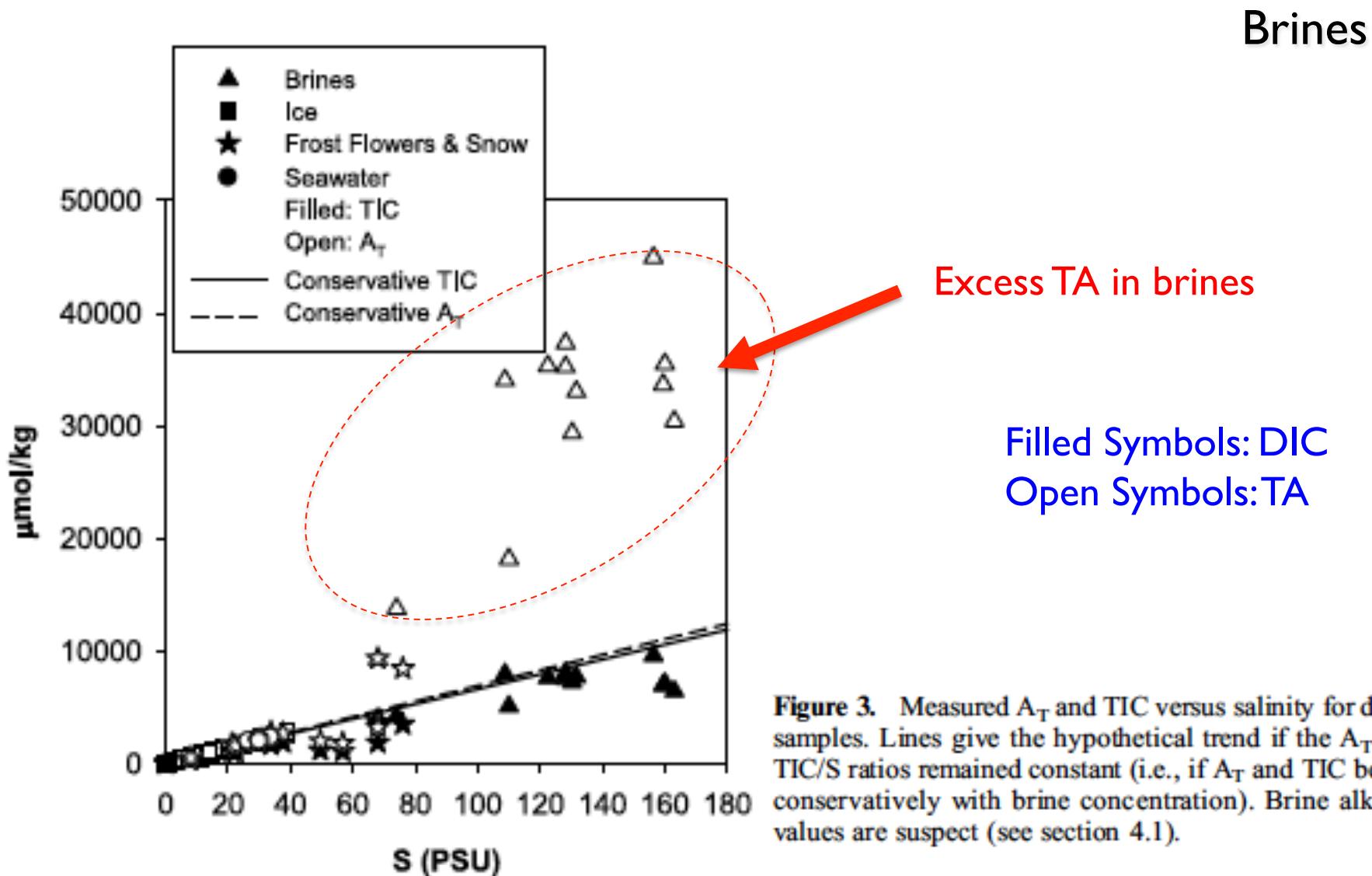
Sea-ice formation/freeze-up

Brines



Sea-ice CO_2 -carbonate chemistry

Sea-ice formation/freeze-up



Sea-ice CO₂-carbonate chemistry

Sea-ice formation/freeze-up

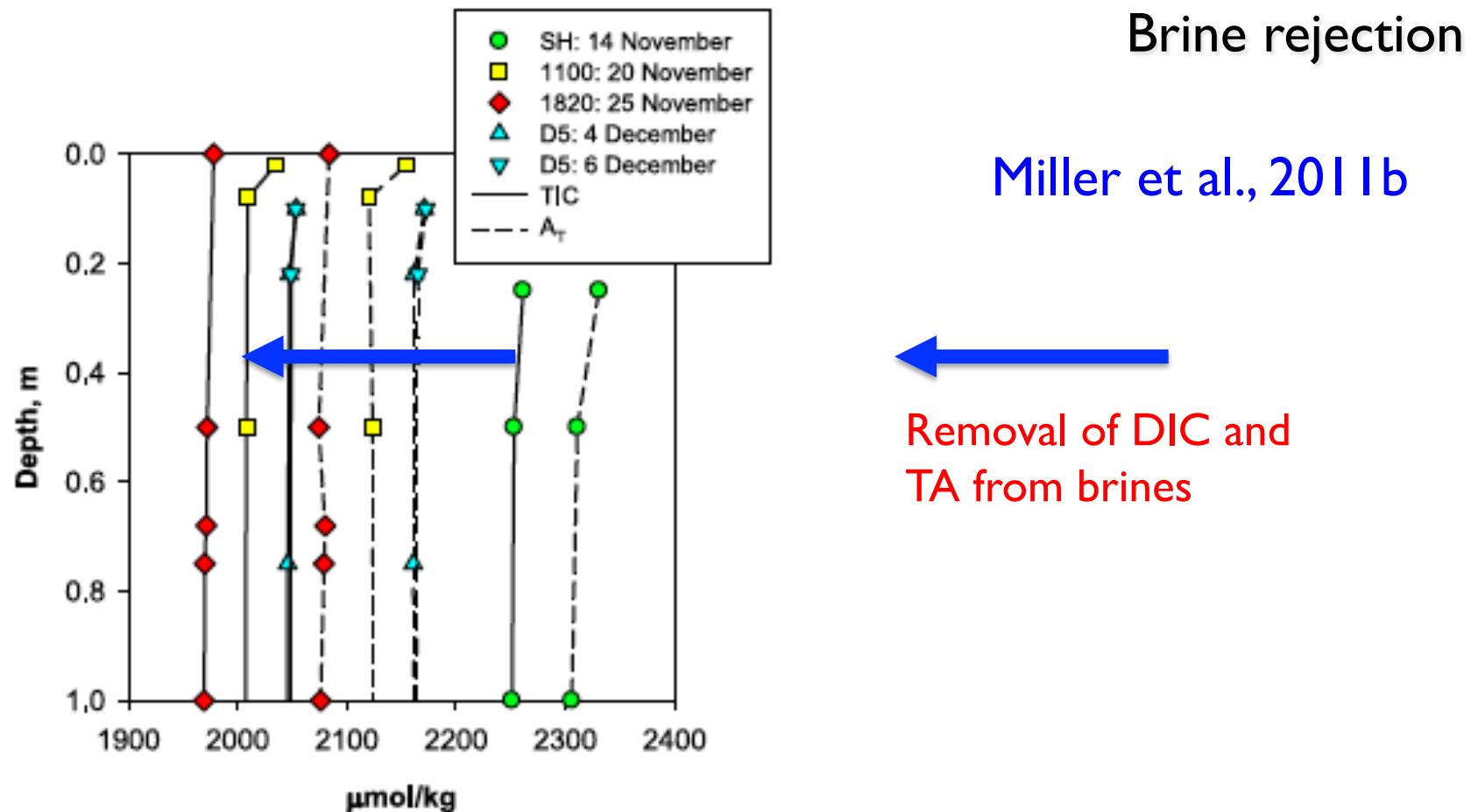


Figure 8. Total inorganic carbon and alkalinity in seawater over the top 1 m under the sea ice at selected stations showing evidence of carbon rejection with brine from the ice. See Figure 1 for station locations.

Sea-ice CO_2 -carbonate chemistry

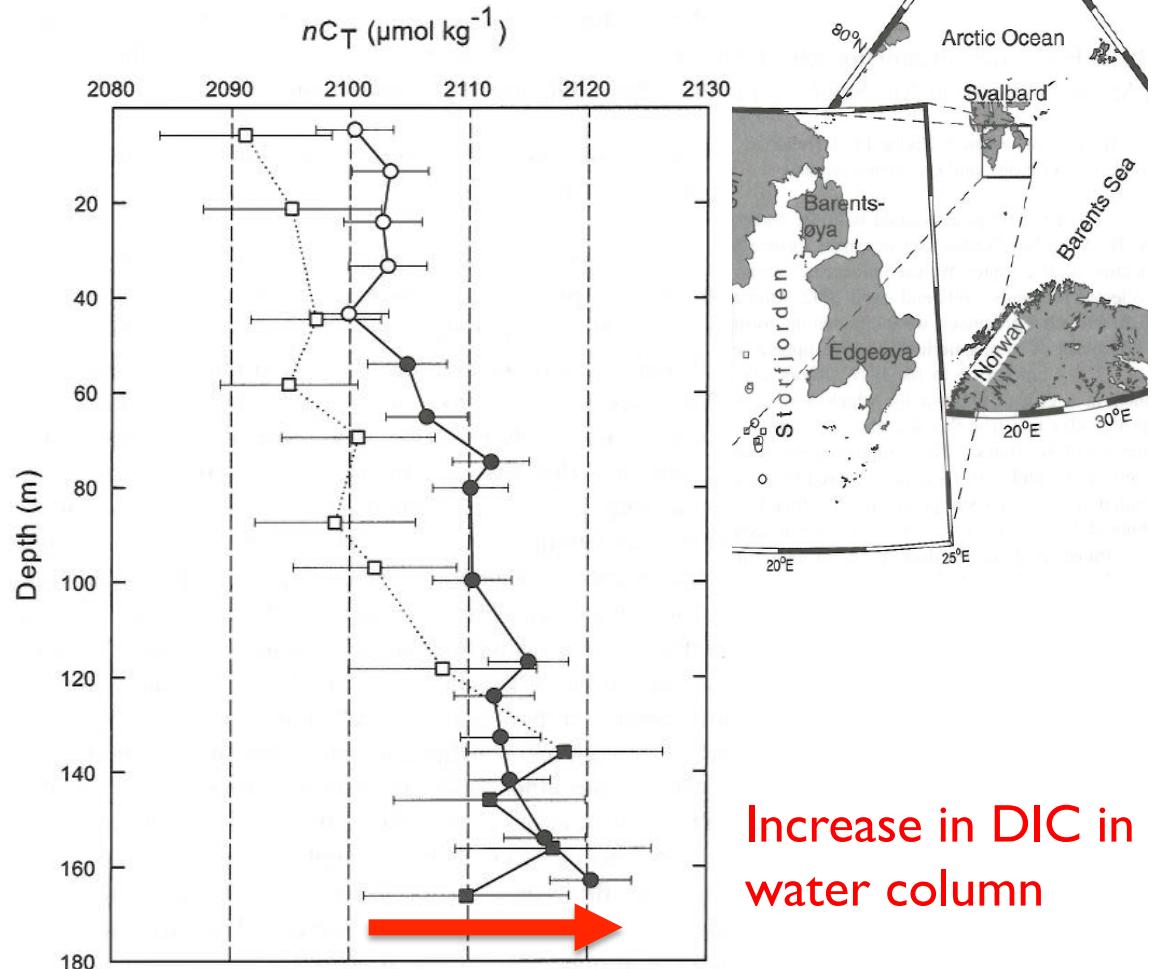
Brine rejection

Omar et al 2005

Physical Processes

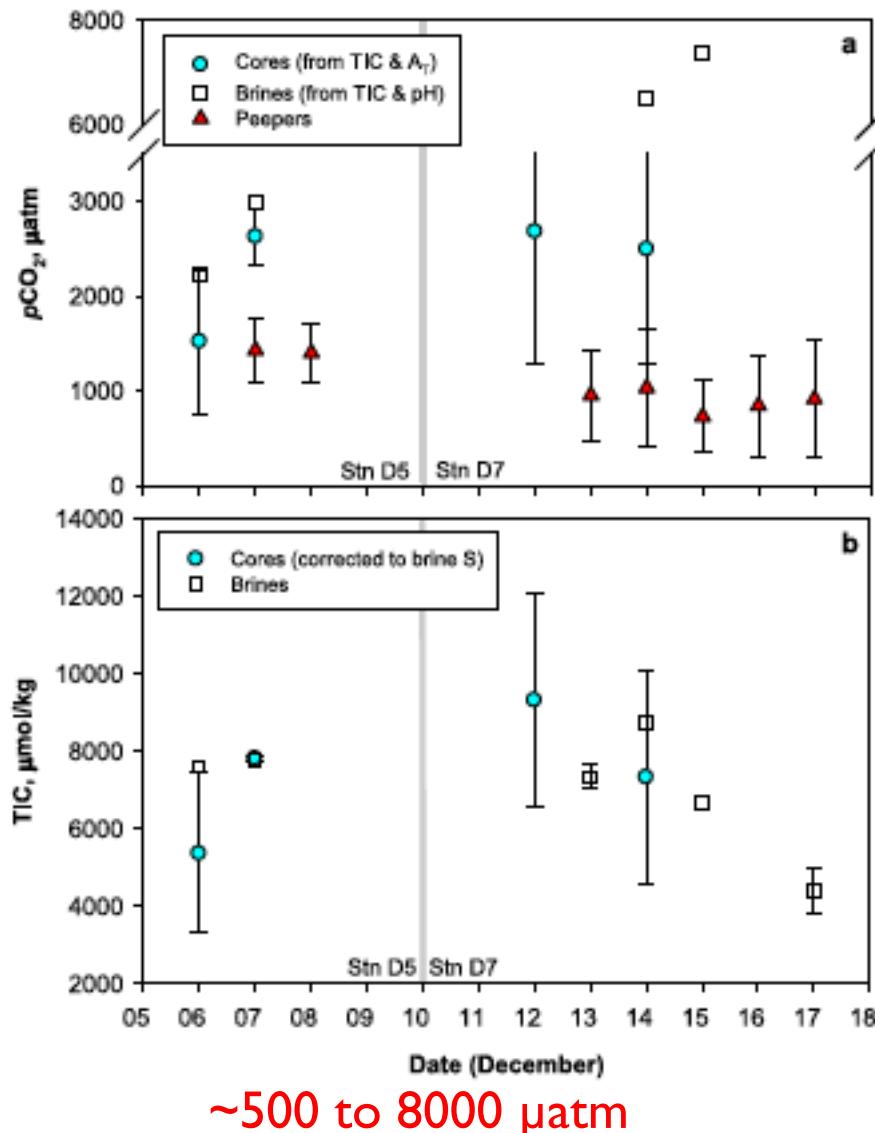
I. Brine rejection

2. During freeze-up, the formation of high salinity brines appears to drive a large uptake of CO_2 from the atmosphere and downward flux of dissolved inorganic carbon (DIC) with cold dense waters formed during brine rejection (e.g., Anderson et al., 2004; Omar et al., 2005; Rysgaard et al., 2007).

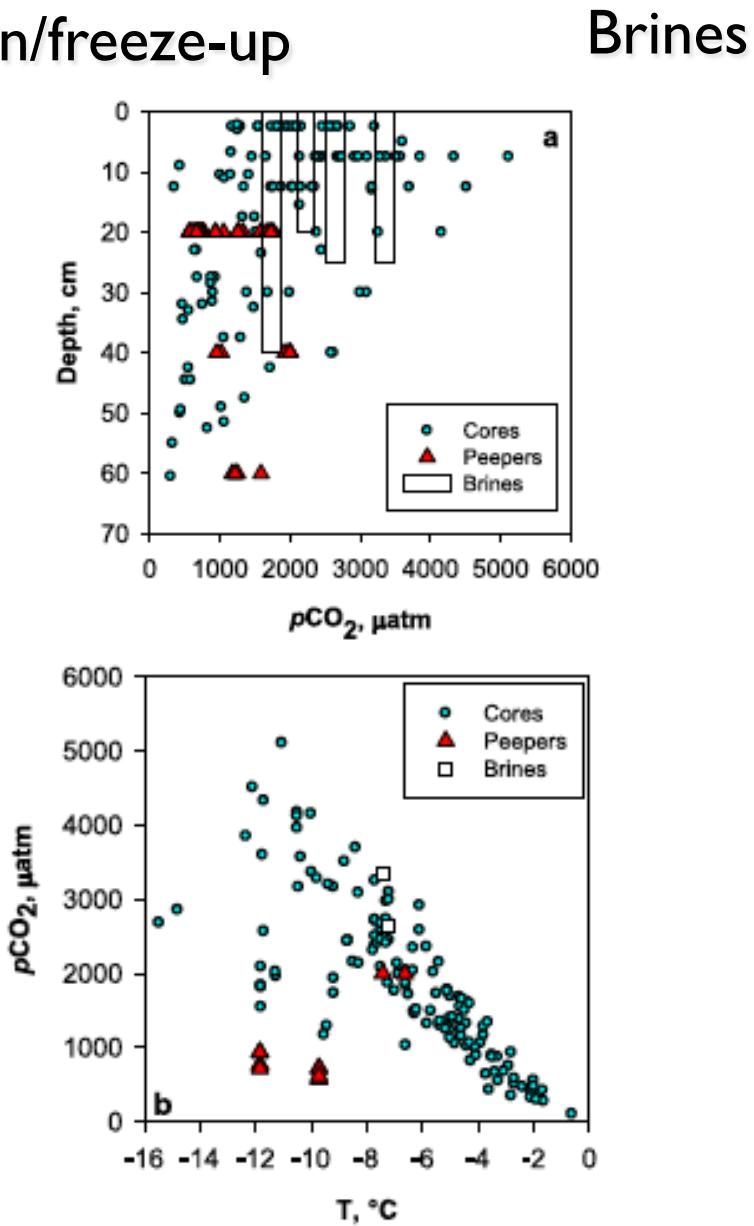


Sea-ice CO_2 -carbonate chemistry

Sea-ice formation/freeze-up



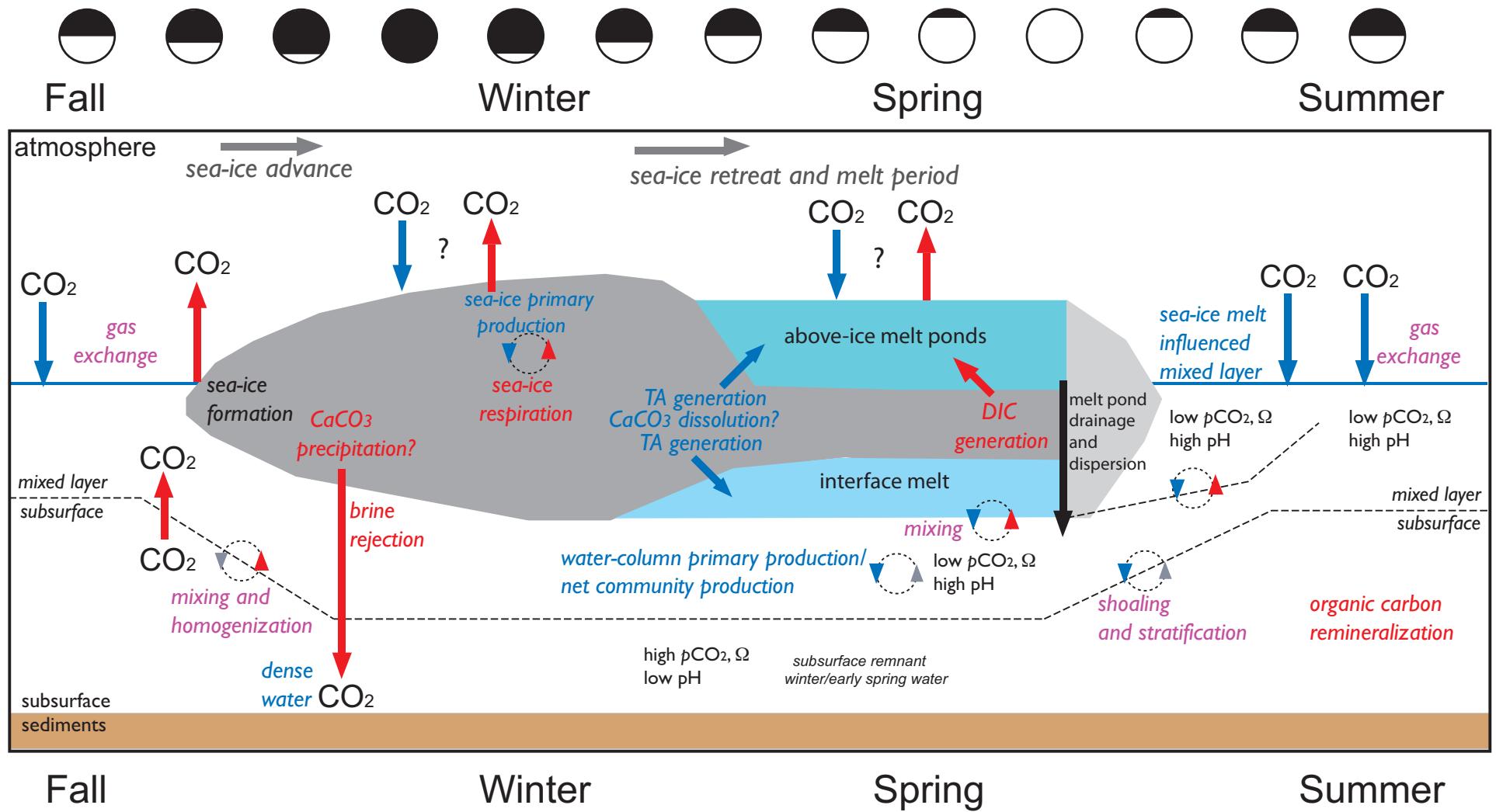
Miller et al., 2011b



Bates et al, OCB Meeting 2014

Sea-ice CO_2 -carbonate chemistry

Winter Observations



Sea-ice CO₂-carbonate chemistry

Sea-ice Brines

Study	Location	Period	Season	pCO ₂ (μatm)	pH	Ω_{calcite}	$\Omega_{\text{aragonite}}$
Brine							
Miller et al., 2011a	Arctic	Nov. to Dec	Fall	<1	12.4	22.5	4.6
Miller et al., 2011b	Arctic	Dec to Mar	Winter	~800 to 12,000	8.2 to 7.1	11.9-1.3	0.8-7.4
Miller et al., 2011b	Arctic	April to June	Spring	~800 to 12,000	8.2 to 7.1	1.3-11.9	0.8-7.4
Geilfus et al. 2012a	Arctic	April	Spring	465 to 1834	8.0	3.0	1.6
Geilfus et al. 2012a	Arctic	May	Spring	147 to 888	8.2	1.5	<0.1
Delille et al., 2007	Antarctic	November	Spring	~100	9.42	>20	>6
Delille et al., 2007	Antarctic	December	Spring	~420	8.38	3.4	1.8
Geilfus et al. 2012a	Arctic	June	Spring	0 to 180	8.3	0.1	<0.1
Geilfus et al. 2014	Arctic	June	Spring	20 to 389			
Fransson et al 2011	Antarctic	Dec. to Jan	Spring	9 to 210	9.3-8.3	3.7-14.8	2.3-9.3

Table 1. Summary of measured and calculated pCO₂ values reported in sea-ice brine, sea-ice and melt ponds. The studies are arranged in seasonal order from fall to spring observations where possible. In most cases, pCO₂, pH, Ω_{calcite} , and $\Omega_{\text{aragonite}}$ were calculated from TA and DIC, or from pCO₂ and pH. In the cases where values were reported in the original study, salinity and temperature values of 4 and 0°C were used in the calculations. (from Bates et al., 2014).

