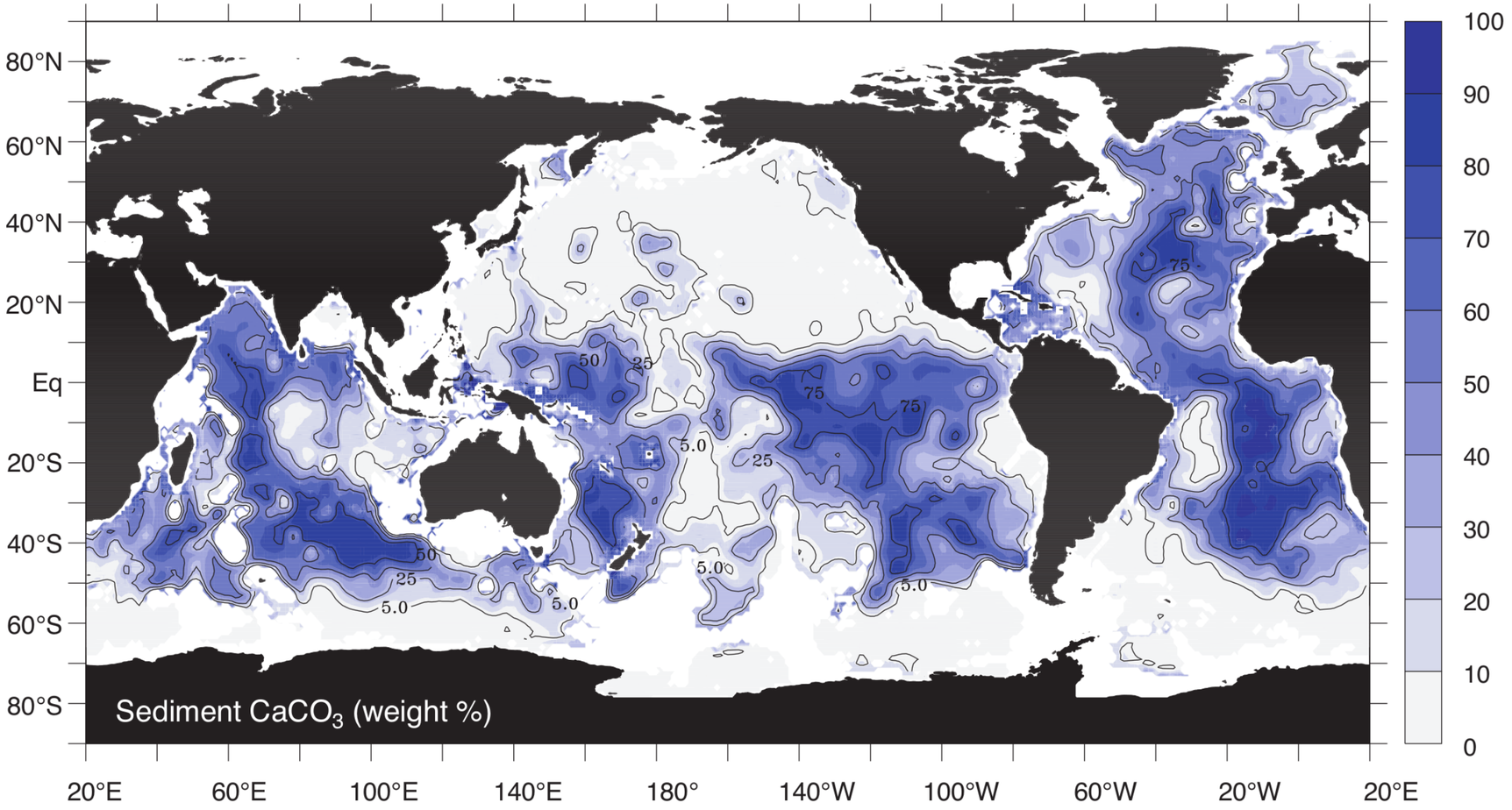
Lecture 21: CaCO3 saturation

1. CaCO3 Saturation and compensation
    A. Seafloor CaCO3
    B. Pressure and Temperature sensitivity of Ksp
    C. [CO_3^{2-}] and reactions that change it
    D. Circulation
    E. Compensation for Alkalinity source changes

We acknowledge and respect the lək$^{\text{w}}$əŋən peoples on whose traditional territory the university stands and the Songhees, Esquimalt and W̱SÁNEĆ peoples whose historical relationships with the land continue to this day.