Sea-ice CO_2 -carbonate chemistry

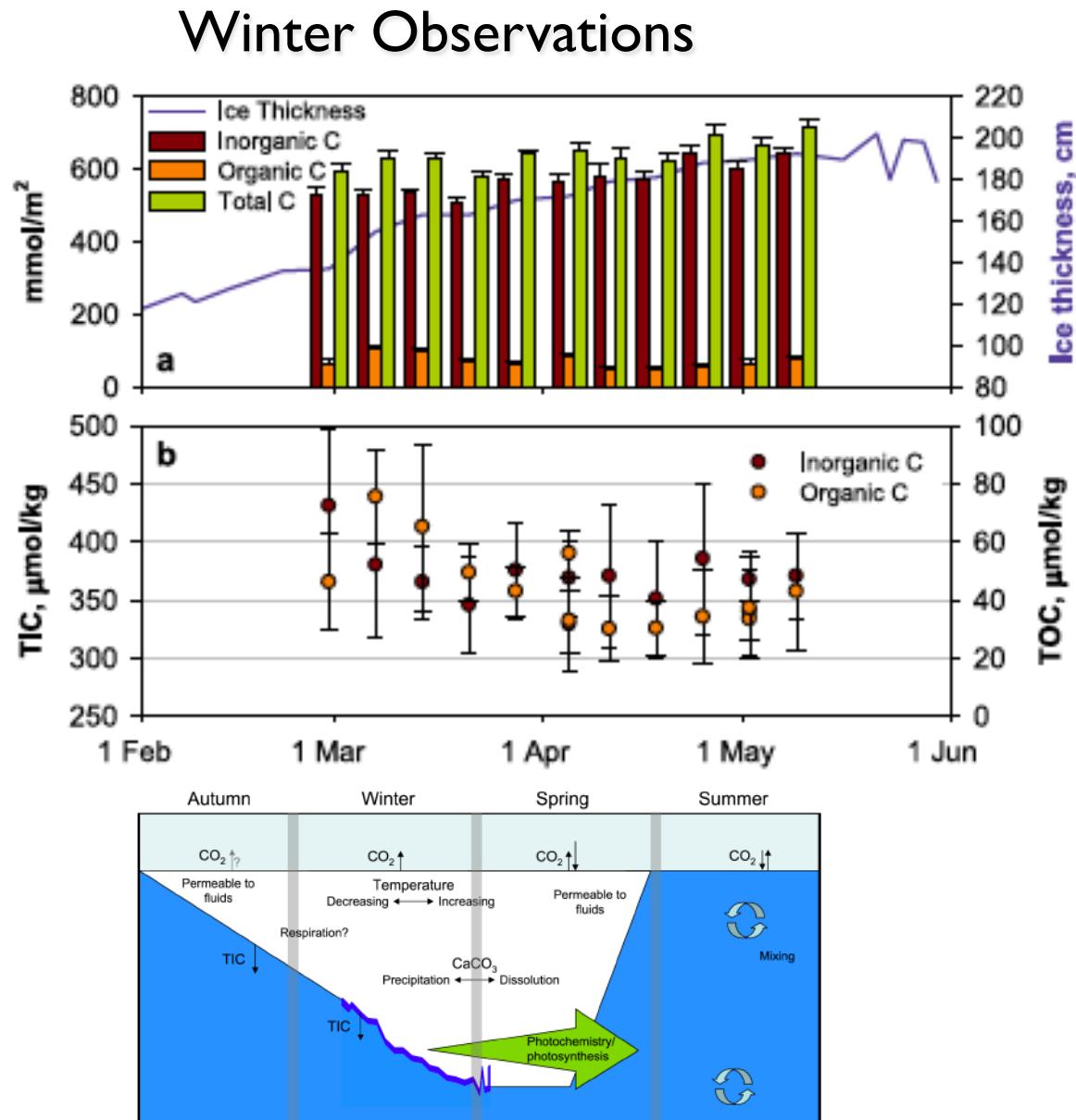
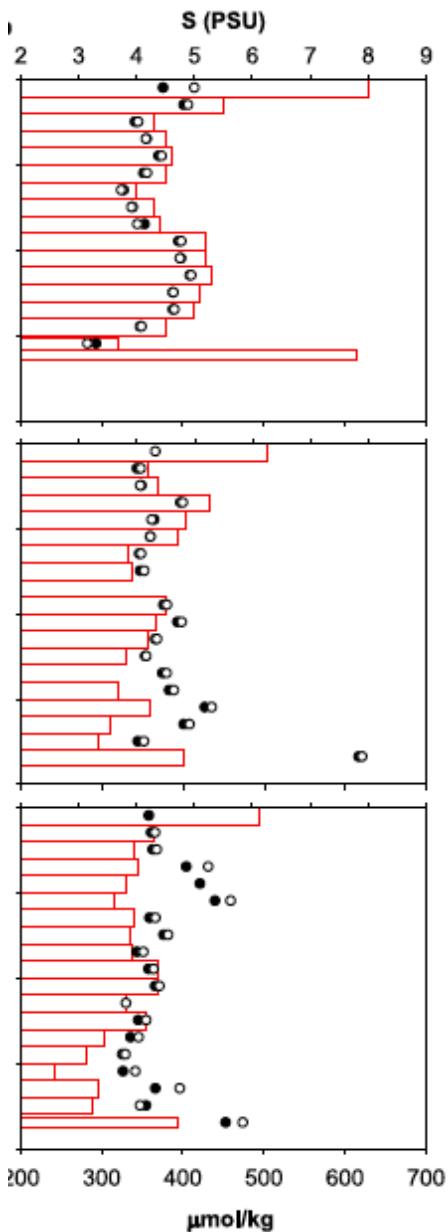
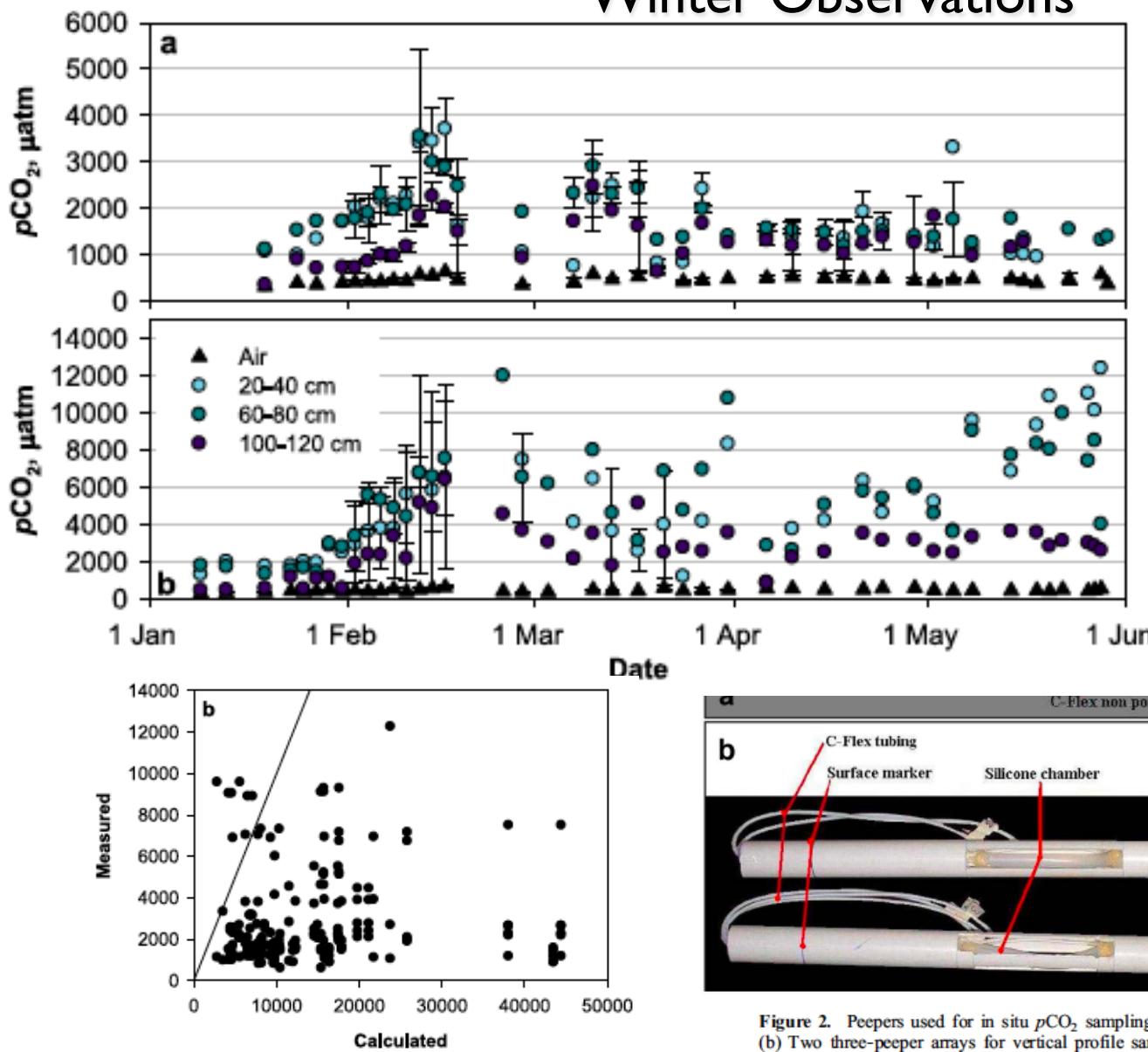


Figure 16. Summary of processes controlling sea ice inorganic carbon dynamics. The dark blue line represents the relative ice thickness during our study (Figure 6a).

Sea-ice CO_2 -carbonate chemistry

Winter Observations



Brines

Miller et al 2011a

~500 to 14,000 μatm

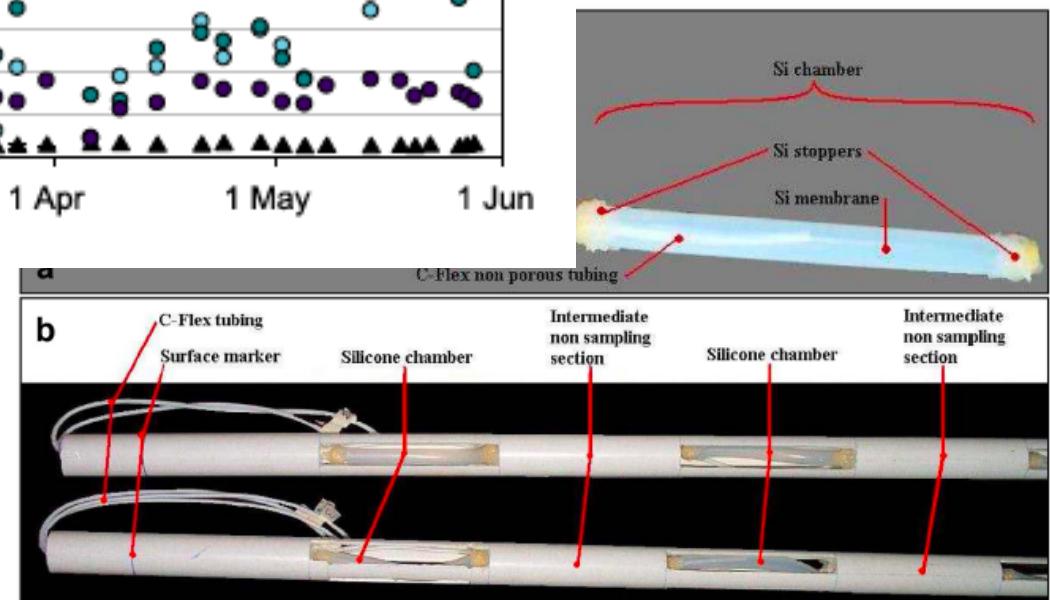
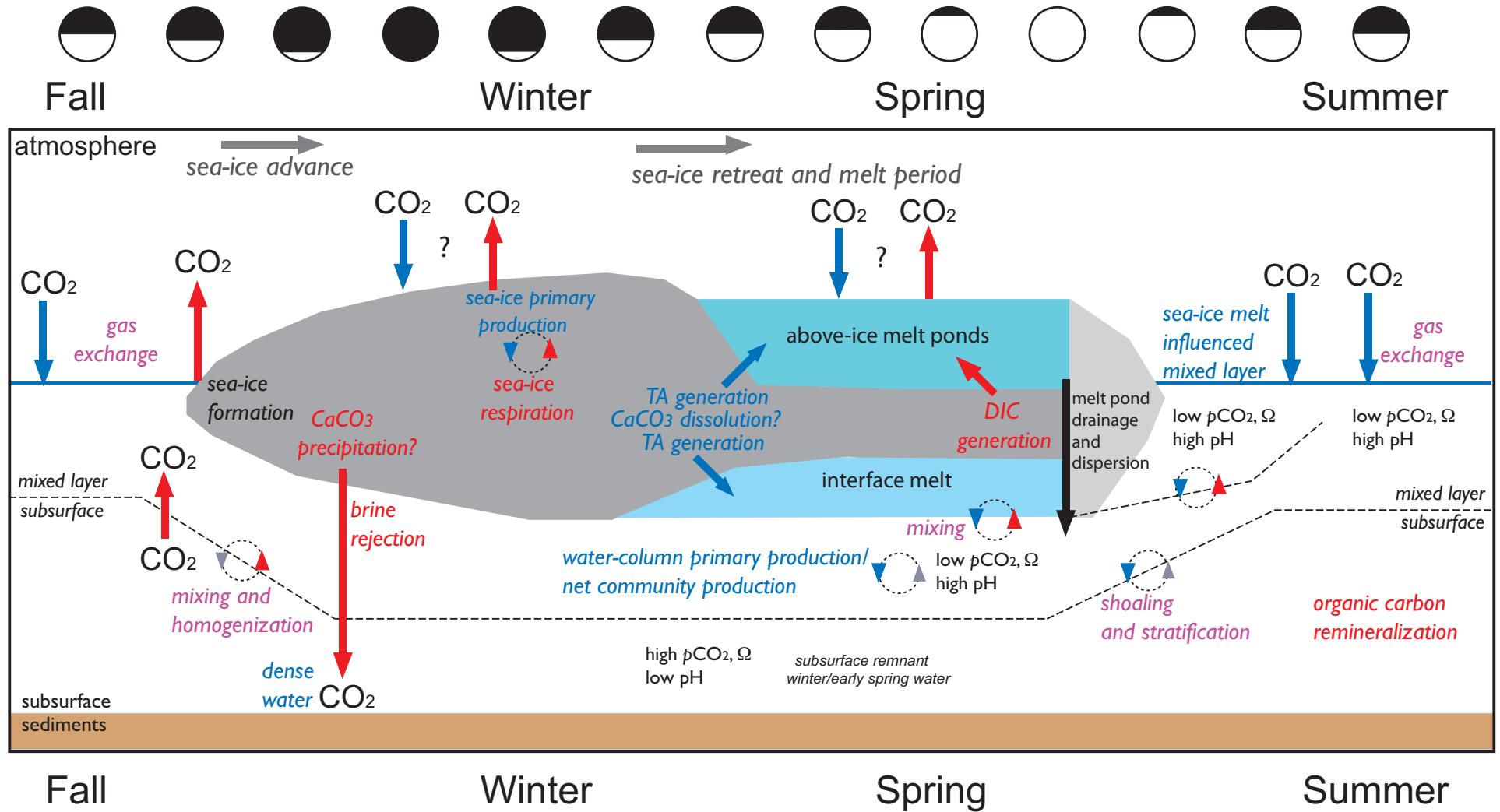


Figure 2. Peepers used for in situ pCO_2 sampling in sea ice. (a) Individual silicone chamber peeper. (b) Two three-peeper arrays for vertical profile sampling. From Owens [2008].

Sea-ice CO₂-carbonate chemistry

Spring Observations



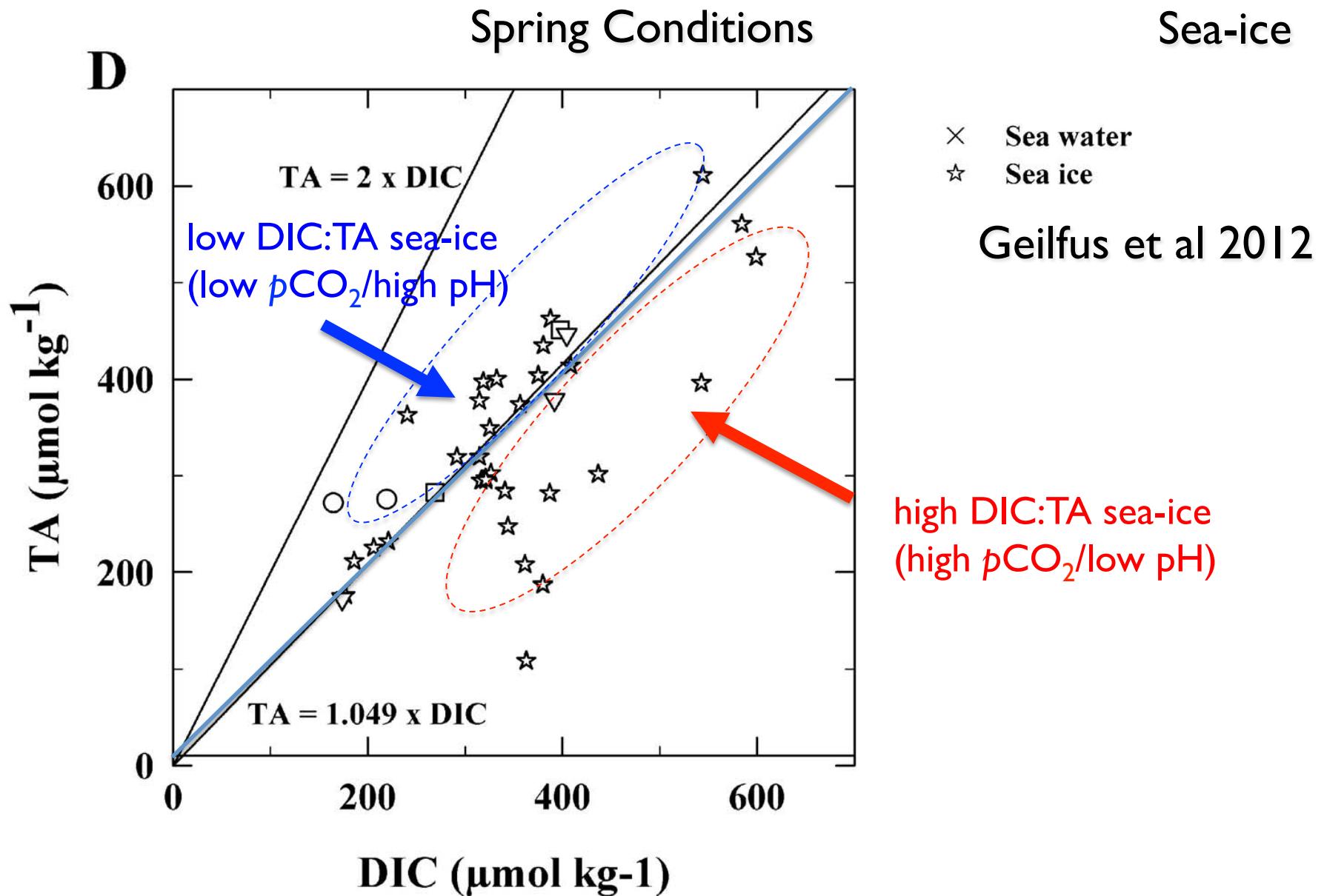
Sea-ice CO₂-carbonate chemistry

Sea-ice

Table 1. Summary of measured and calculated $p\text{CO}_2$ values reported in sea-ice brine, sea-ice and melt ponds. The studies are arranged in seasonal order from fall to spring observations where possible (from Bates et al., 2014).

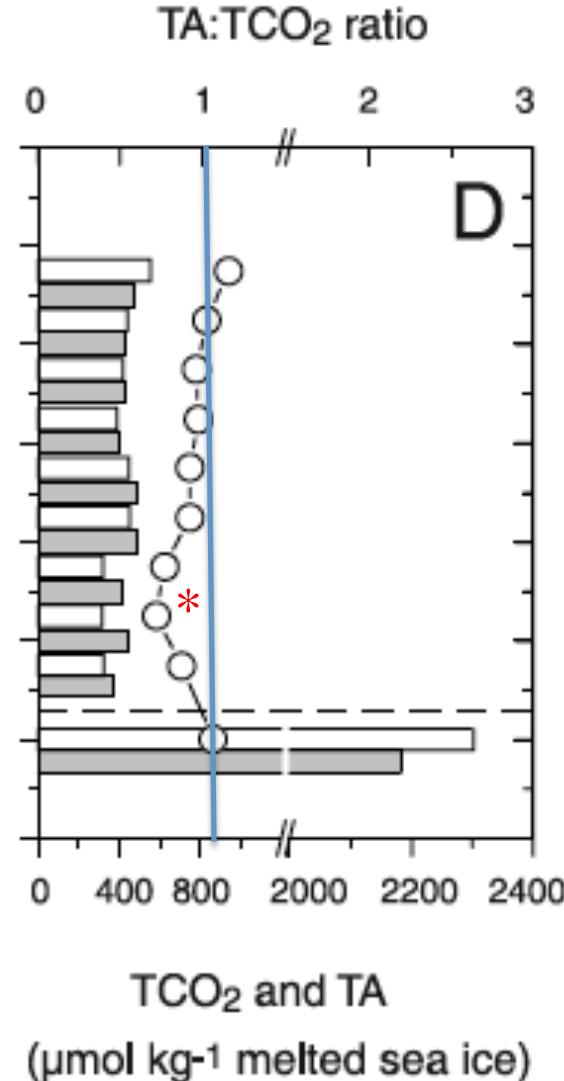
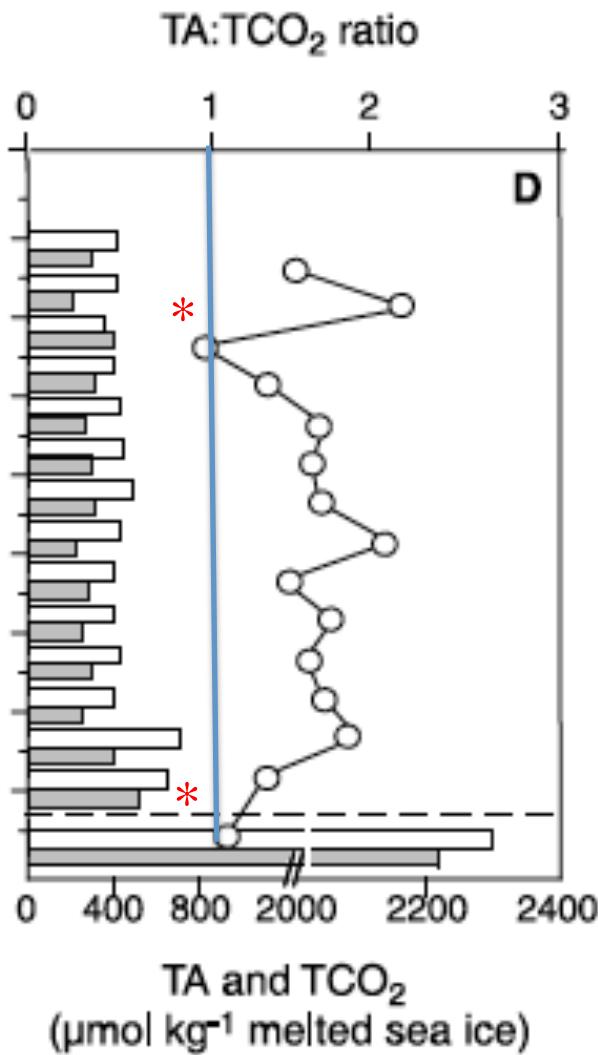
Study	Location	Period	Season	$p\text{CO}_2$ (μatm)	pH	Ω_{calcite}	$\Omega_{\text{aragonite}}$
Sea-Ice							
Miller et al., 2011a	Arctic	Nov. to Dec	Fall	<1	8.20	0.42	0.25
Miller et al., 2011a	Arctic	Nov. to Dec	Fall	<1	8.97	1.75	0.96
Rysgaard et al. 2007	Arctic	March	Spring	<1 to 6	9.1-10.4	1.6-5.5	0.86-3.0
Crabeck et al. 2014	Arctic	March	Spring	60 to 330 (1)			
Miller et al., 2011b	Arctic	April to June	Spring	103 to 197	7.7-7.97	<0.1	<0.1
Sejr et al. 2011	Greenland	March/April	Spring	165 and 195			
Rysgaard et al. 2007	Arctic	April	Spring	204 to 522	7.36-7.8	<0.05	<0.05
Delille et al., 2007	Antarctic	Nov. to Dec	Spring	<10 to 420	8.0-8.7	0.5	0.3-0.19
Sogaard et al., 2013	Arctic	April	Spring	<2 to ~10			
Sogaard et al., 2013	Arctic	May	Spring	~5 to ~145			
Geilfus et al. 2012a	Arctic	June	Spring	50 to 1800	8.4-6.2	0.56-<0.1	0.3-<0.1
Fransson et al 2011	Antarctic	Dec. to Jan	Spring	<10	9.3	14.8	9.3
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Sea-ice CO_2 -carbonate chemistry



Sea-ice CO₂-carbonate chemistry

Spring Conditions



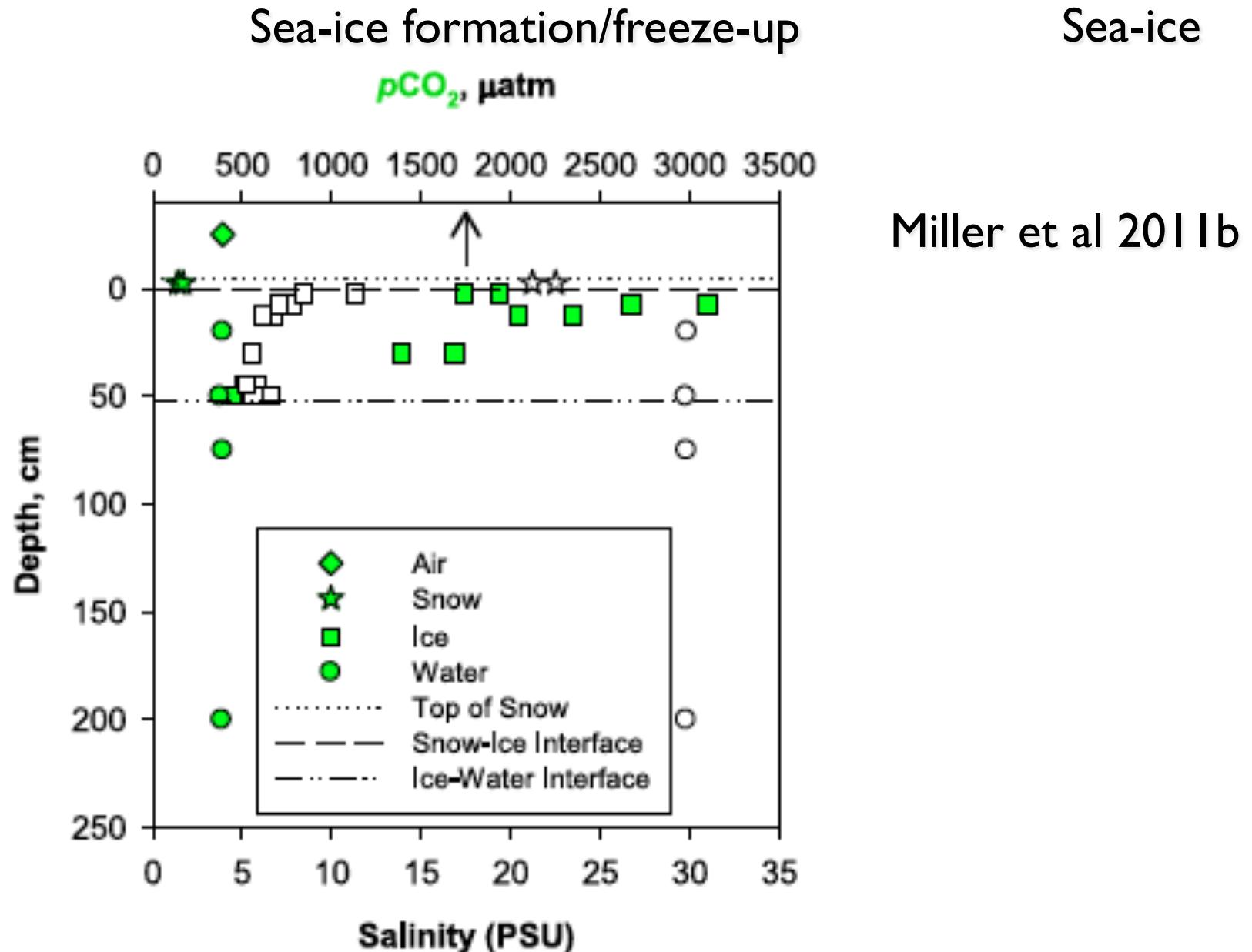
Sea-ice
Geilfus et al 2012

DIC>TA in sea-ice
(high $p\text{CO}_2$ /low pH)

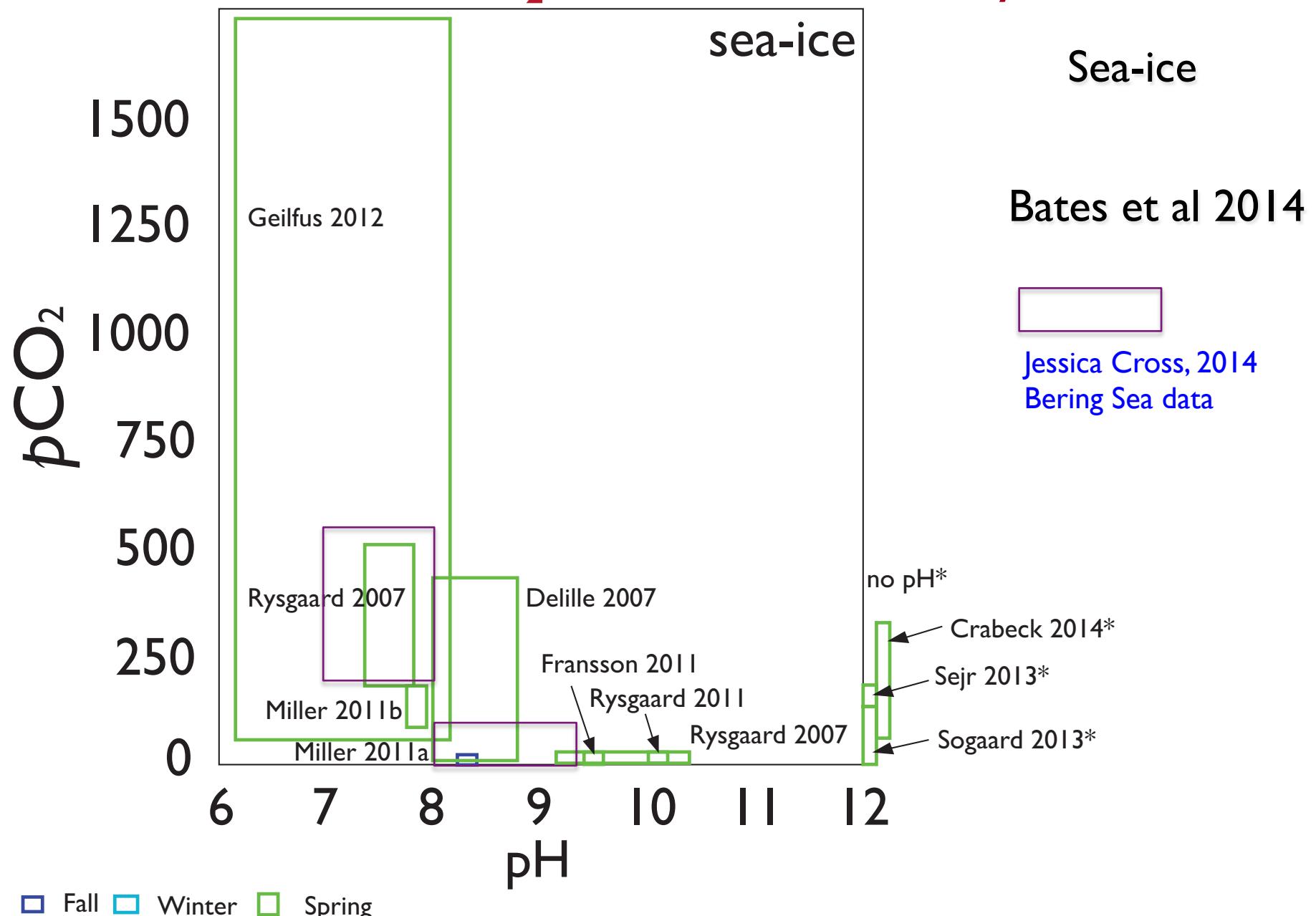
TA, $\mu\text{mol kg}^{-1}$ Melted Sea Ice	TCO ₂ , $\mu\text{mol kg}^{-1}$ Melted Sea Ice	TA:TCO ₂ , mol mol ⁻¹
426 ± 15	320 ± 18	1.33 ± 0.05
403 ± 20	278 ± 16	1.45 ± 0.06
457 ± 19	369 ± 7	1.24 ± 0.06
425 ± 26	285 ± 21	1.49 ± 0.08
573 ± 25	258 ± 19	2.22 ± 0.19
424 ± 24	463 ± 15	0.92 ± 0.03
414 ± 11	425 ± 23	0.97 ± 0.03
406 ± 26	439 ± 13	0.93 ± 0.03
541 ± 34	465 ± 27	1.16 ± 0.01

ice as in Figure 1. YS represents Young Sound, and FB

Sea-ice CO_2 -carbonate chemistry



Sea-ice CO₂-carbonate chemistry



Sea-ice CO₂-carbonate chemistry

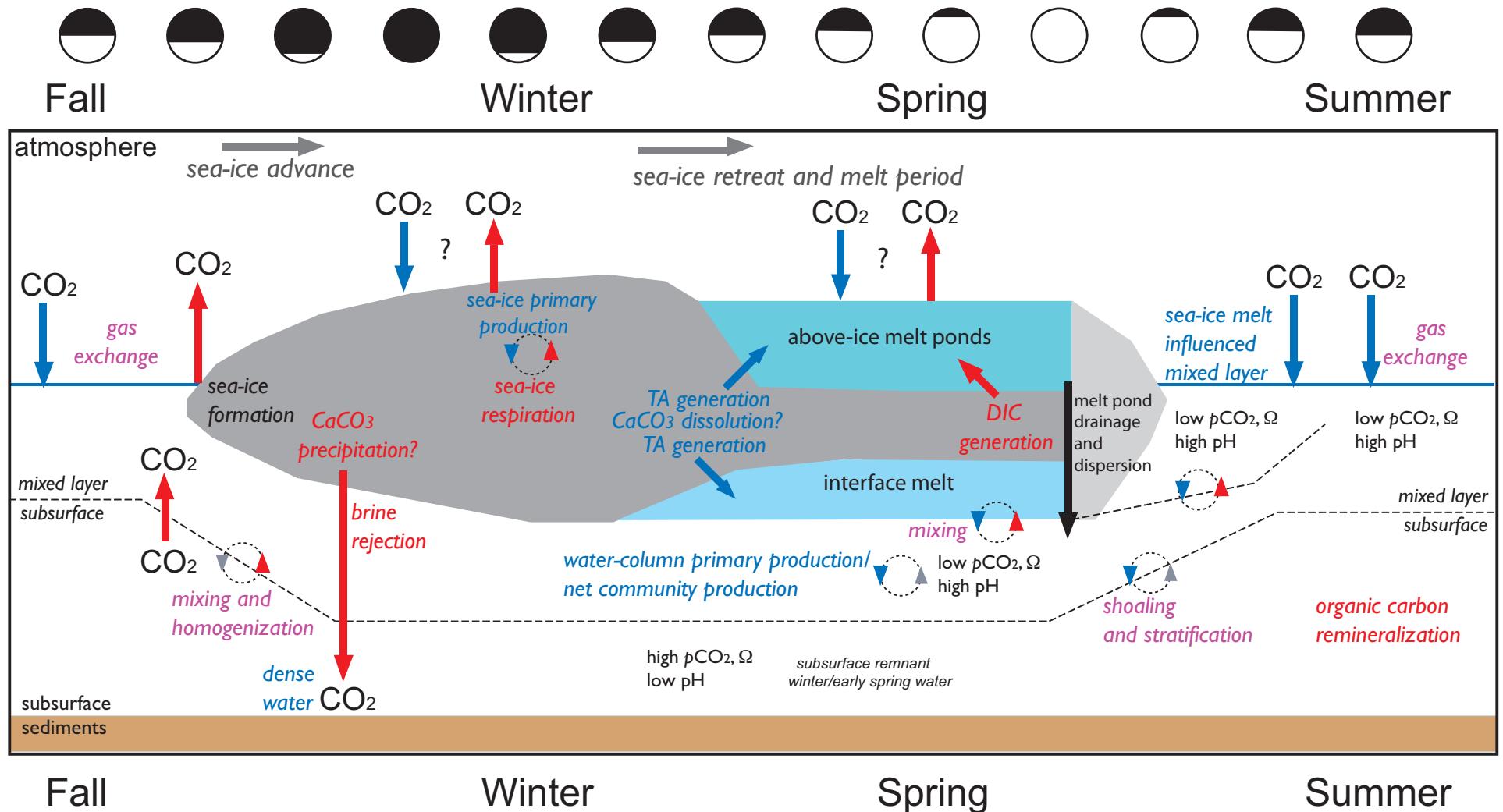
Sea-ice

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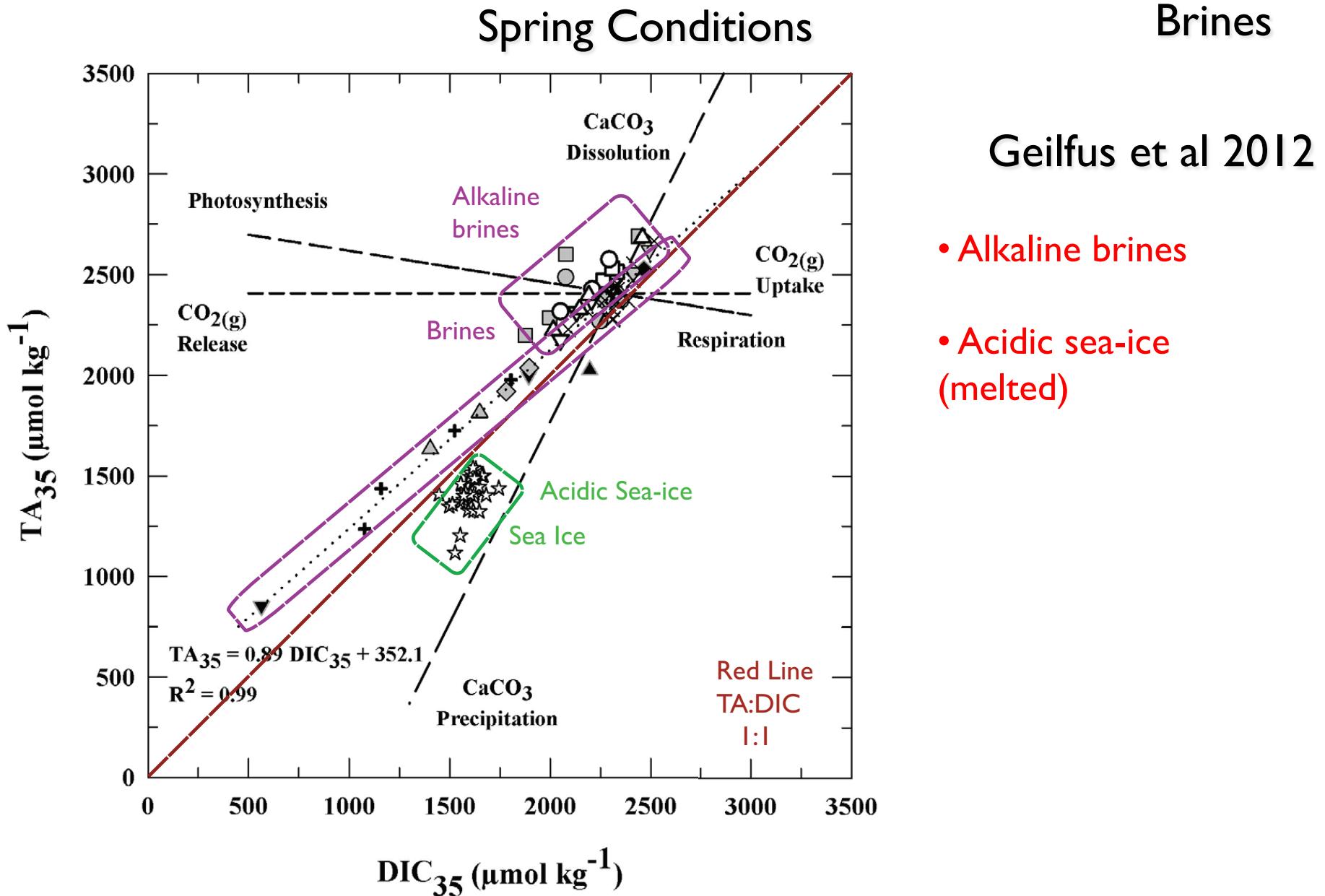
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Sea-ice CO₂-carbonate chemistry

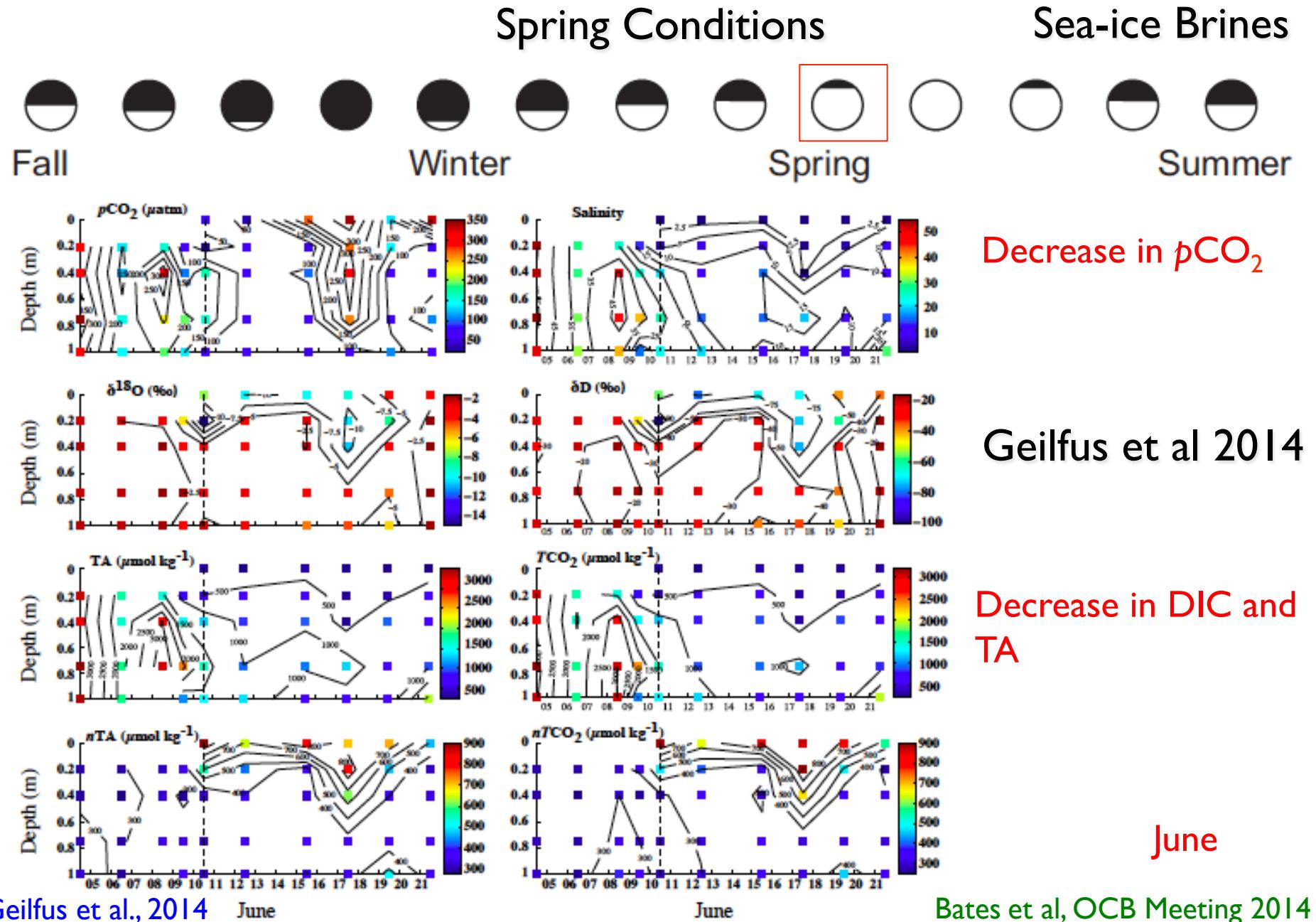
Seasonal changes in generic sea-ice impacted shelf



Sea-ice CO_2 -carbonate chemistry

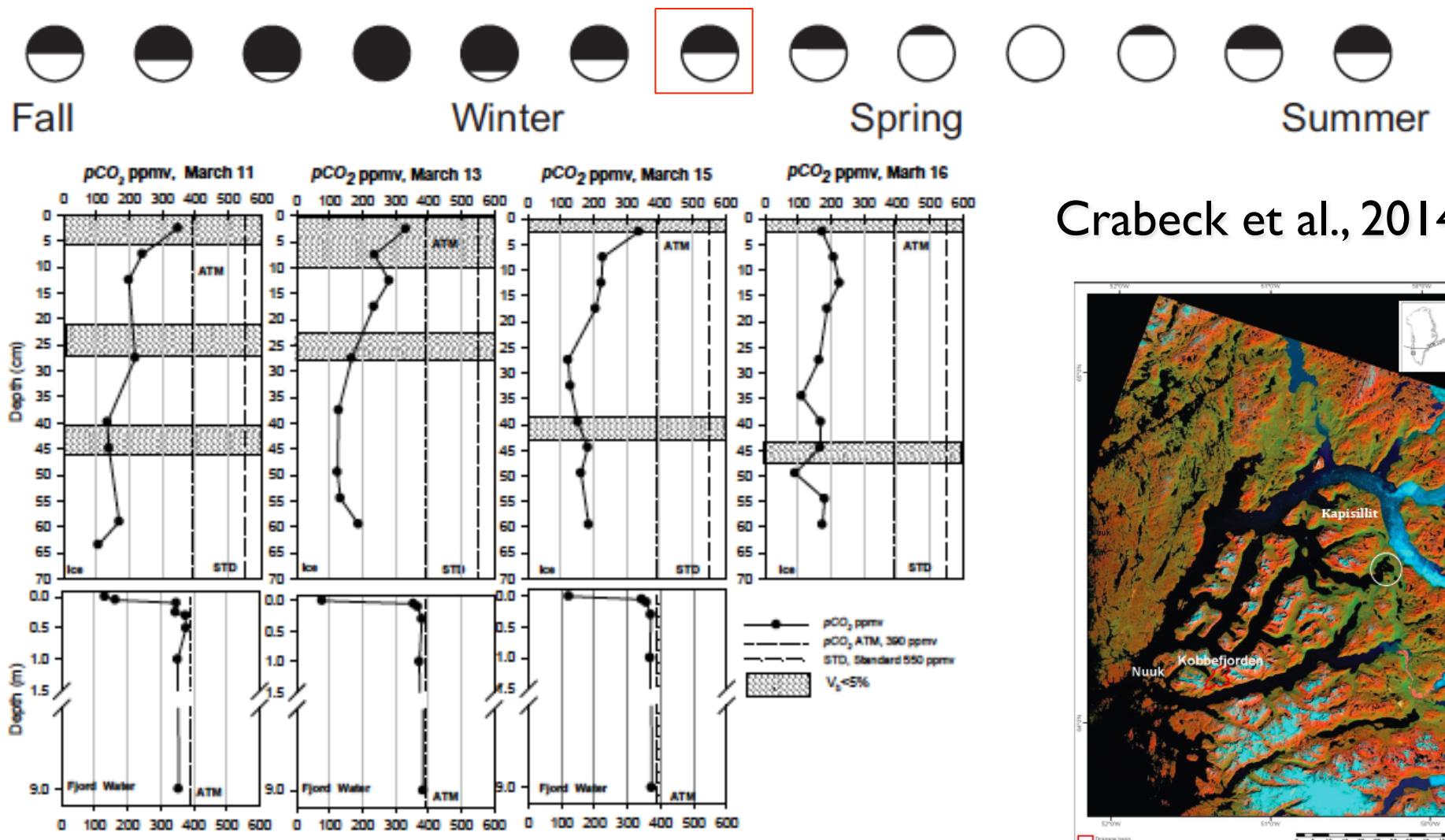


Sea-ice CO₂-carbonate chemistry



Sea-ice CO_2 -carbonate chemistry

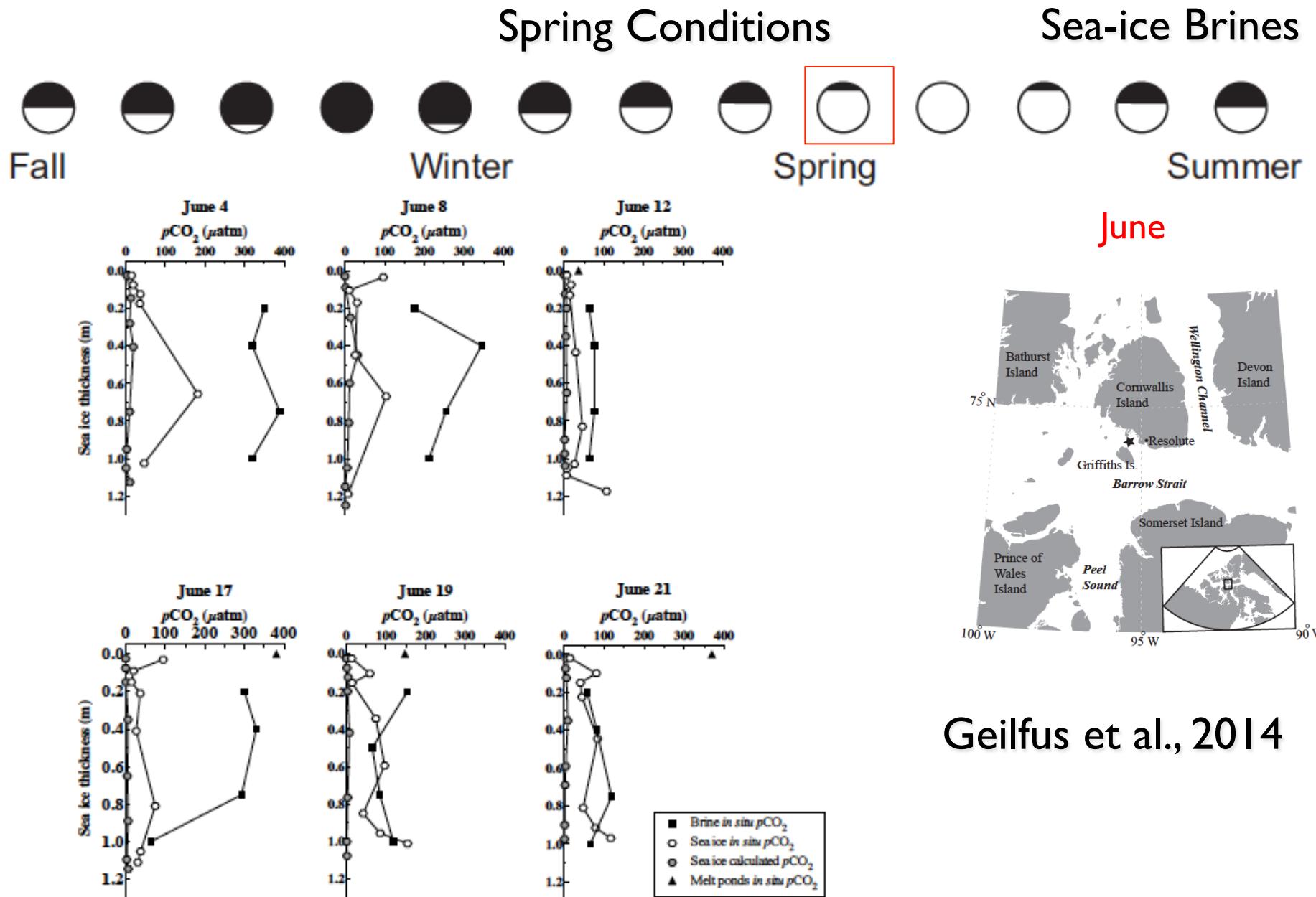
Spring Conditions



Crabeck et al., 2014

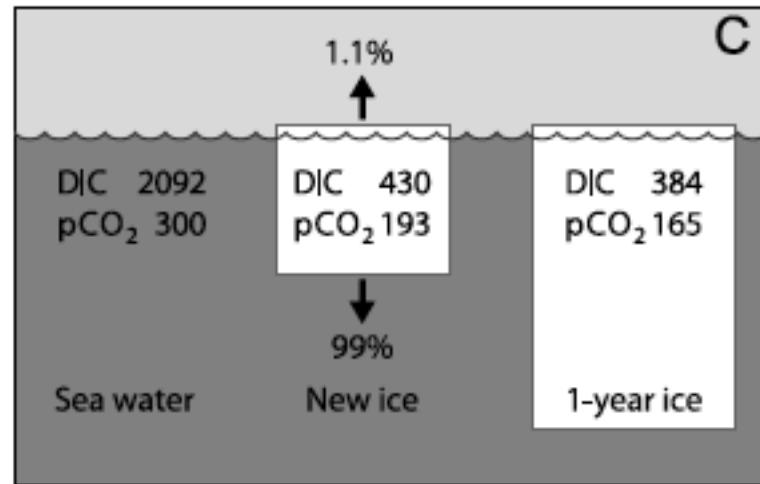
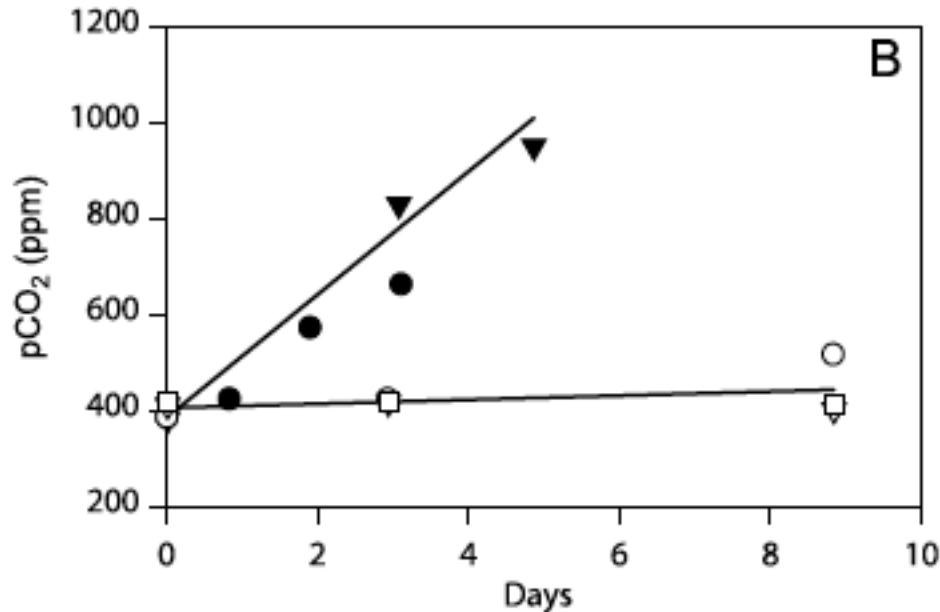
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Sea-ice CO₂-carbonate chemistry