80°N
60°N
40°N
20°N
Eq
20°S
40°S
60°S
80°S
20°E
60°E
100°E
140°E
180°
140°W
100°W
60°W
20°W
20°E
100
90
80
70
60
50
40
30
20
10
0
Sediment CaCO3 (weight %)
75
50
25
5.0

$$CaCO_3 \longleftrightarrow Ca^{2+} + CO_3^{2-}$$

$$K_{sp} = \frac{[Ca^{2+}][CO_3^{2-}]}{1}$$

Saturation State

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

$\Omega = 1$ equilibrium

$\Omega > 1$ super saturated (min precipitates)

$\Omega < 1$ under saturated (min dissolves)

Calcite

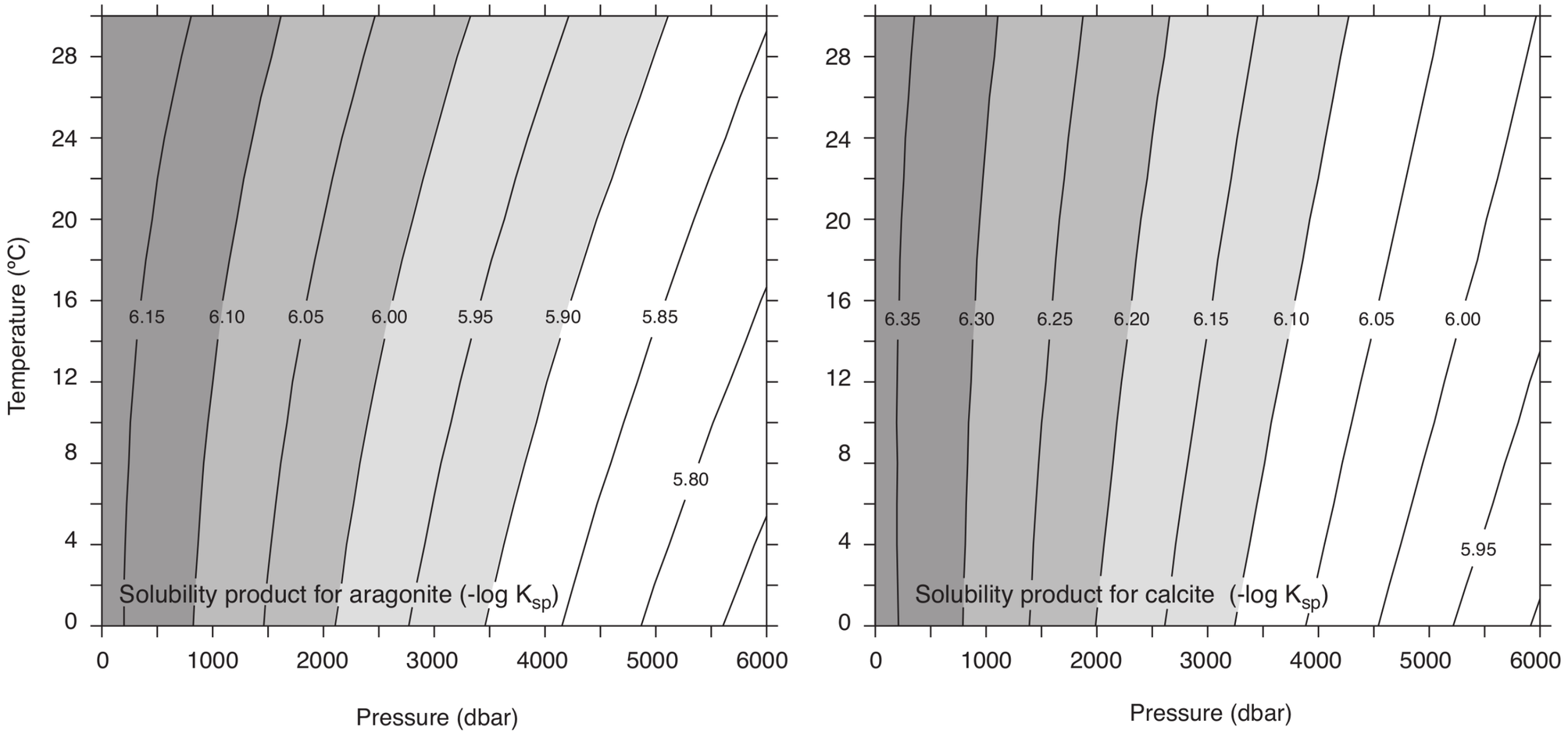
$K_{sp} = 10^{-6.37}$

Aragonite

$K_{sp} = 10^{-6.19}$

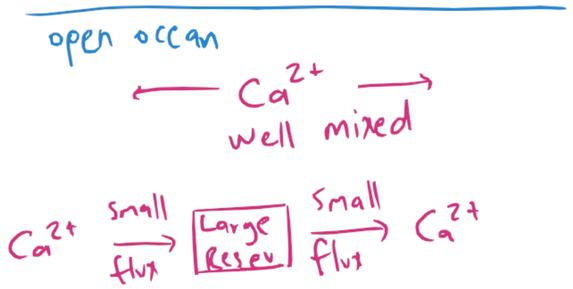
Which mineral is more soluble in seawater?