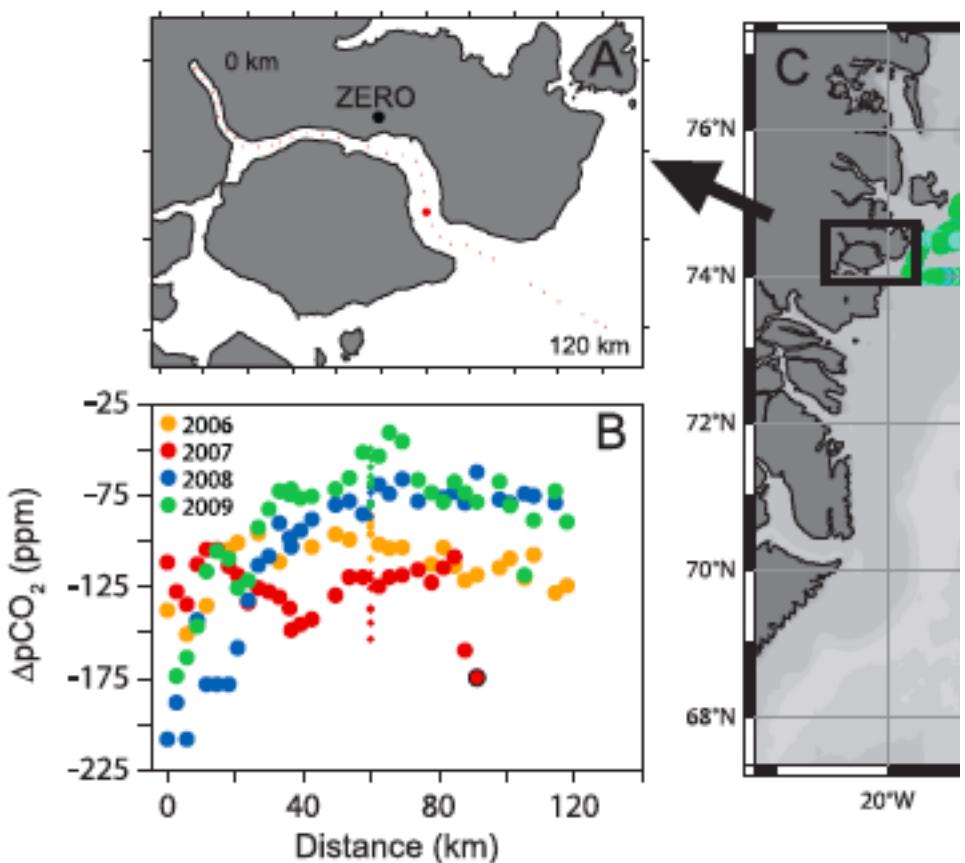


Sea-ice CO_2 -carbonate chemistry

Brines

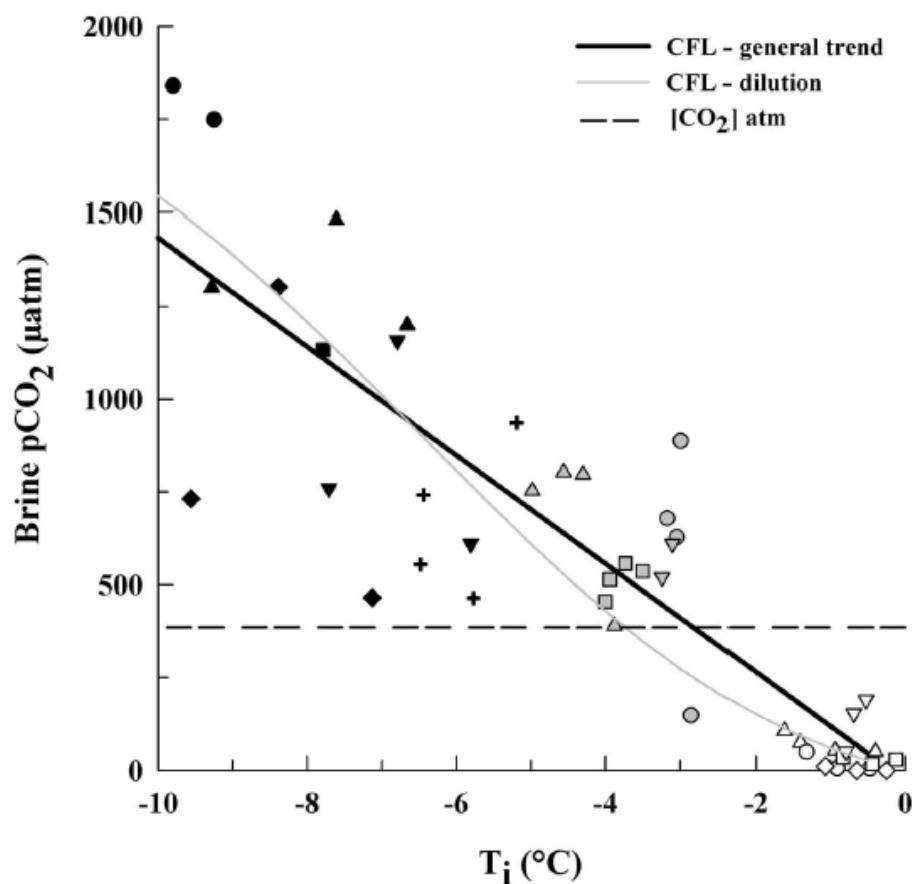


Sejr et al 2012

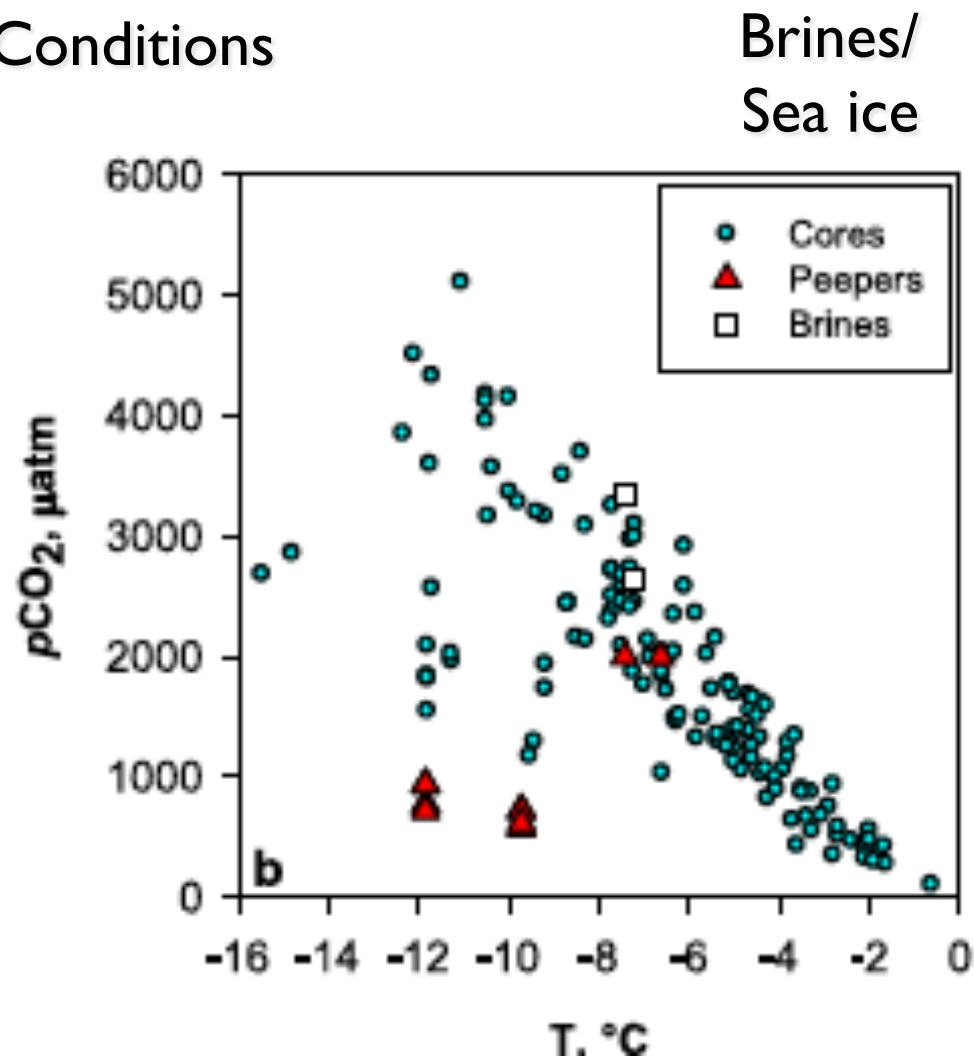


Sea-ice CO_2 -carbonate chemistry

Spring Conditions



Geilfus et al., 2012

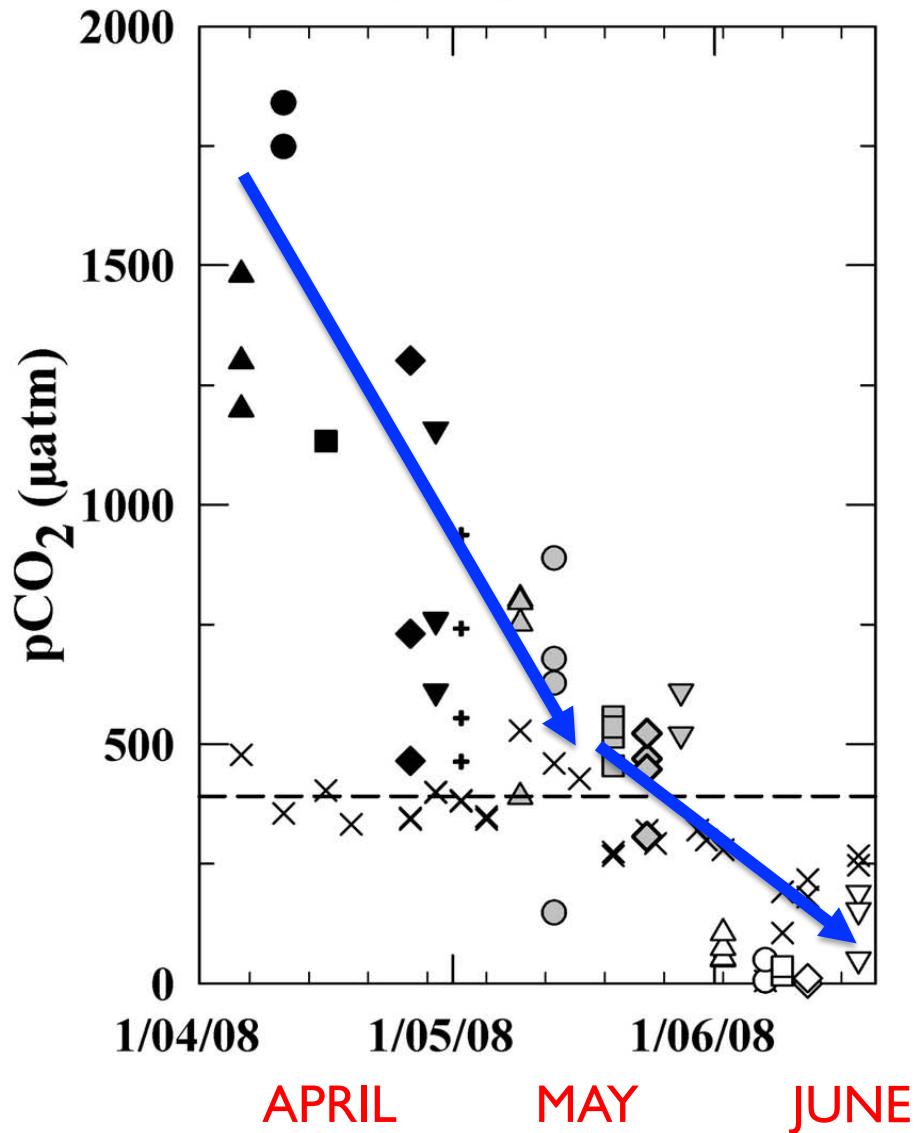


Miller et al., 2011b

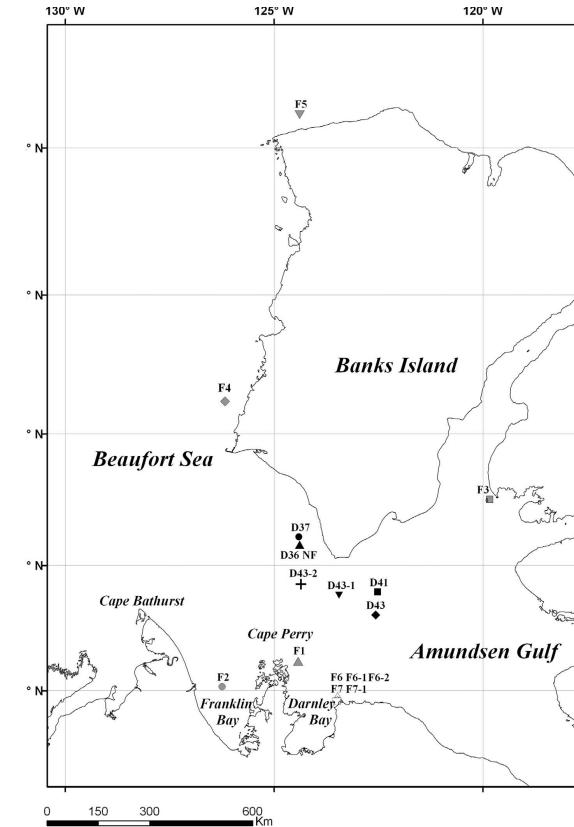
Bates et al, OCB Meeting 2014

Sea-ice CO₂-carbonate chemistry

Spring Conditions: Seasonal Changes



seasonal decrease of
pCO₂ in brines

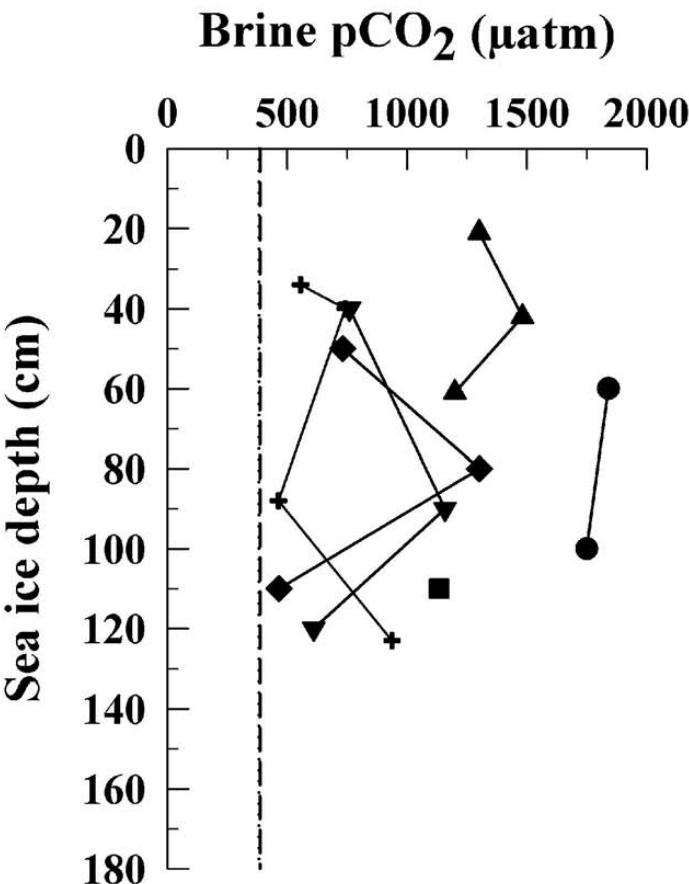


Sea-ice CO_2 -carbonate chemistry

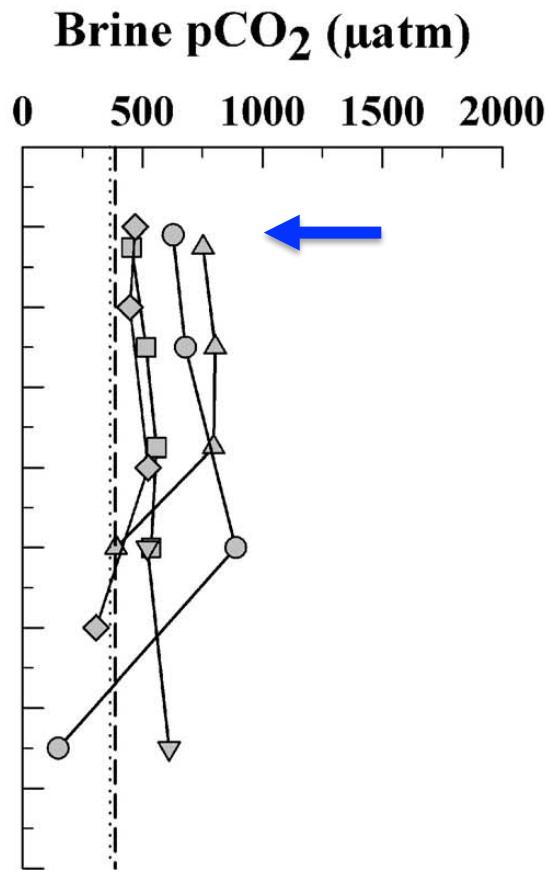
Geilfus et al., 2012

Brines

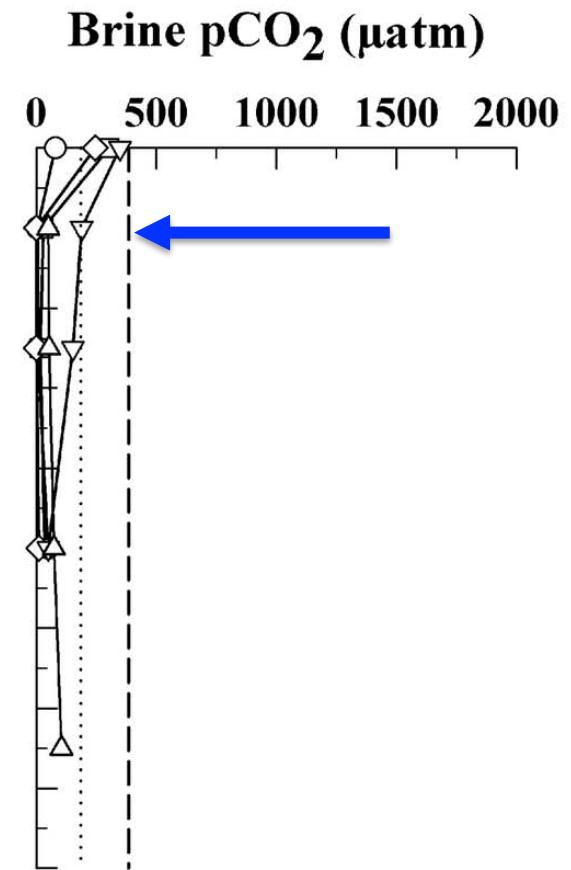
April



May

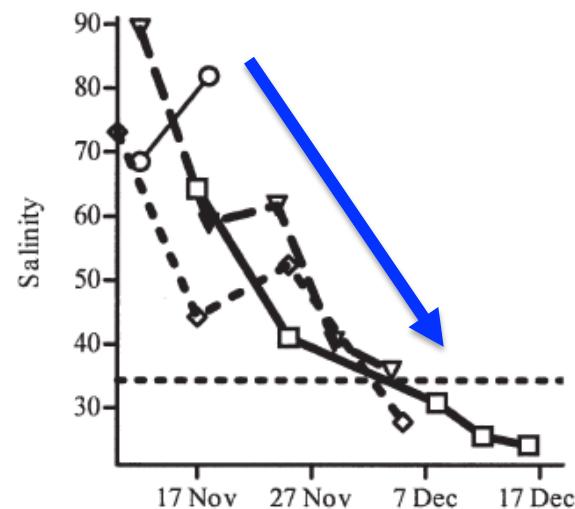
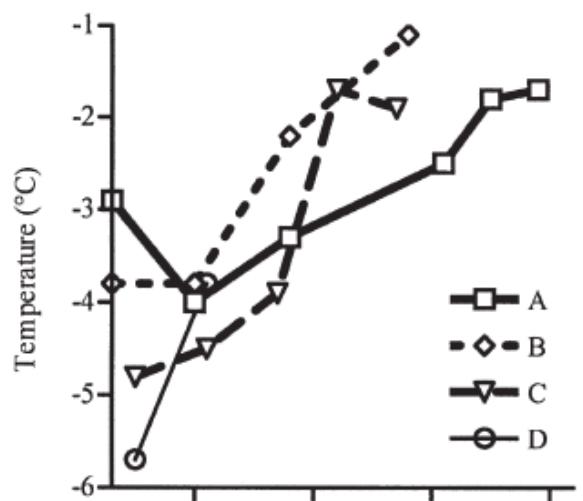


June

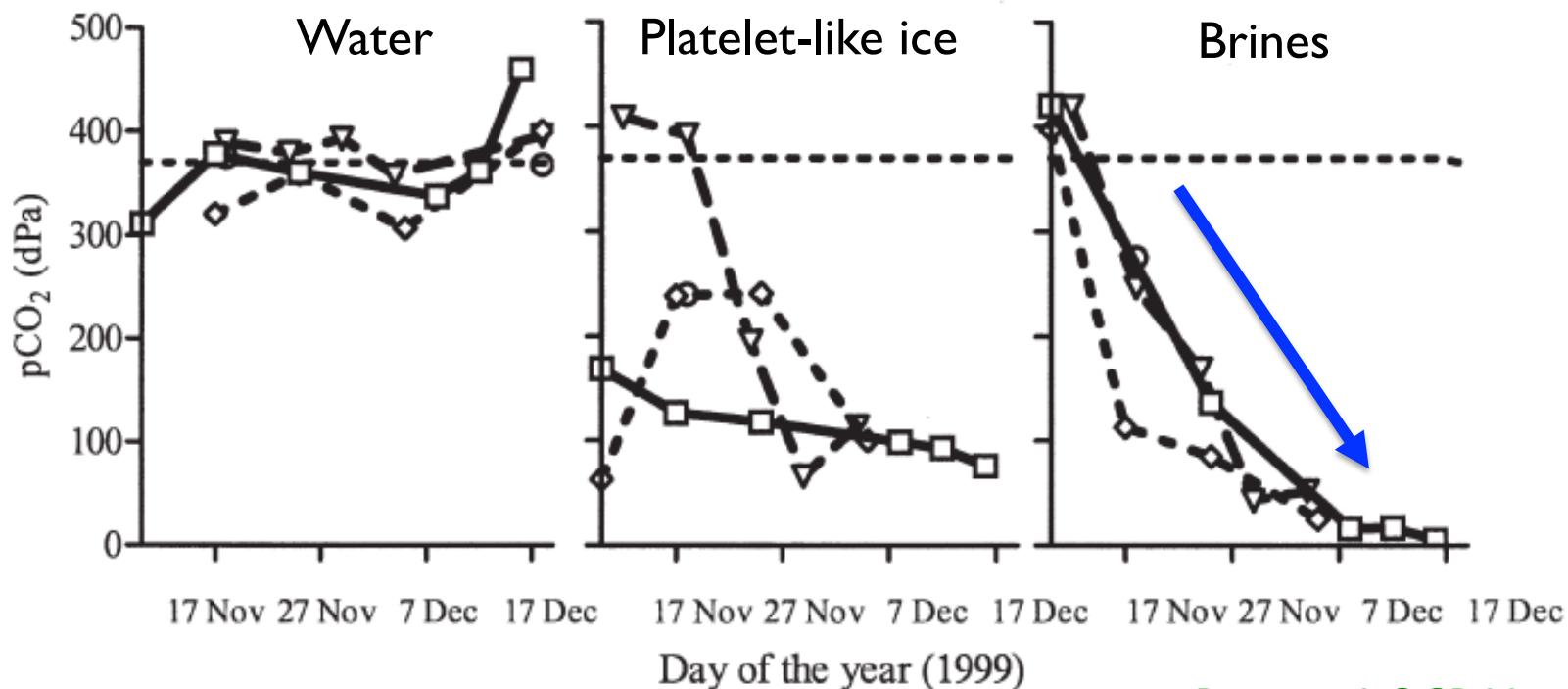


seasonal decrease of pCO_2 in brines

Sea-ice CO_2 -carbonate chemistry



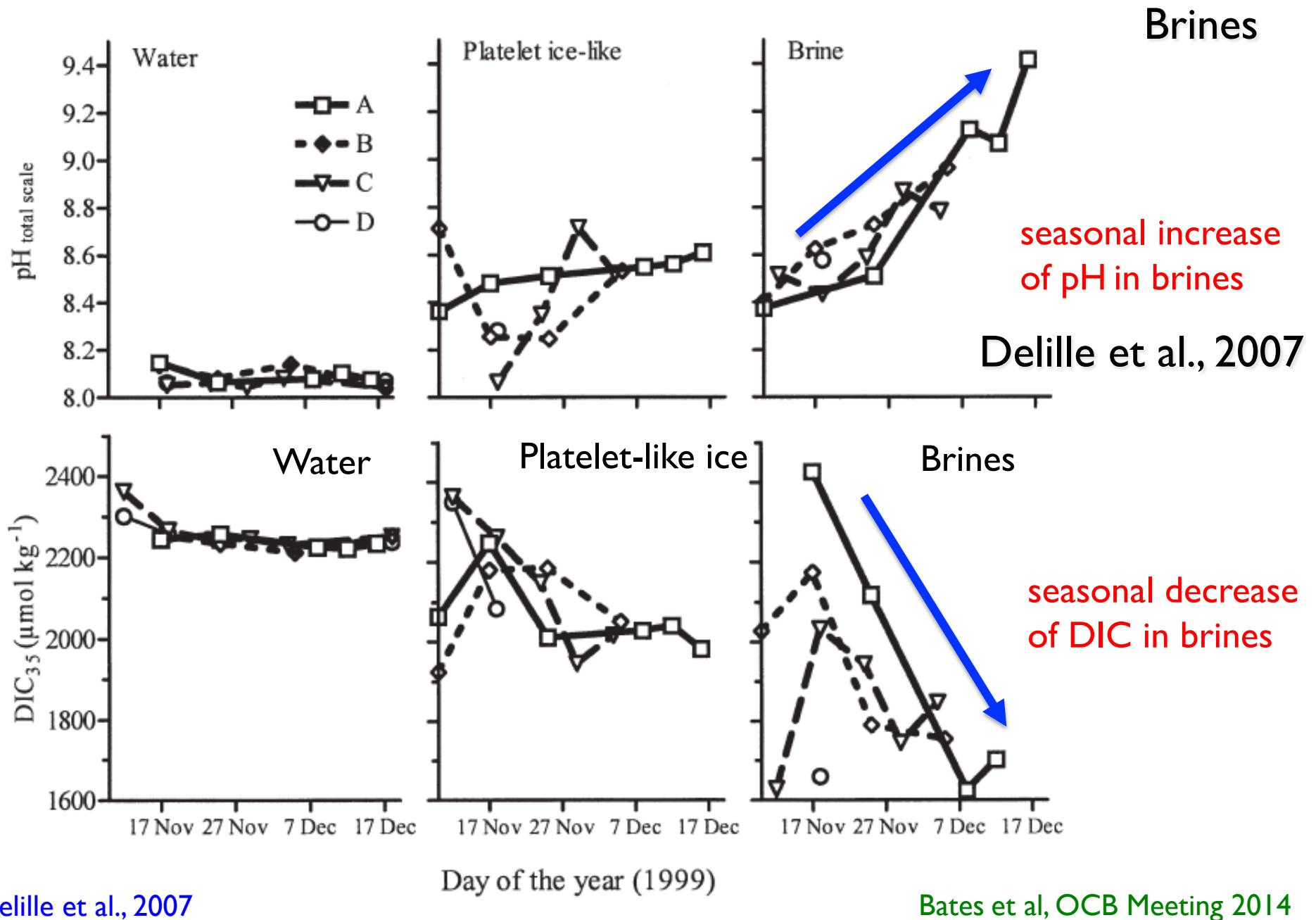
Delille et al., 2007



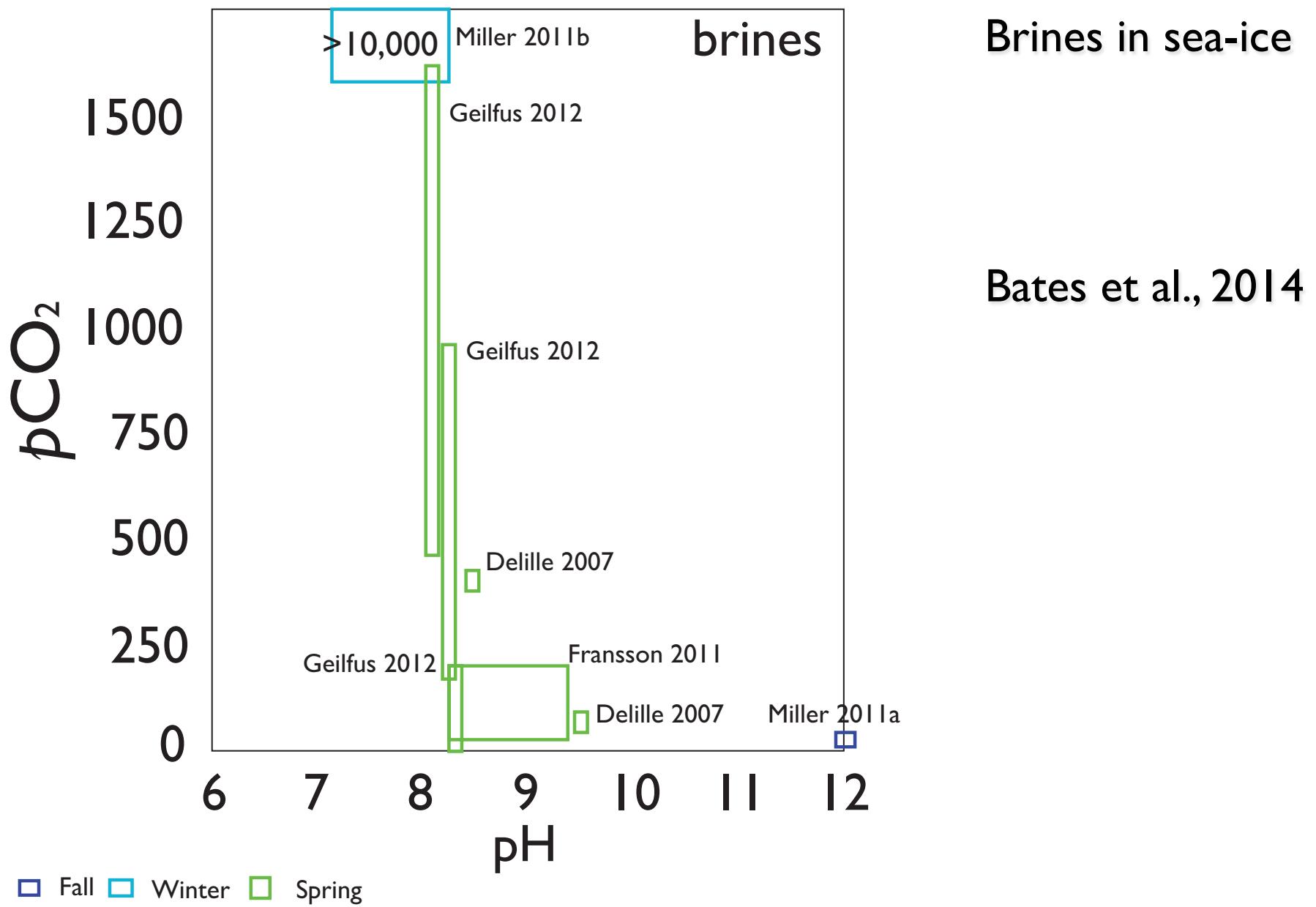
Delille et al., 2007

Bates et al, OCB Meeting 2014

Sea-ice CO_2 -carbonate chemistry



Sea-ice CO₂-carbonate chemistry



Bates et al., 2014

Bates et al., 2014

Sea-ice CO₂-carbonate chemistry

Sea-ice Brines

Study	Location	Period	Season	$p\text{CO}_2$ (μatm)	pH	Ω_{calcite}	$\Omega_{\text{aragonite}}$
Brine							
Miller et al., 2011a	Arctic	Nov. to Dec	Fall	<1	12.4	22.5	4.6
Miller et al., 2011b	Arctic	Dec to Mar	Winter	~800 to 12,000	8.2 to 7.1	11.9-1.3	0.8-7.4
Miller et al., 2011b	Arctic	April to June	Spring	~800 to 12,000	8.2 to 7.1	1.3-11.9	0.8-7.4
Geilfus et al. 2012a	Arctic	April	Spring	465 to 1834	8.0	3.0	1.6
Geilfus et al. 2012a	Arctic	May	Spring	147 to 888	8.2	1.5	<0.1
Delille et al., 2007	Antarctic	November	Spring	~100	9.42	>20	>6
Delille et al., 2007	Antarctic	December	Spring	~420	8.38	3.4	1.8
Geilfus et al. 2012a	Arctic	June	Spring	0 to 180	8.3	0.1	<0.1
Geilfus et al. 2014	Arctic	June	Spring	20 to 389			
Fransson et al 2011	Antarctic	Dec. to Jan	Spring	9 to 210	9.3-8.3	3.7-14.8	2.3-9.3

Table 1. Summary of measured and calculated $p\text{CO}_2$ values reported in sea-ice brine, sea-ice and melt ponds. The studies are arranged in seasonal order from fall to spring observations where possible. In most cases, $p\text{CO}_2$, pH, Ω_{calcite} , and $\Omega_{\text{aragonite}}$ were calculated from TA and DIC, or from $p\text{CO}_2$ and pH. In the cases where values were reported in the original study, salinity and temperature values of 4 and 0°C were used in the calculations. (from Bates et al., 2014).

Sea-ice CO₂-carbonate chemistry

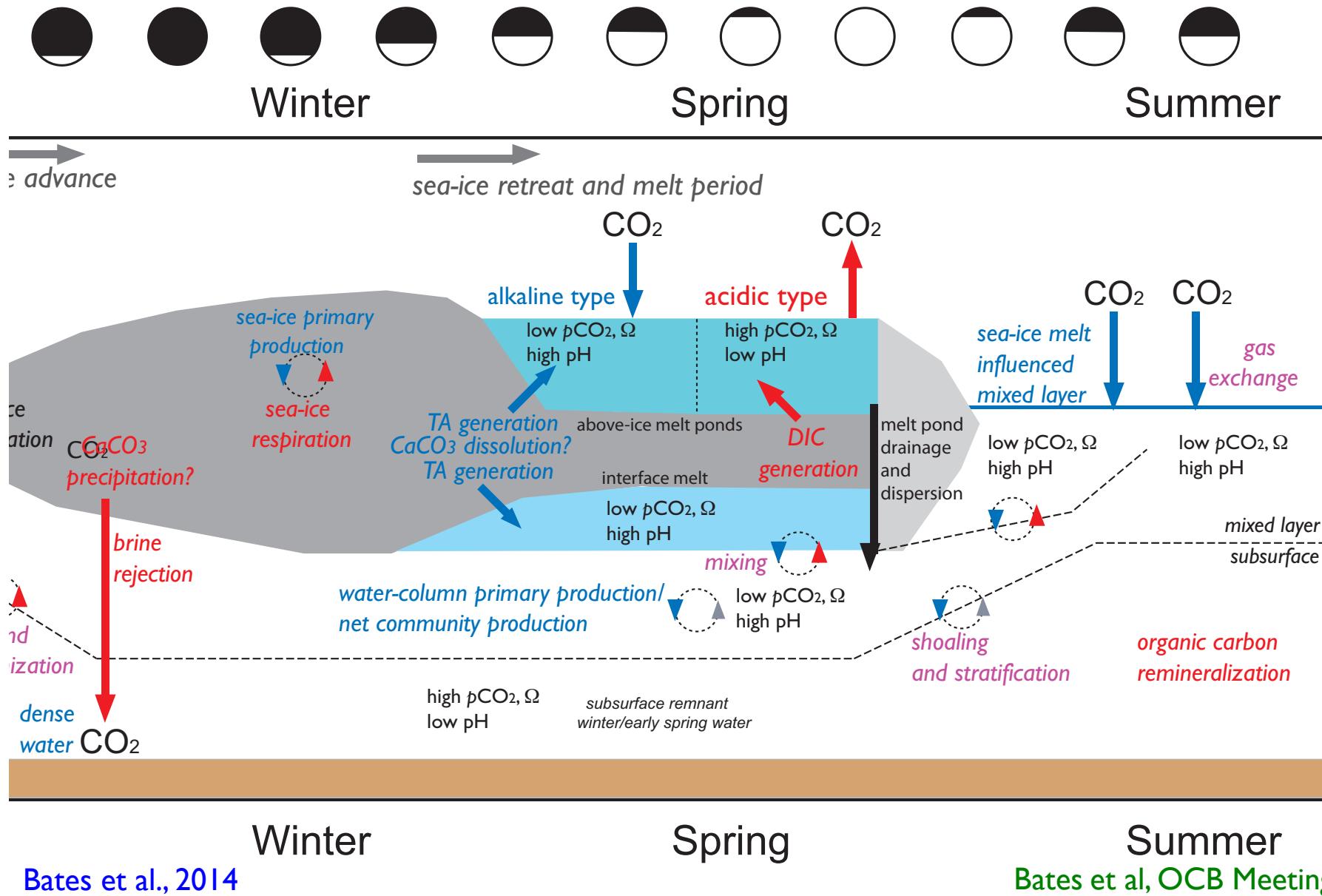
Sea-ice

Study	Location	Period	Season	pCO ₂ (μatm)	pH	Ω_{calcite}	$\Omega_{\text{aragonite}}$
Sea-Ice							
Miller et al., 2011a	Arctic	Nov. to Dec	Fall	<1	8.20	0.42	0.25
Miller et al., 2011a	Arctic	Nov. to Dec	Fall	<1	8.97	1.75	0.96
Rysgaard et al. 2007	Arctic	March	Spring	<1 to 6	9.1-10.4	1.6-5.5	0.86-3.0
Crabeck et al. 2014	Arctic	March	Spring	60 to 330 (1)			
Miller et al., 2011b	Arctic	April to June	Spring	103 to 197	7.7-7.97	<0.1	<0.1
Sejr et al. 2011	Greenland	March/April	Spring	165 and 195			
Rysgaard et al. 2007	Arctic	April	Spring	204 to 522	7.36-7.8	<0.05	<0.05
Delille et al., 2007	Antarctic	Nov. to Dec	Spring	<10 to 420	8.0-8.7	0.5	0.3-0.19
Sogaard et al., 2013	Arctic	April	Spring	<2 to ~10			
Sogaard et al., 2013	Arctic	May	Spring	~5 to ~145			
Geilfus et al. 2012a	Arctic	June	Spring	50 to 1800	8.4-6.2	0.56-<0.1	0.3-<0.1
Fransson et al. 2011	Antarctic	Dec. to Jan	Spring	<10	9.3	14.8	9.3
Rysgaard et al. 2011	Arctic	not given	Spring	< 1	10.0	<0.1	<0.1
Rysgaard et al. 2011	Antarctic	not given	Spring	< 1	10.0	<0.1	<0.1

Table 1. Summary of measured and calculated pCO₂ values reported in sea-ice brine, sea-ice and melt ponds. The studies are arranged in seasonal order from fall to spring observations where possible (from Bates et al., 2014).

Sea-ice CO_2 -carbonate chemistry

Seasonal sea-ice melt ponds



Bates et al., 2014

Bates et al., OCB Meeting 2014

Sea-ice CO₂-carbonate chemistry

Seasonal sea-ice melt ponds

Karen Frey Photo

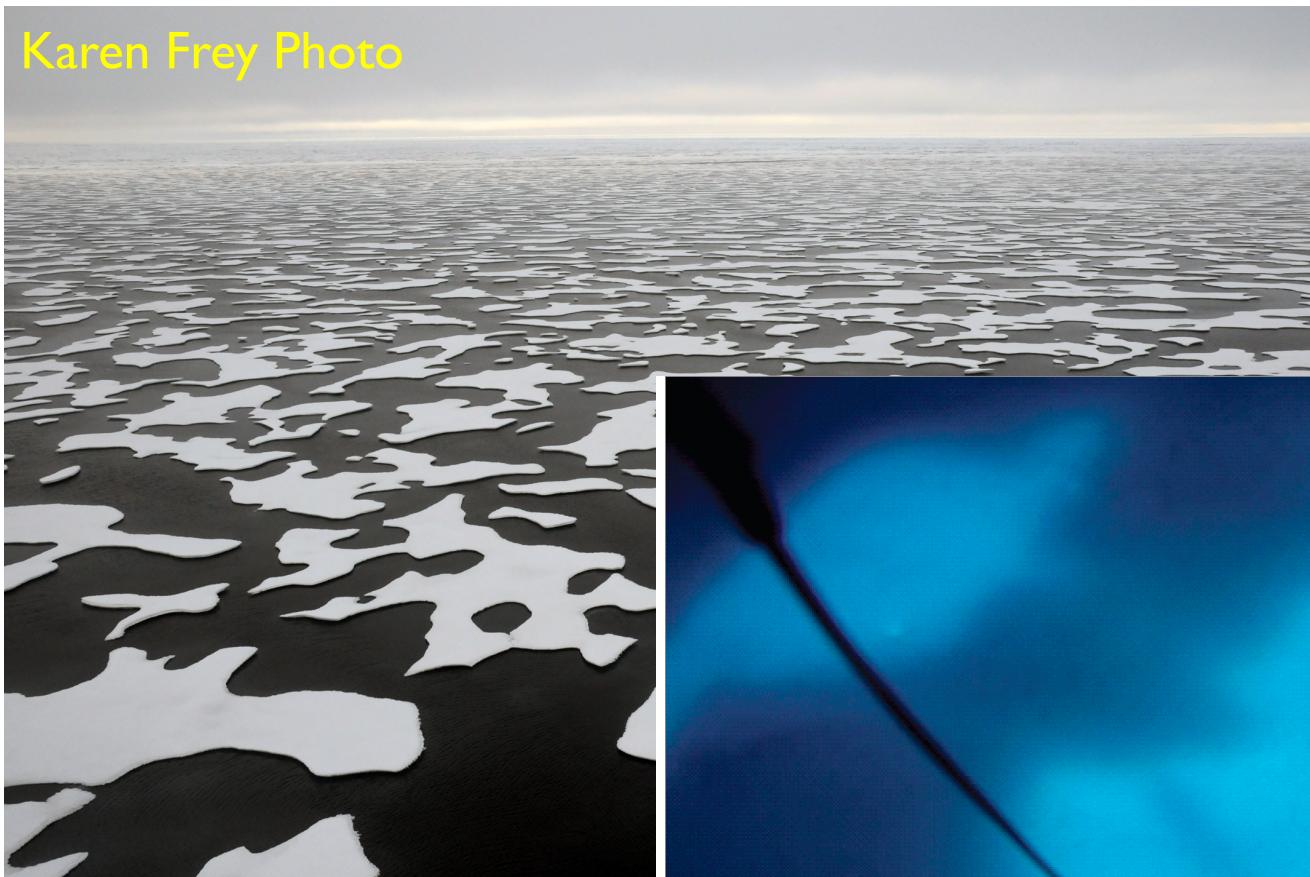


- 12 million km² extent in Arctic at present
- ~20% to 50% cover
- 2 to 4 week duration

Sea-ice CO₂-carbonate chemistry

Seasonal sea-ice melt ponds

Karen Frey Photo



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Karen Frey Photo



Bates et al., 2014

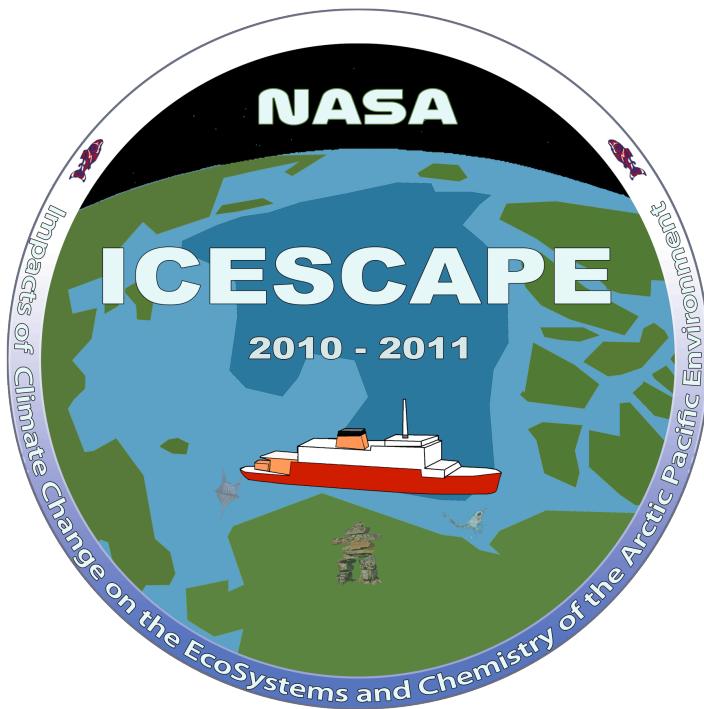
Bates et al, OCB Meeting 2014

Sea-ice CO₂-carbonate chemistry

Sea-ice melt ponds

Bates et al., 2014

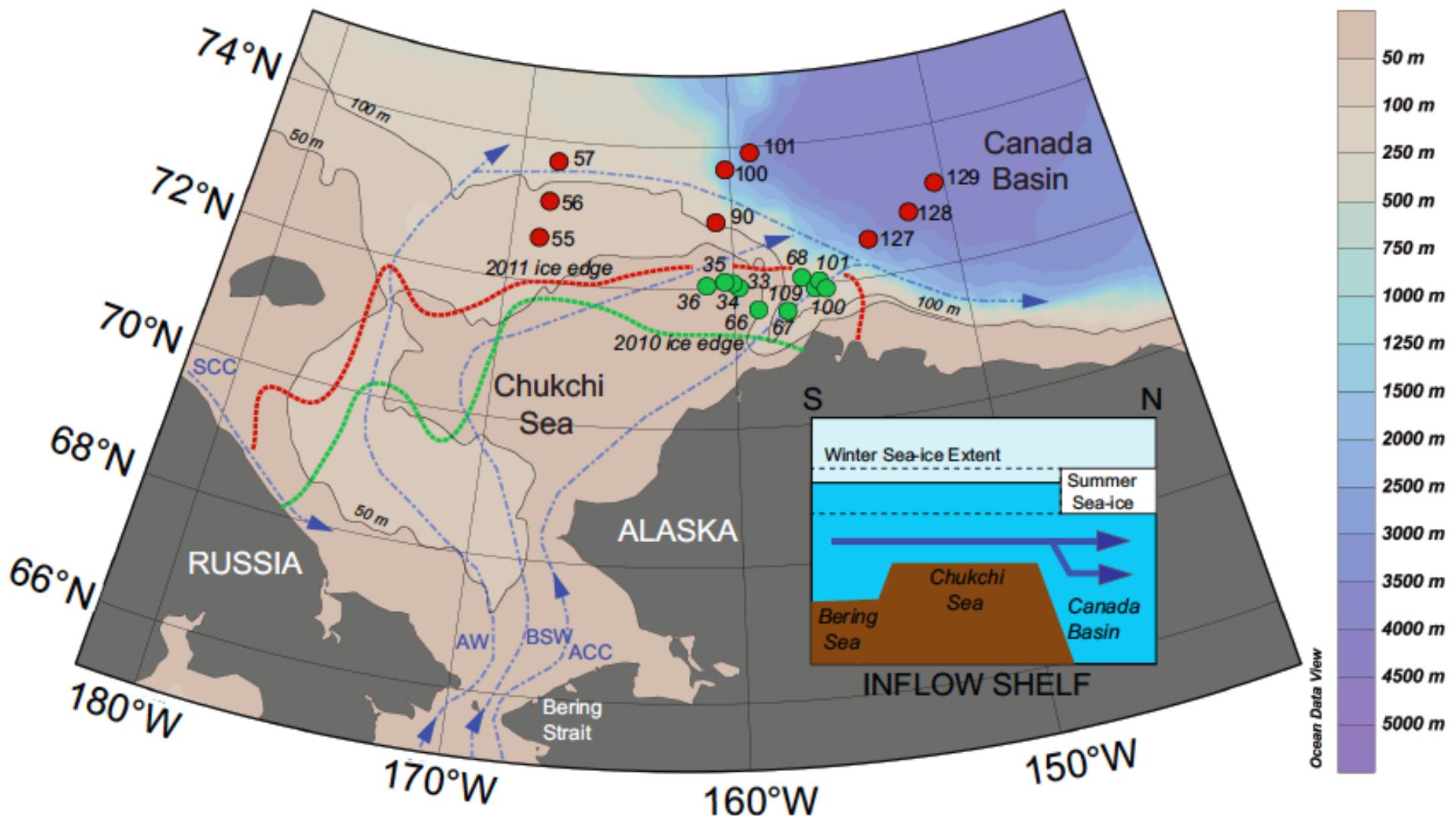
Study	Location	Period	Season	pCO ₂ (μatm)	pH	Ω _{calcite}	Ω _{aragonite}
Ice melt ponds							
Geilfus et al. 2012a	Arctic	June	Spring	79 to 348	n/a	n/a	n/a
this study (acidic type)	Arctic	June/July	Spring	355-1516	7.4 to 6.1	<0.1	<0.1
this study (alkaline)	Arctic	June/July	Spring	<1 to 60	10.8 to 8.6	2.6 to 0.2	1.5 to <0.1



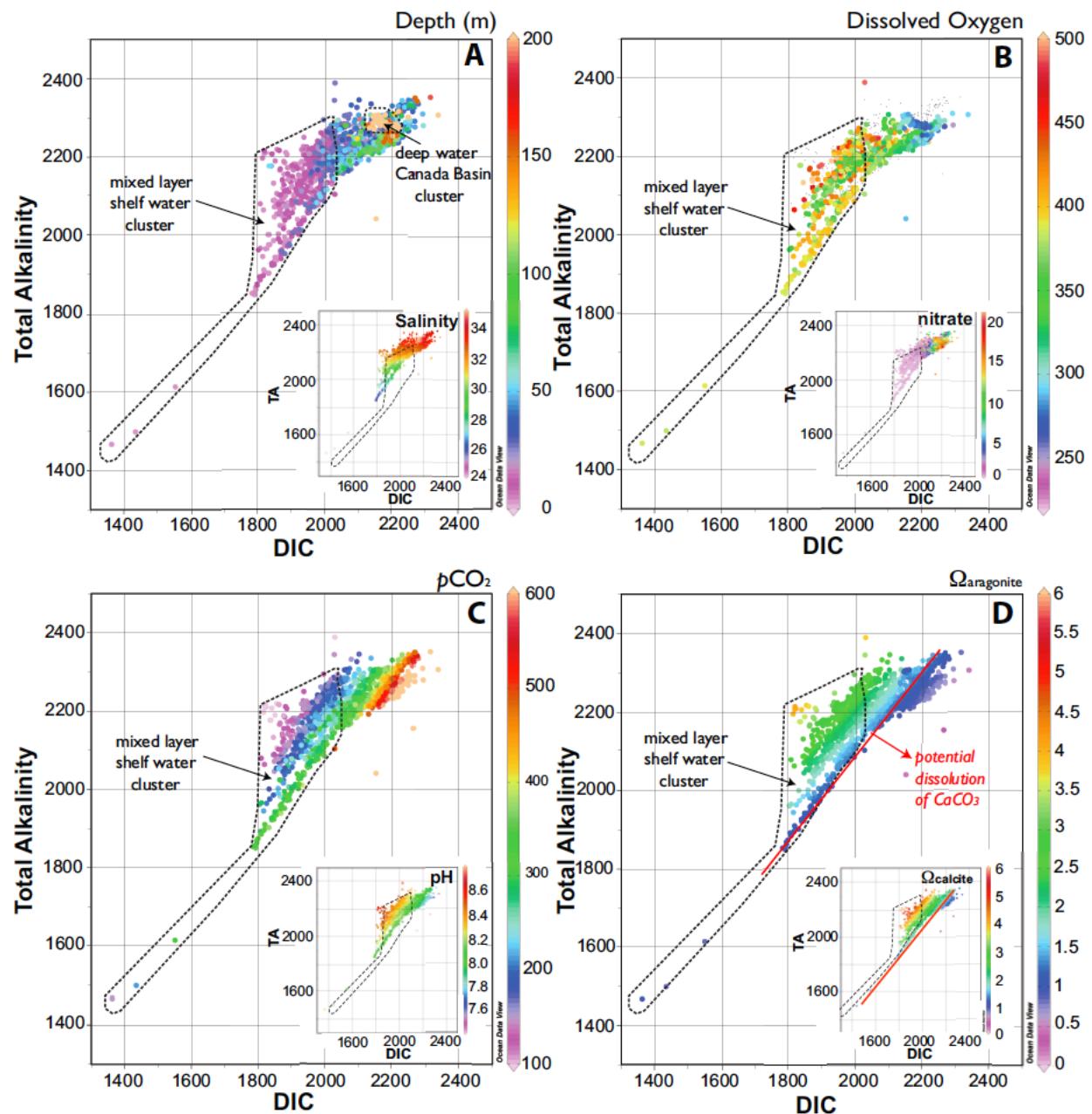
Karen Frey Photo

Sea-ice CO₂-carbonate chemistry

Sea-ice melt ponds



Sea-ice CO₂-carbonate chemistry



Bates et al., 2014

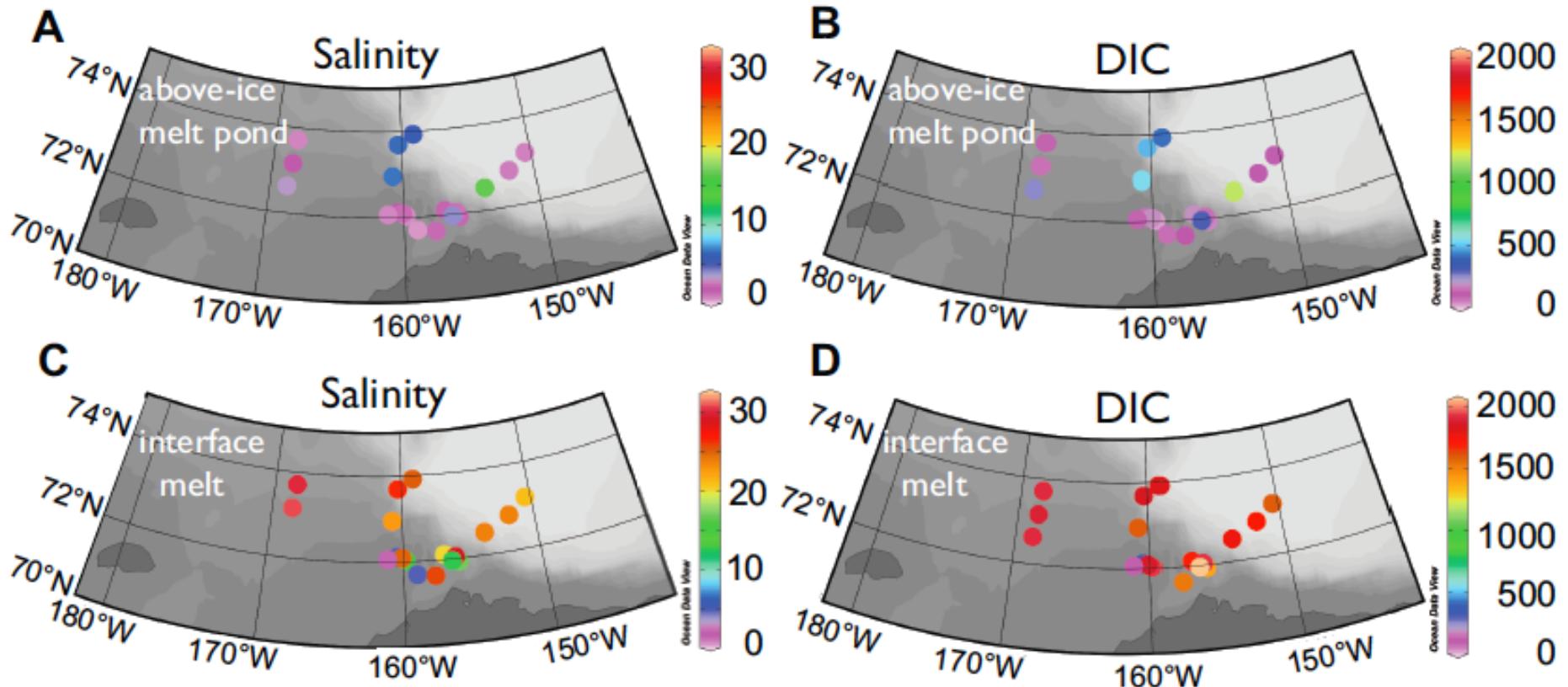
Sea-ice melt ponds

Bates et al., 2014

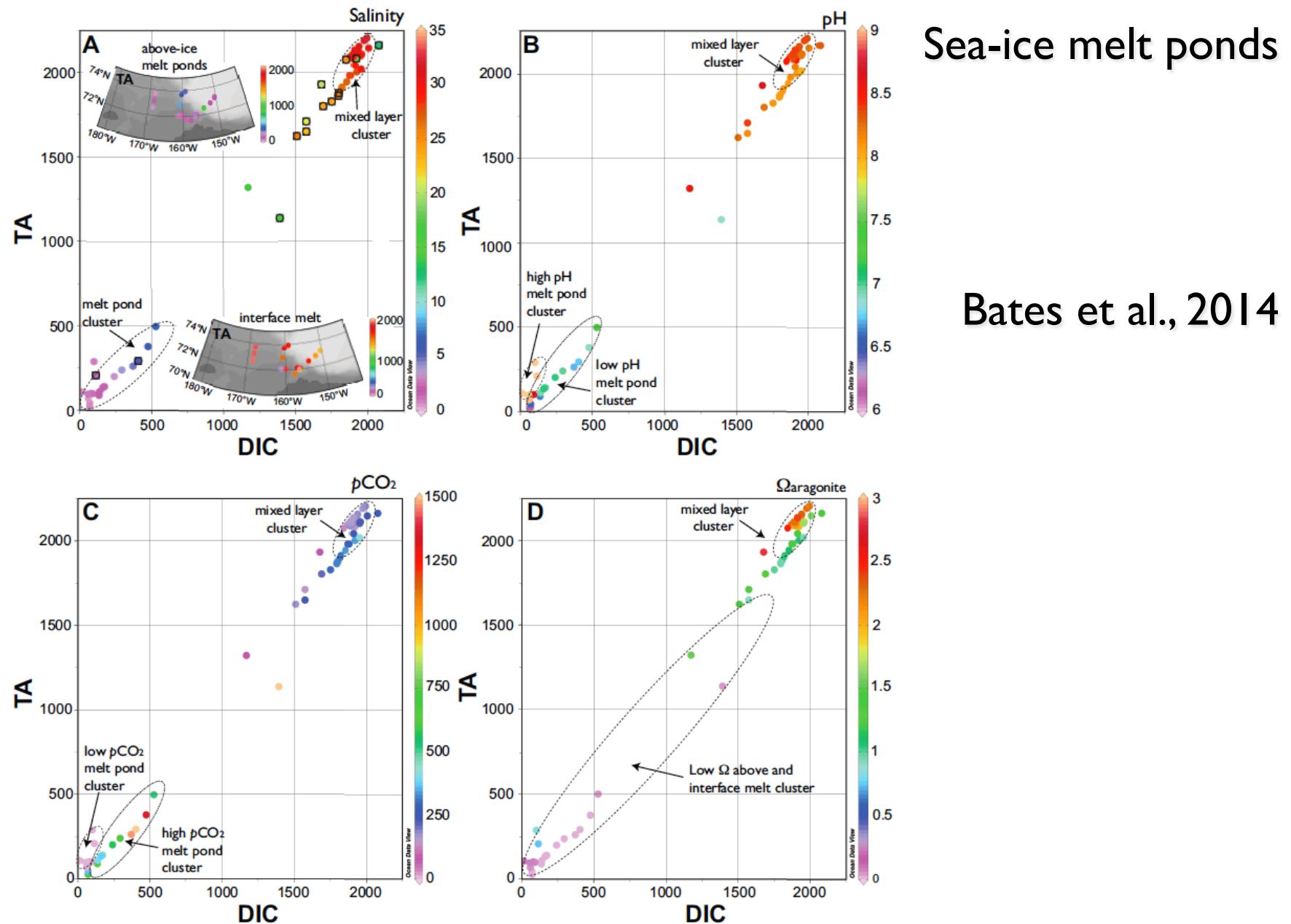
Bates et al, OCB Meeting 2014

Sea-ice CO₂-carbonate chemistry

Sea-ice melt ponds



Sea-ice CO_2 -carbonate chemistry



Bates et al., 2014

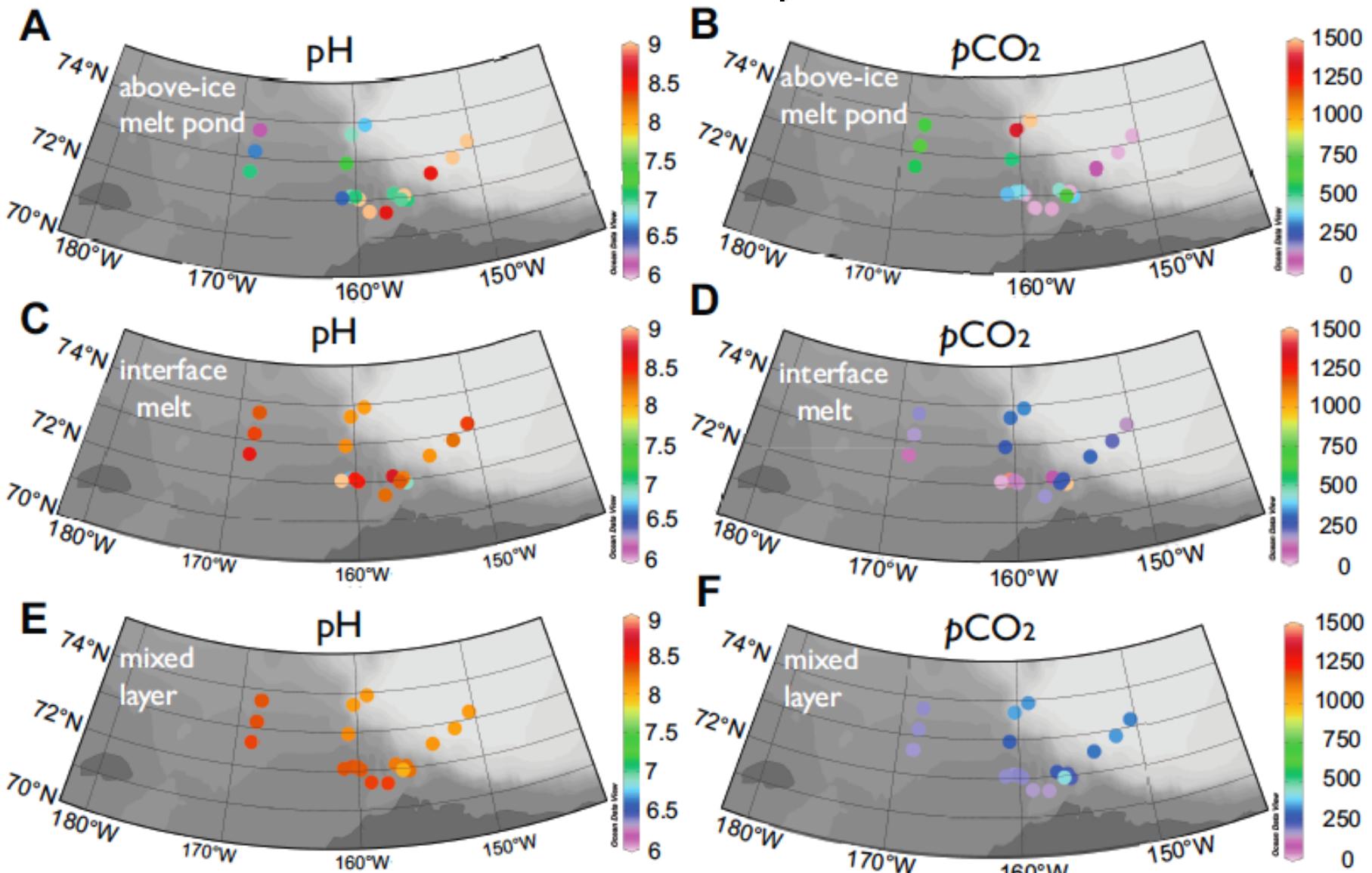
Sea-ice melt ponds

Bates et al., 2014

Bates et al, OCB Meeting 2014

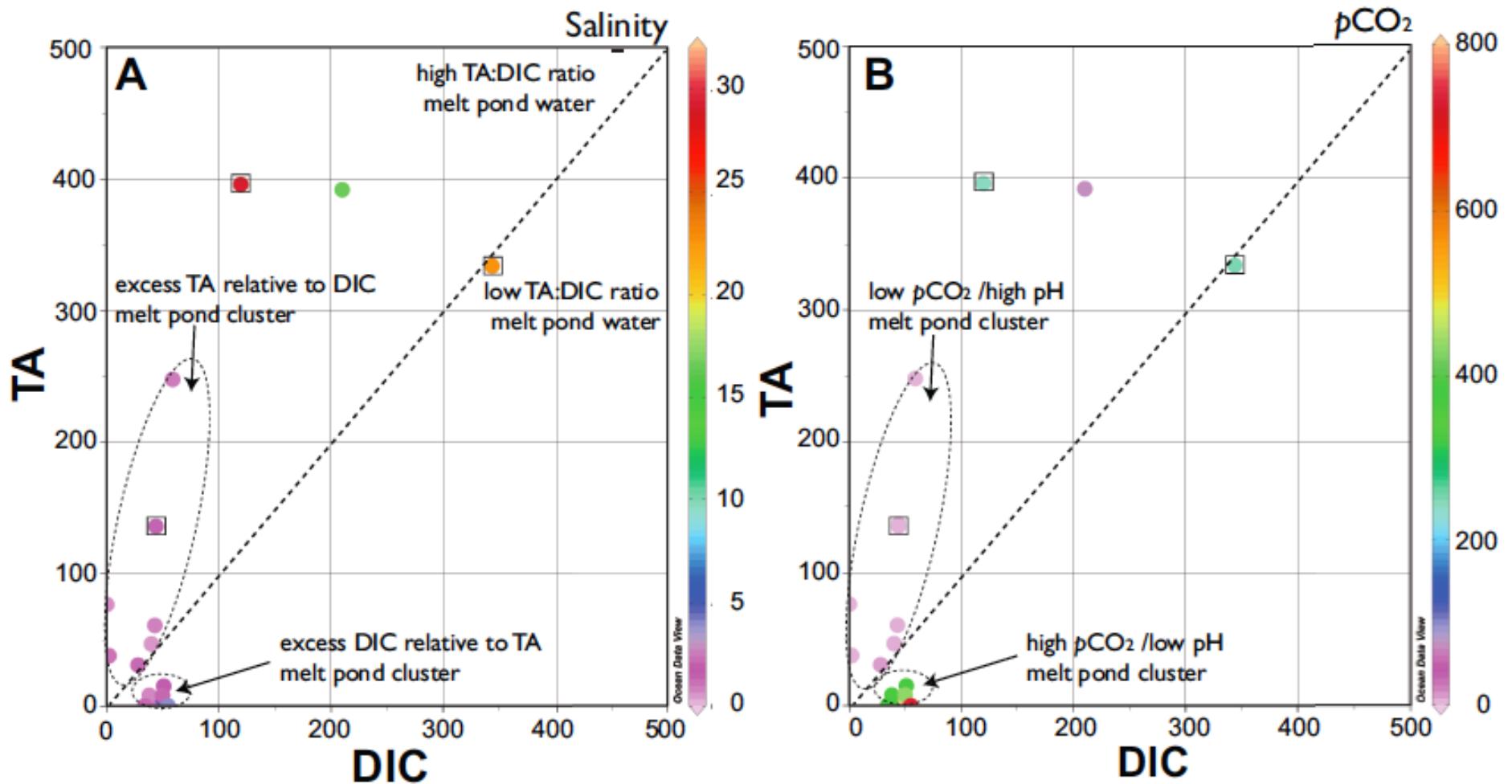
Sea-ice CO₂-carbonate chemistry

Sea-ice melt ponds



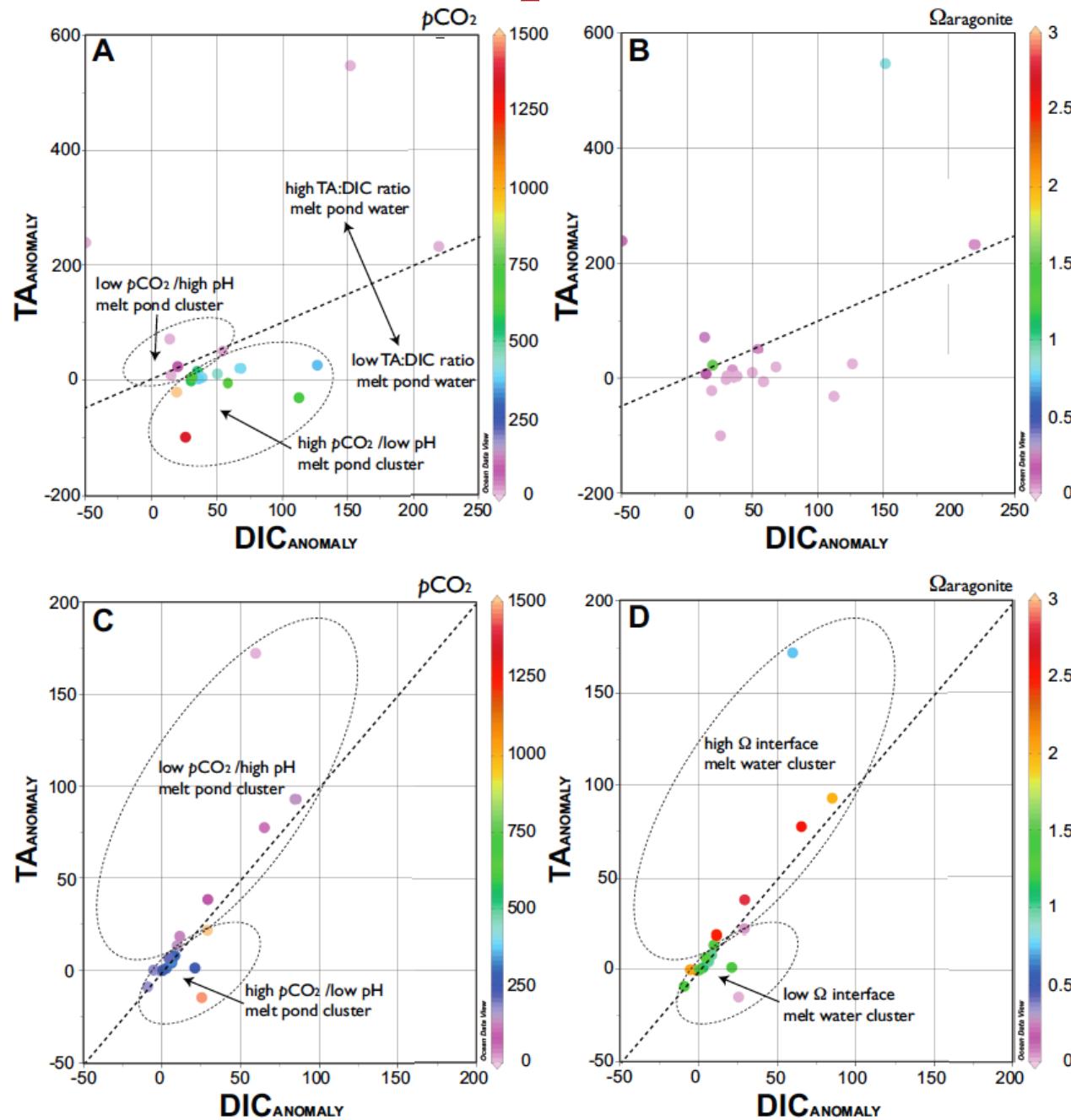
Sea-ice CO₂-carbonate chemistry

Sea-ice melt ponds

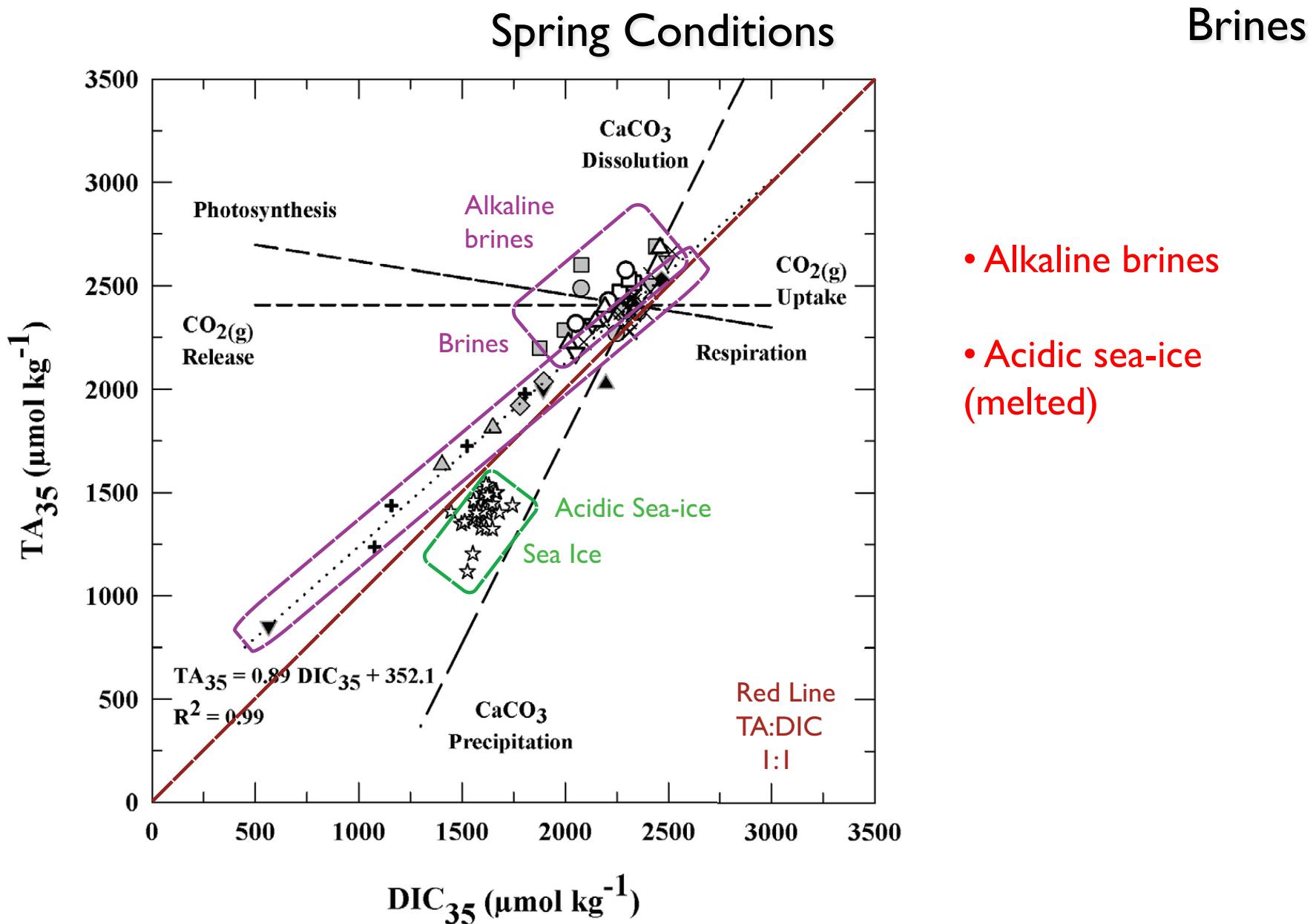


Sea-ice CO₂-carbonate chemistry

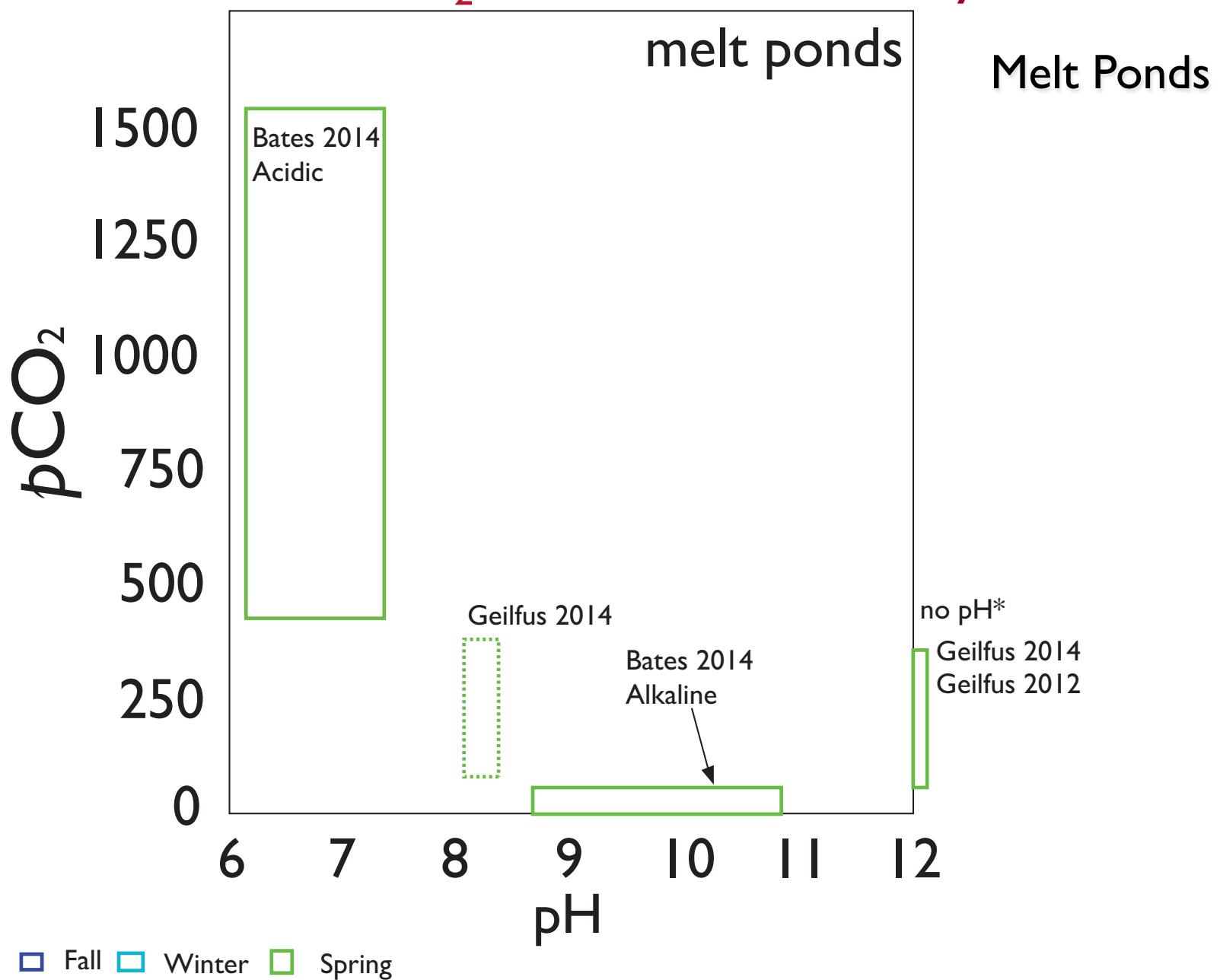
Sea-ice
melt ponds



Sea-ice CO_2 -carbonate chemistry

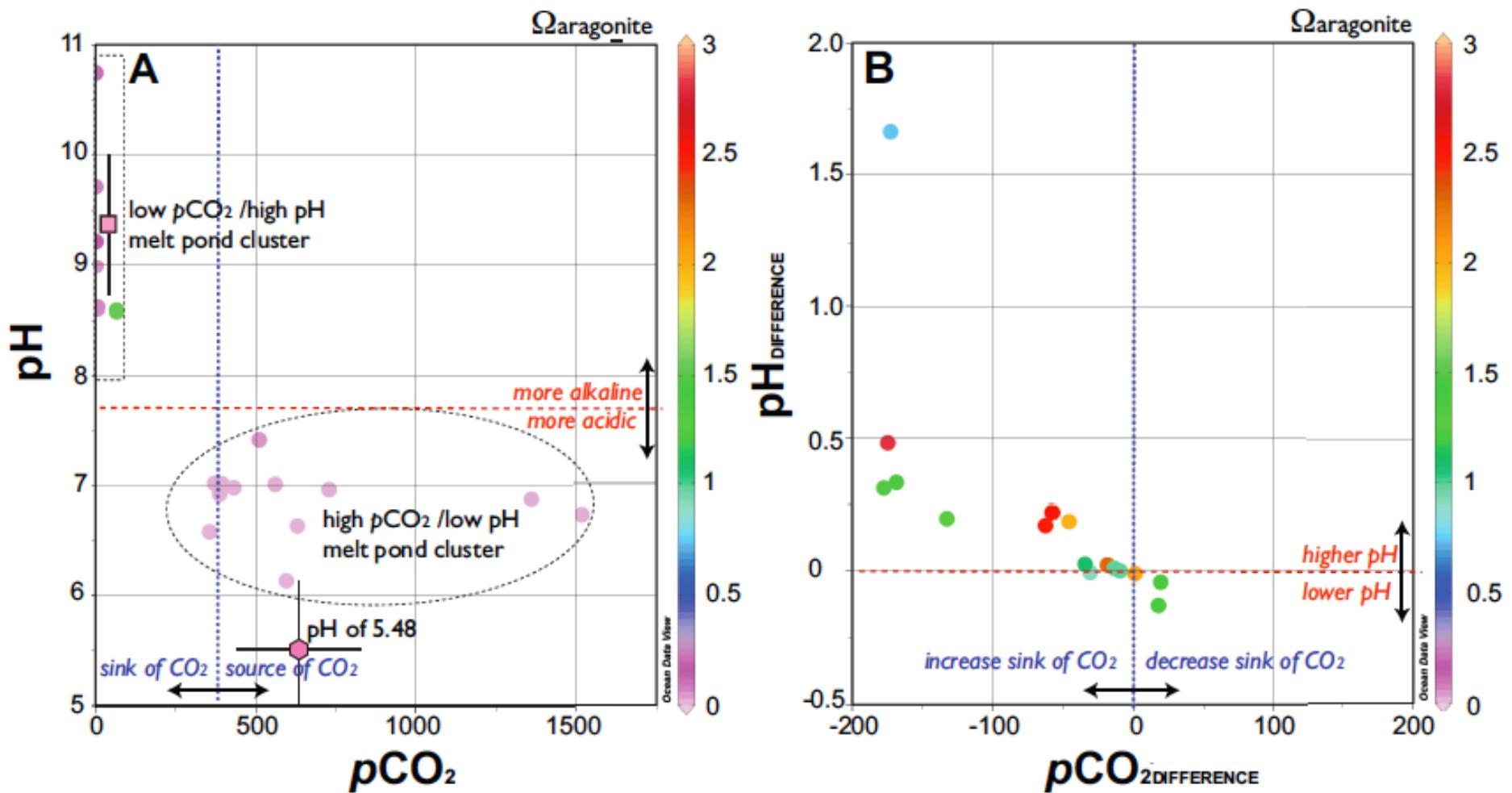


Sea-ice CO_2 -carbonate chemistry



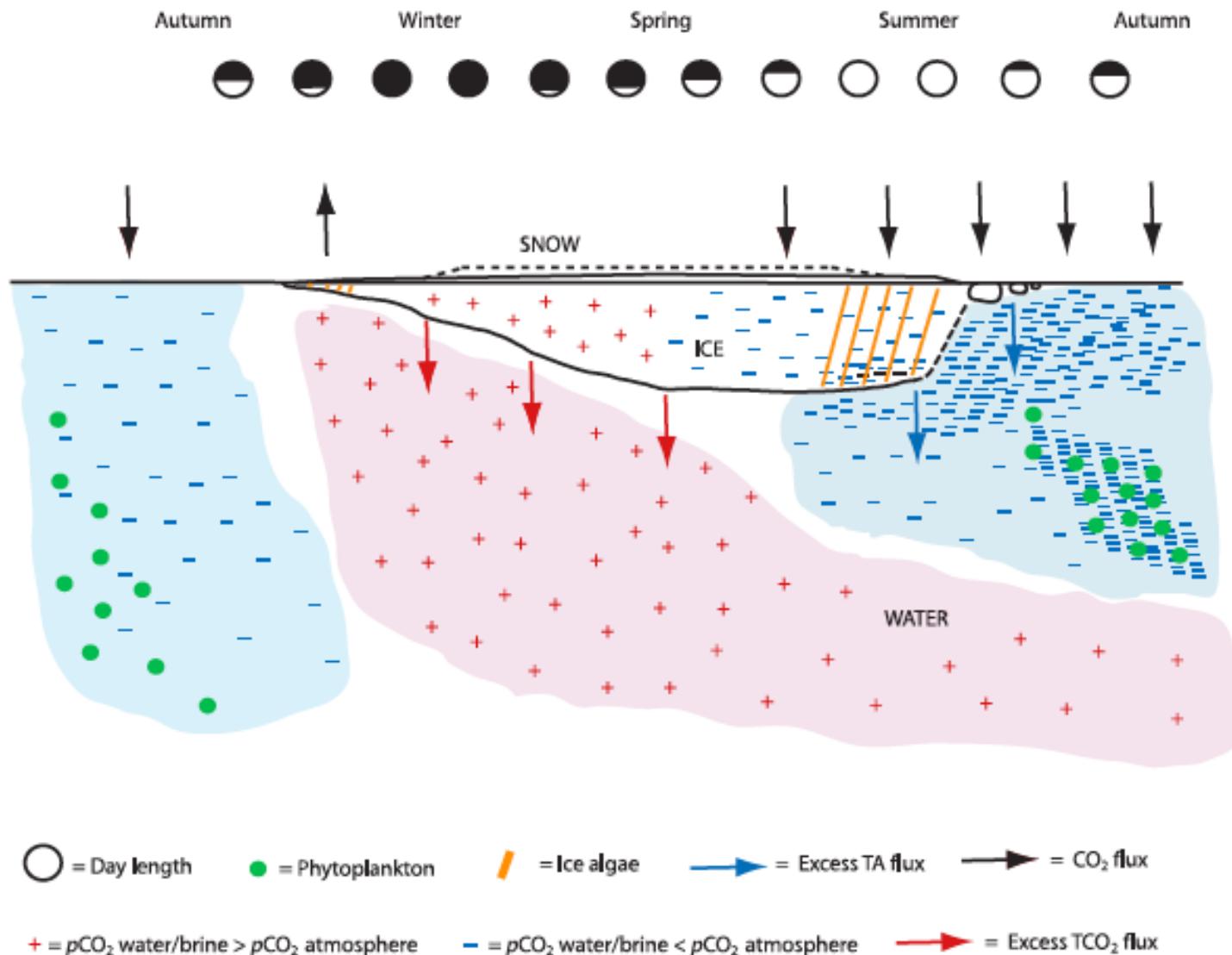
Sea-ice CO_2 -carbonate chemistry

Sea-ice melt ponds

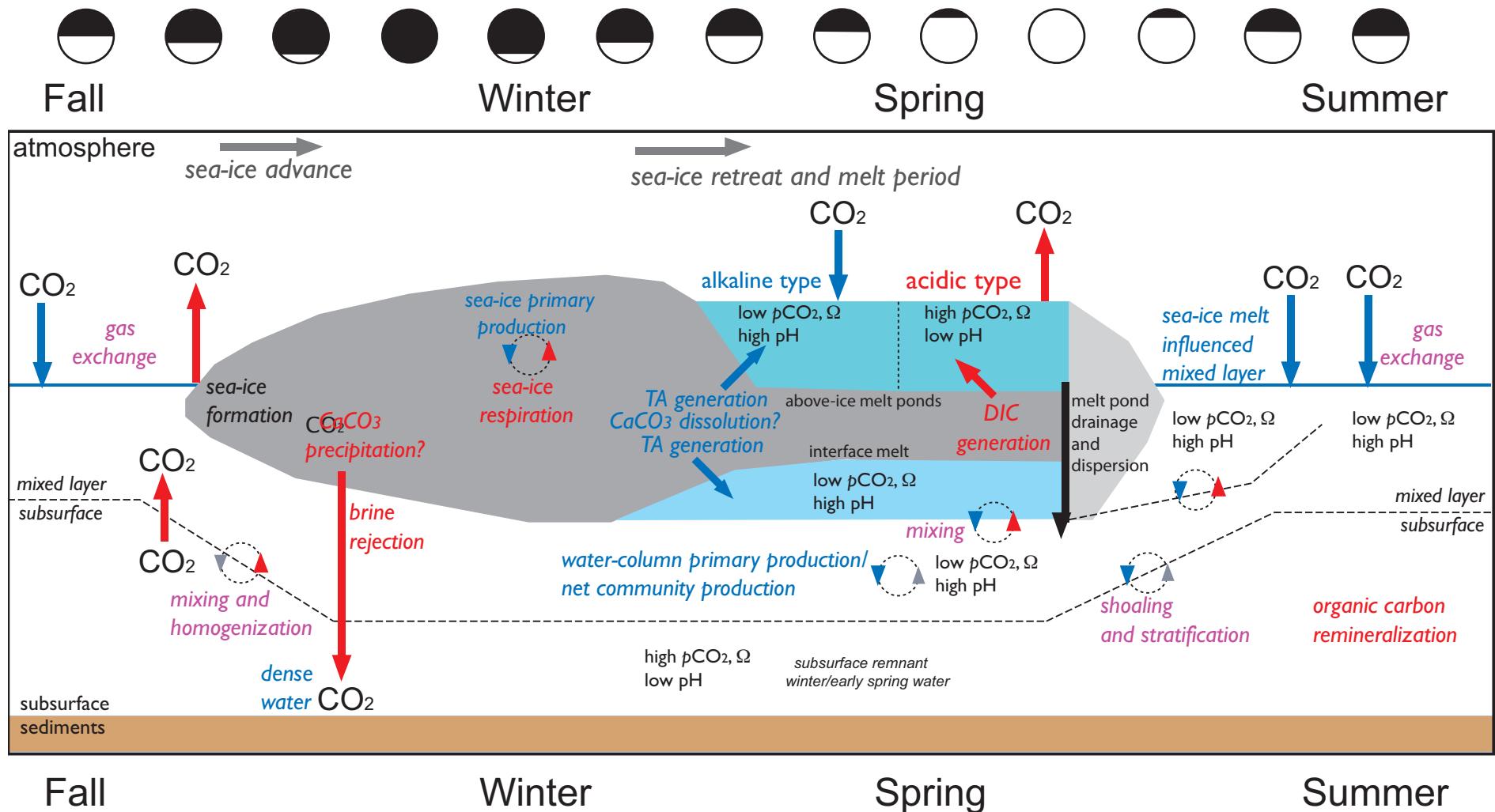


Sea-ice CO₂-carbonate chemistry

Sea-ice melt ponds

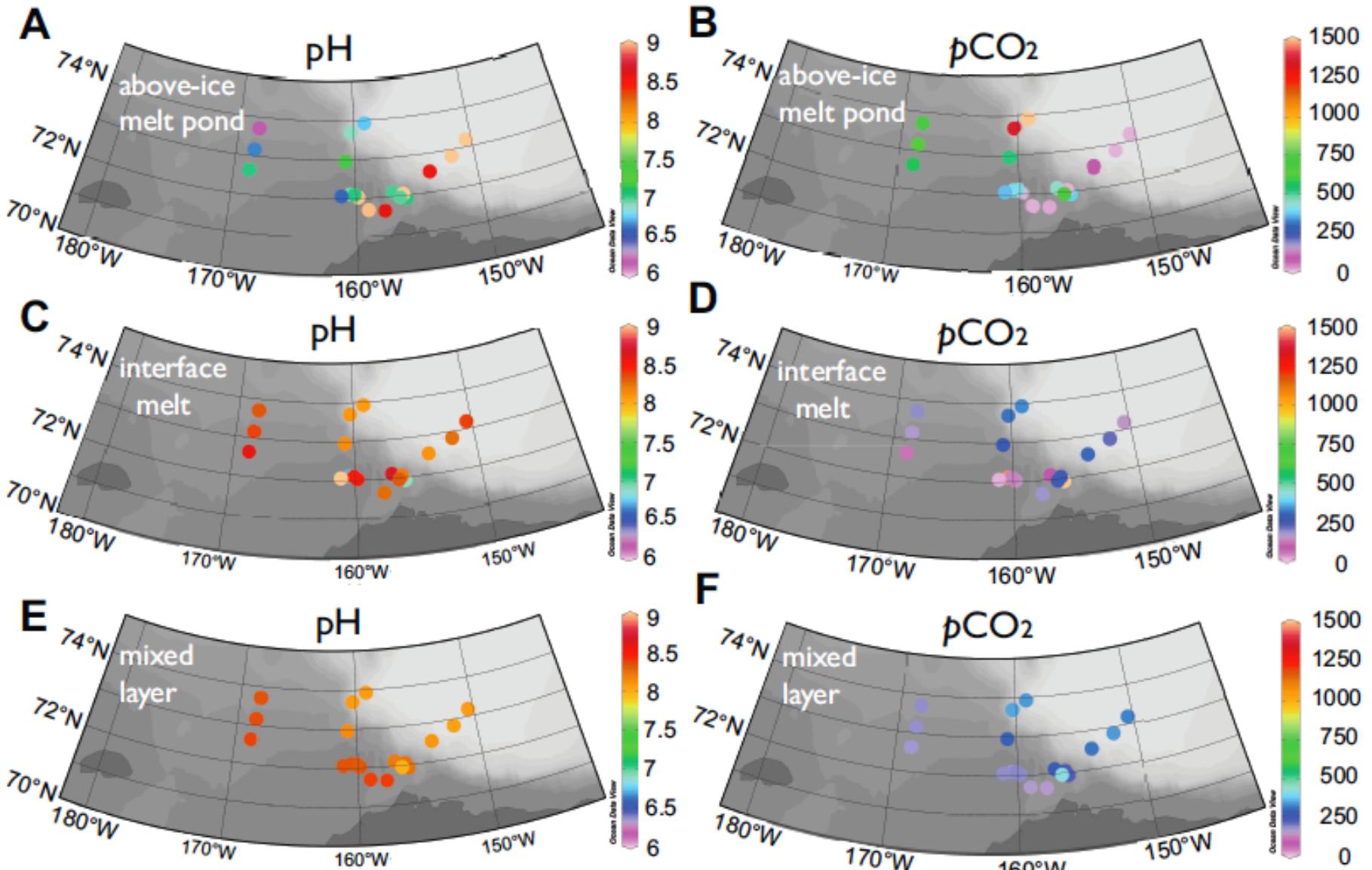


Sea-ice CO_2 -carbonate chemistry



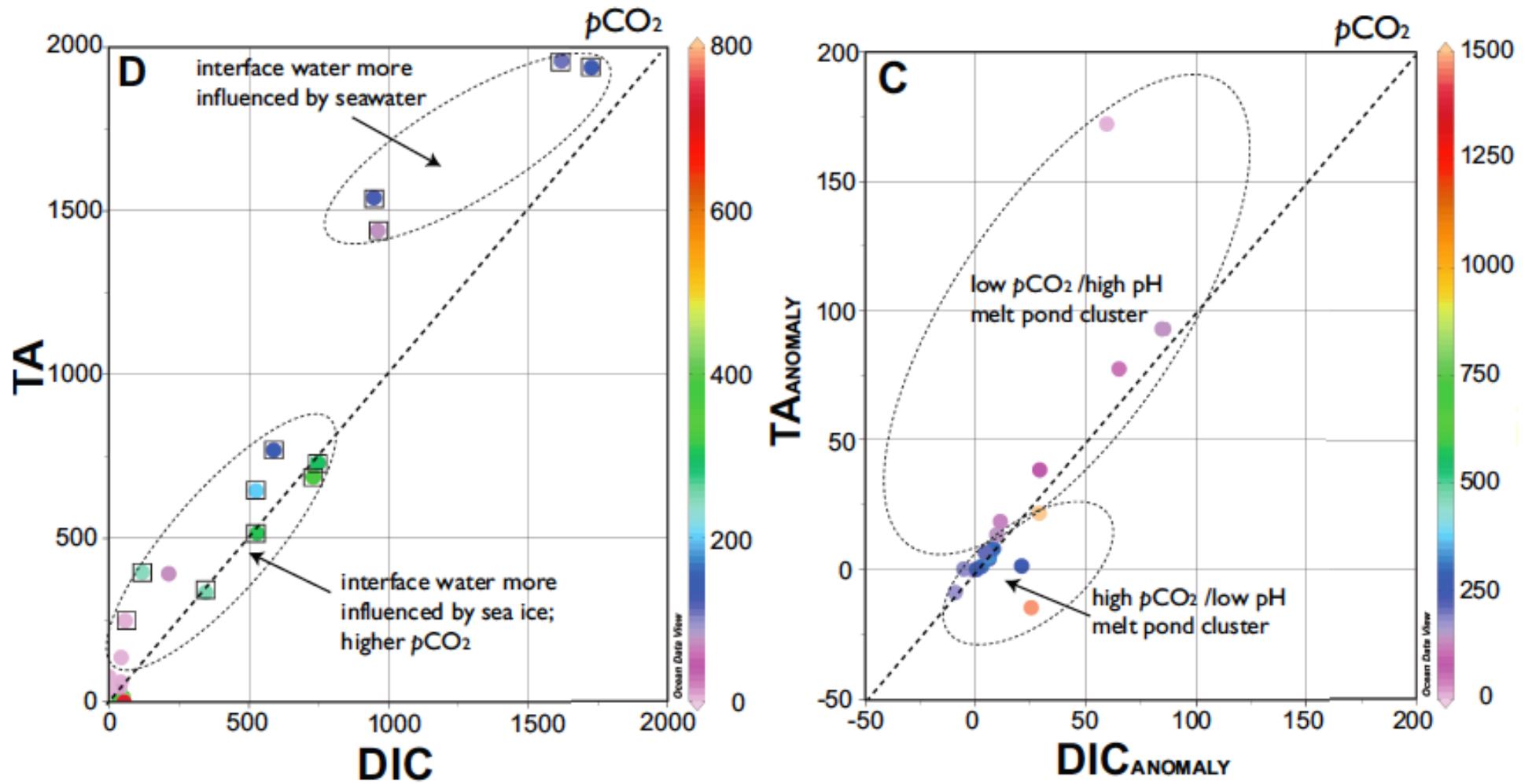
Sea-ice CO_2 -carbonate chemistry

Below-ice interface water



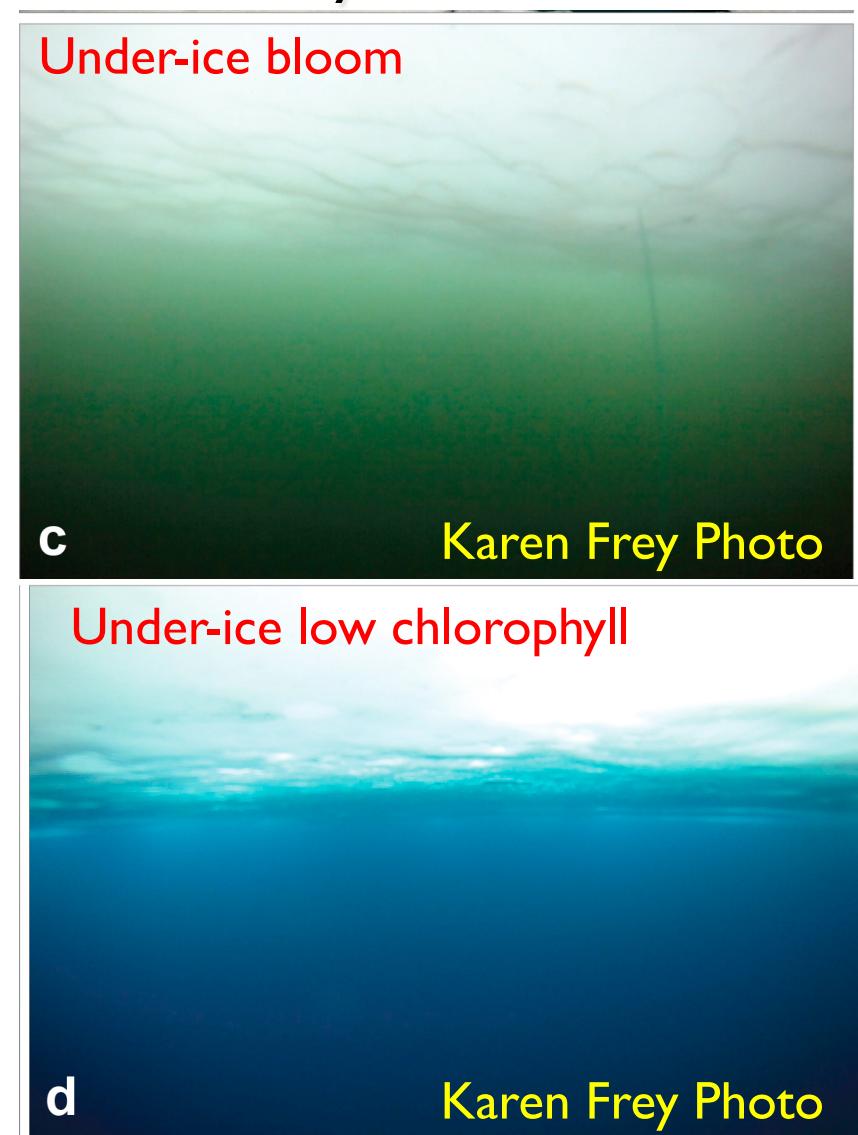
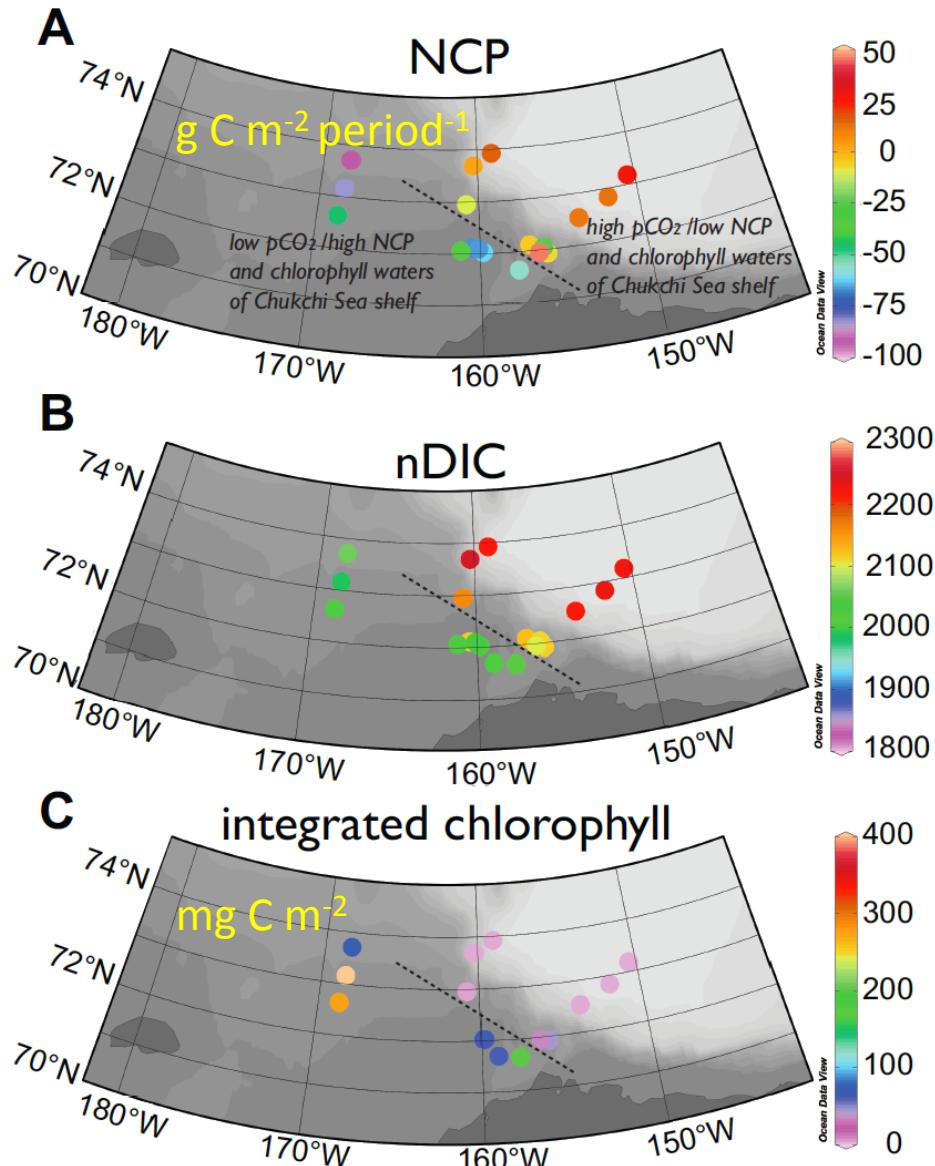
Sea-ice CO_2 -carbonate chemistry

Below-ice interface water



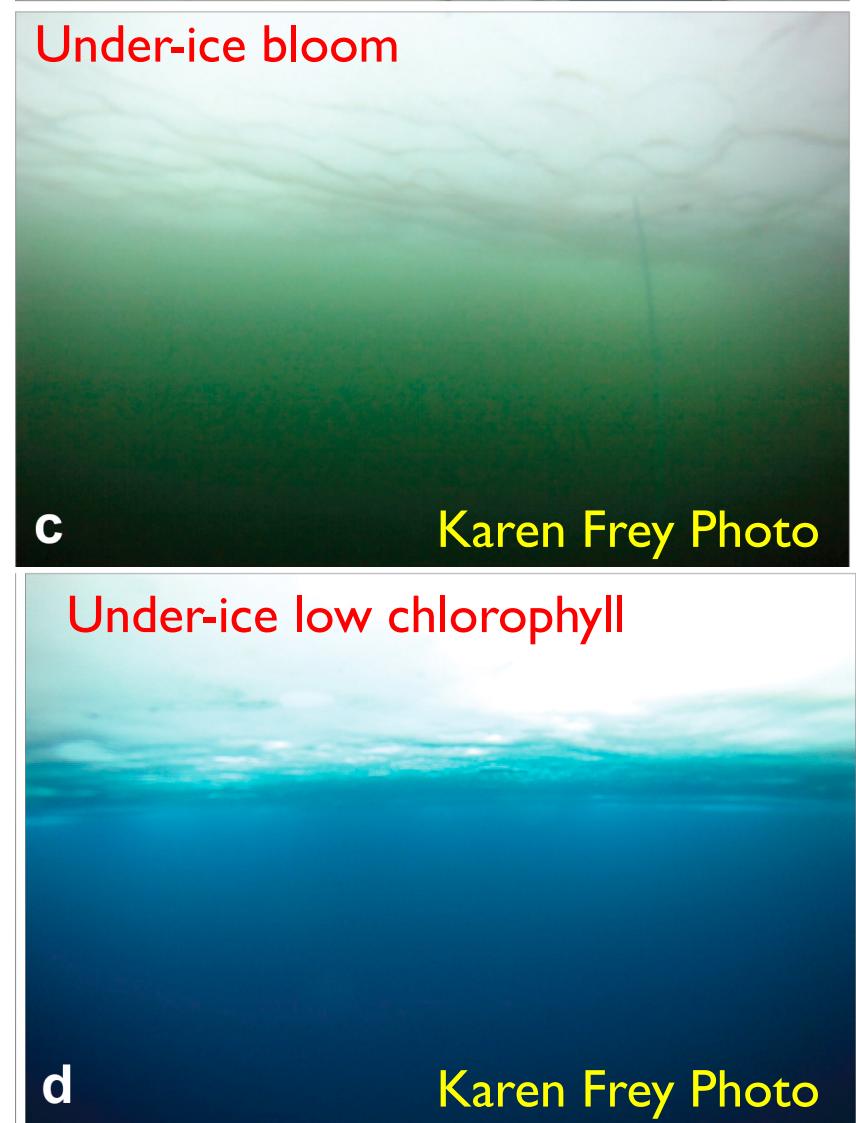
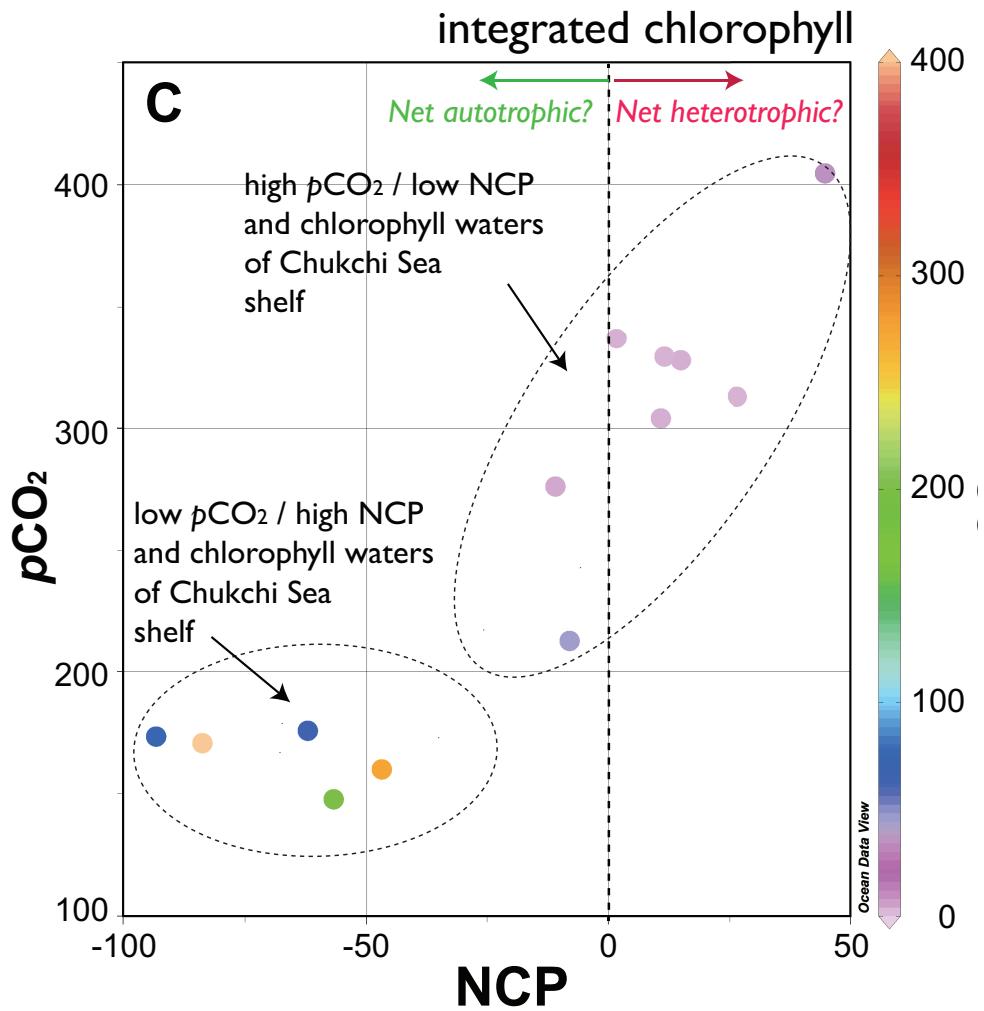
Sea-ice CO_2 -carbonate chemistry

Melt water contributions to mixed layer water



Sea-ice CO_2 -carbonate chemistry

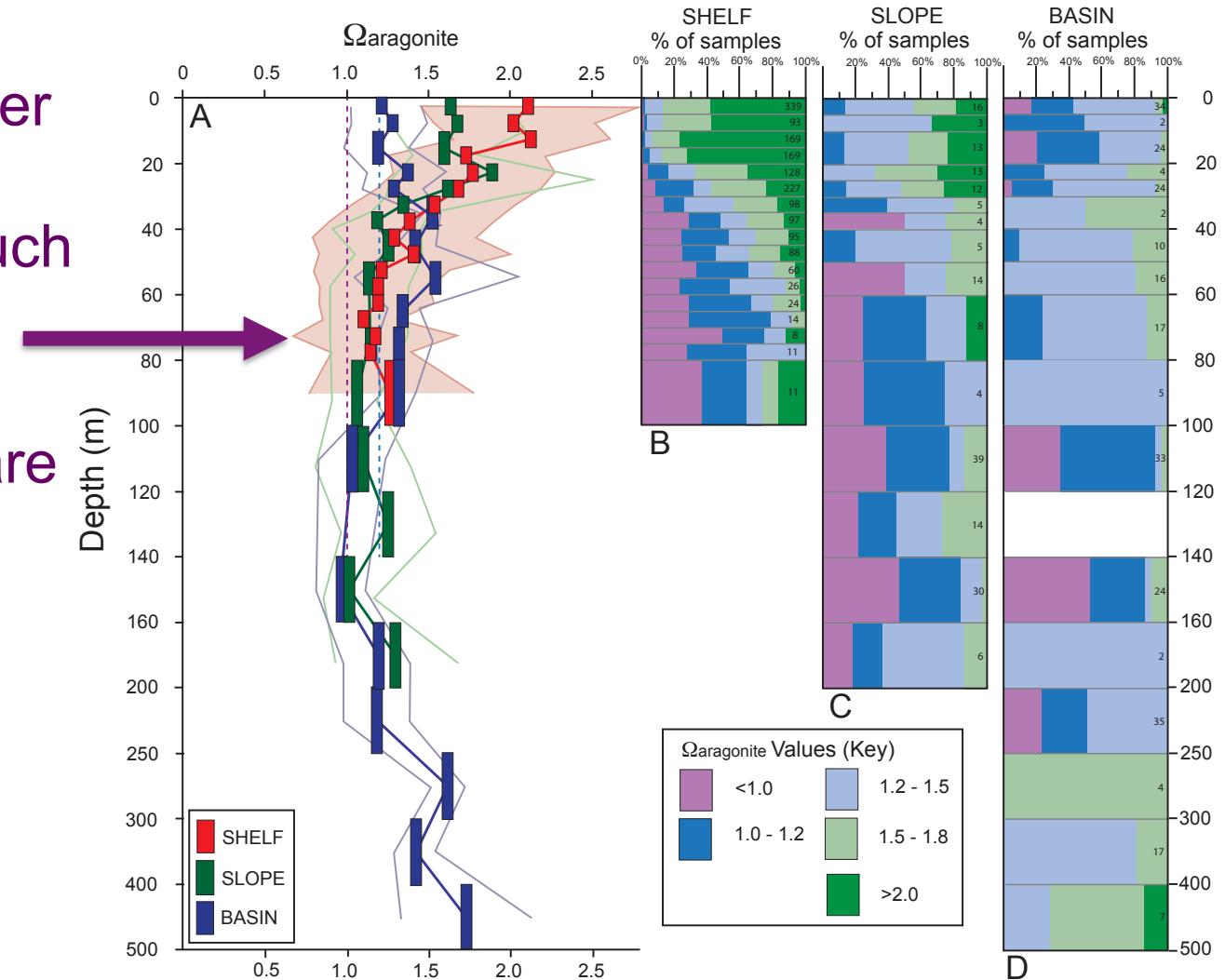
Melt water contributions to mixed layer water



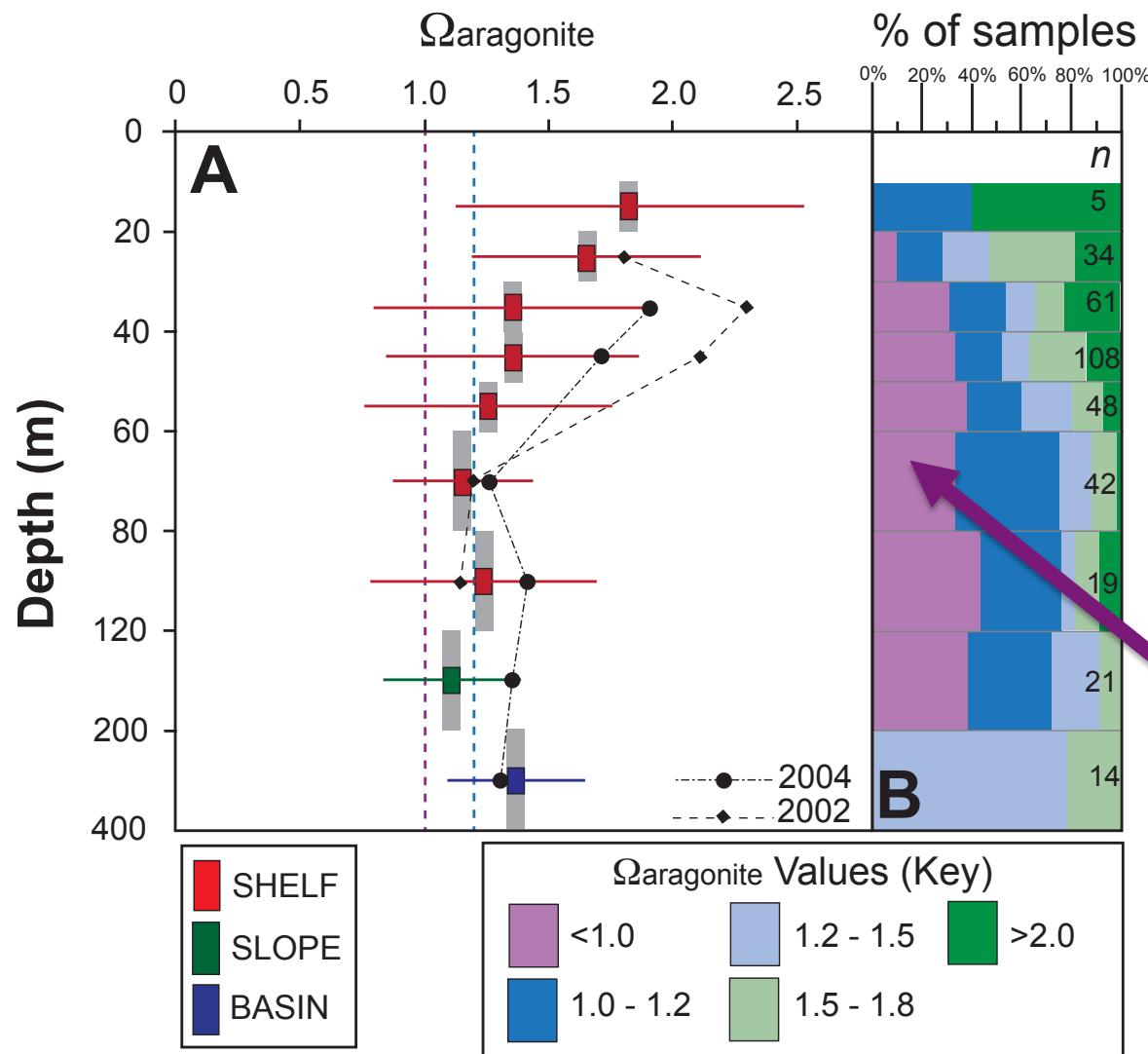
Western Arctic OA vulnerability

Arctic highly vulnerable to OA

Areas of low seawater saturation state for CaCO_3 minerals. Much of the Chukchi Sea benthos exposed to bottom waters that are corrosive to CaCO_3 during summertime.



Western Arctic OA vulnerability

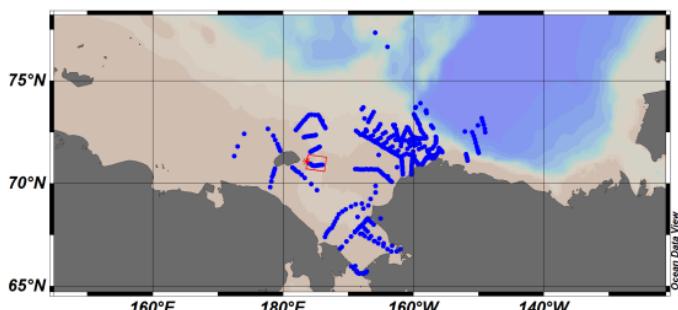
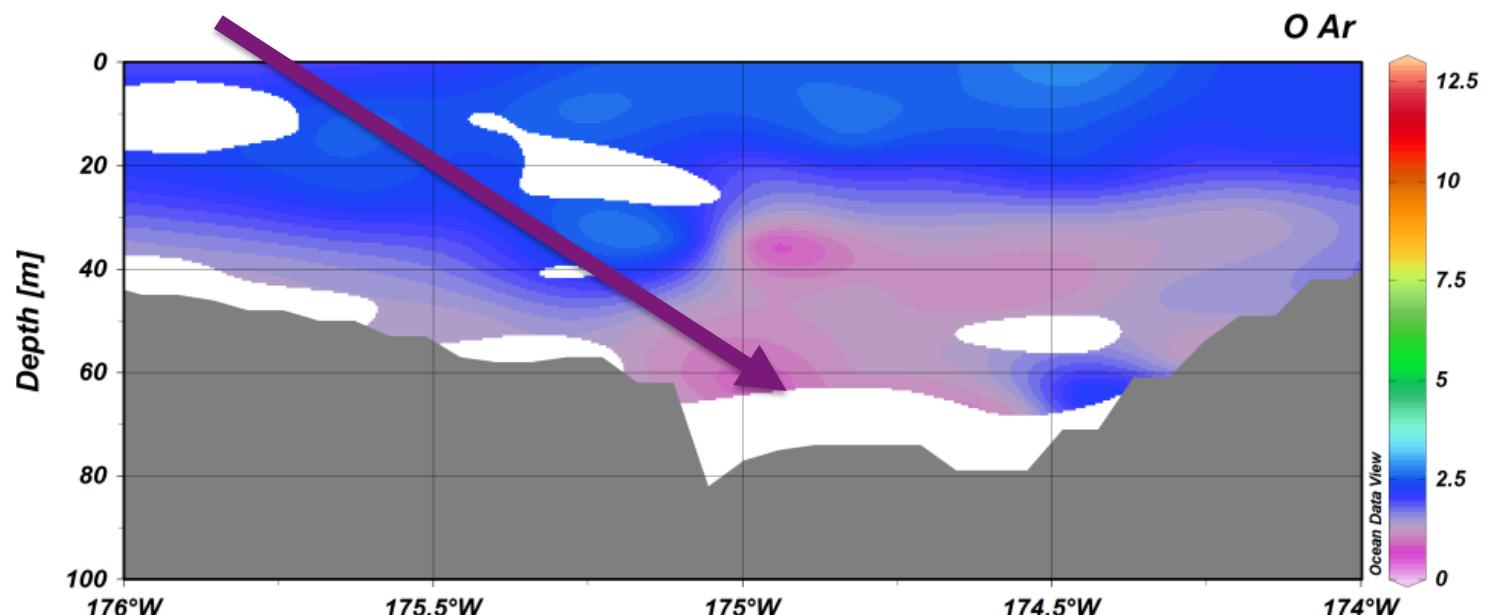


Areas of low seawater saturation state for CaCO_3 minerals. At least 40% of the Chukchi Sea benthos is exposed to bottom waters that are corrosive to CaCO_3 during summertime

Western Arctic OA vulnerability

Outflow of corrosive
bottom waters
through Herald Valley

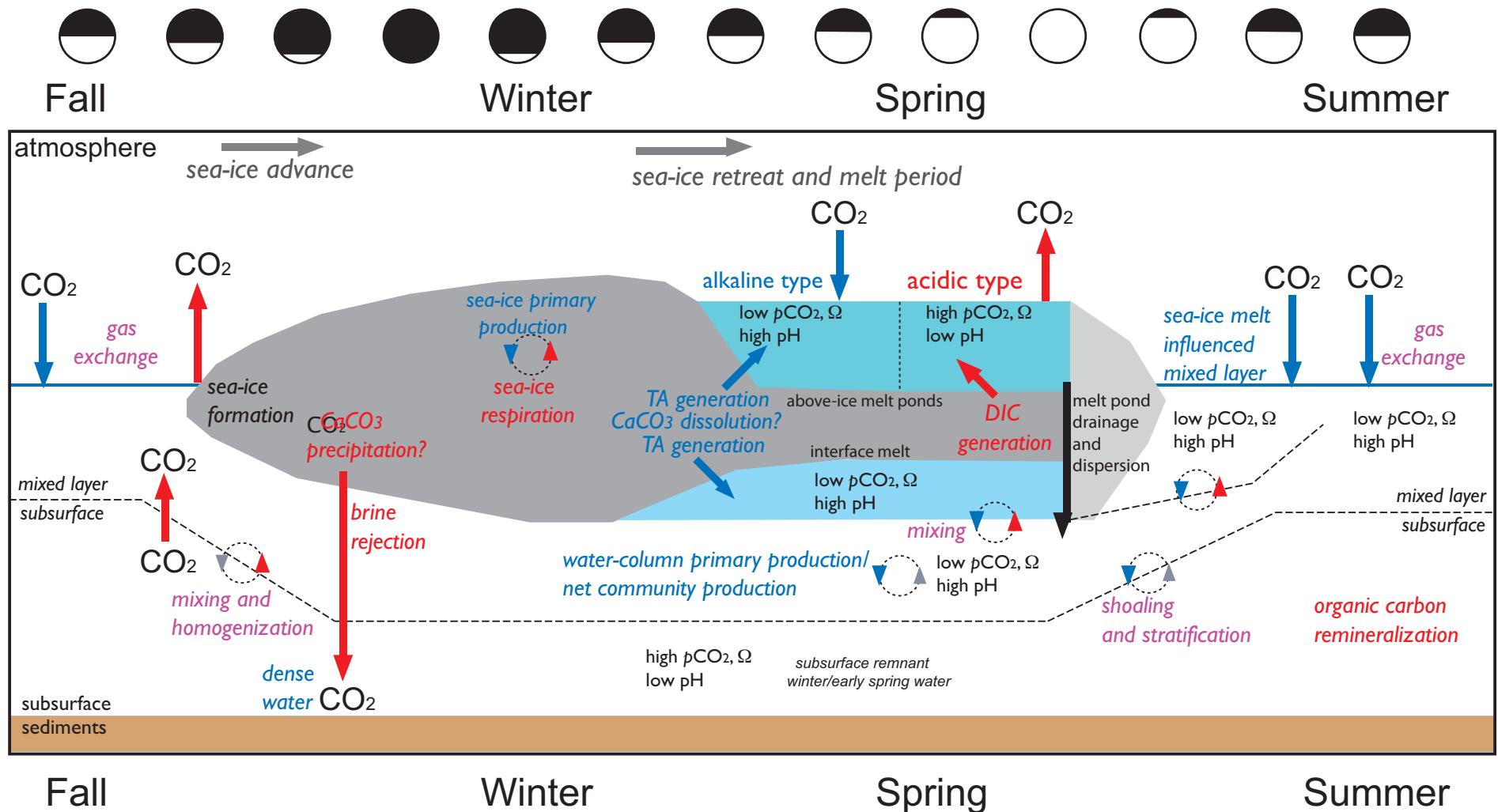
Chukchi Sea and ESS highly
vulnerable to OA



Bates et al., 2013

Bates et al, OCB Meeting 2014

Sea-ice CO_2 -carbonate chemistry



Sea-ice CO₂-carbonate chemistry

Conclusions

- Sea-ice CO₂-carbonate chemistry:
some issues and caveats with limited data
- Fall/freeze-up data
very limited data
- Sea-ice chemistry
relatively low $p\text{CO}_2$ (<100-400 μatm)
- Sea-ice brines
highly variable $p\text{CO}_2$ (<1-2,000 μatm)
- Melt ponds and interface waters
alkaline and acidic melt ponds
- Impacts on underlying water column
ocean acidification and NCP impacts