*Aragonite higher K_{sp} so "easier" to dissolve.

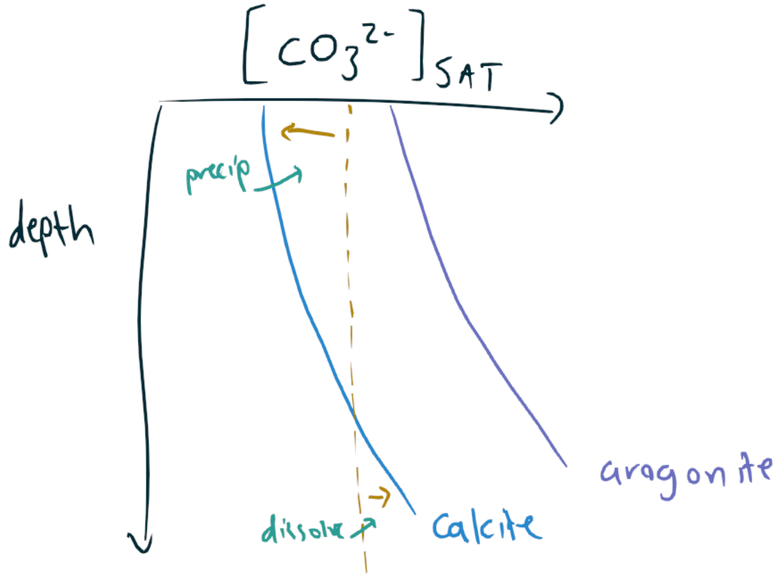


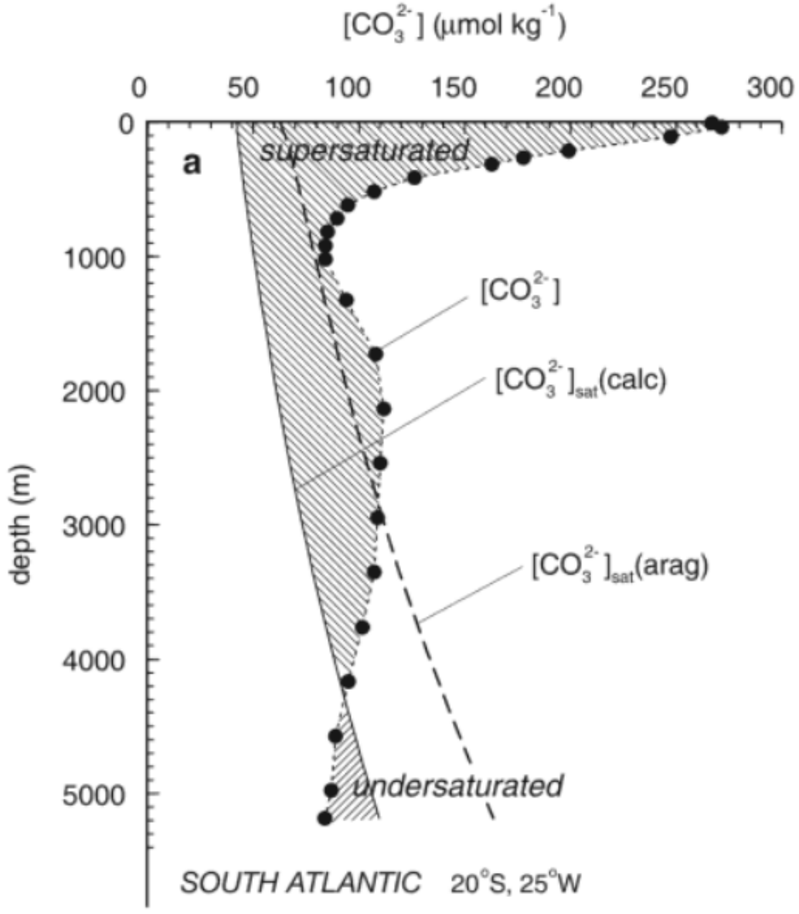
Note: 1 dbar is approximately the hydrostratic pressure for 1 meter of water depth

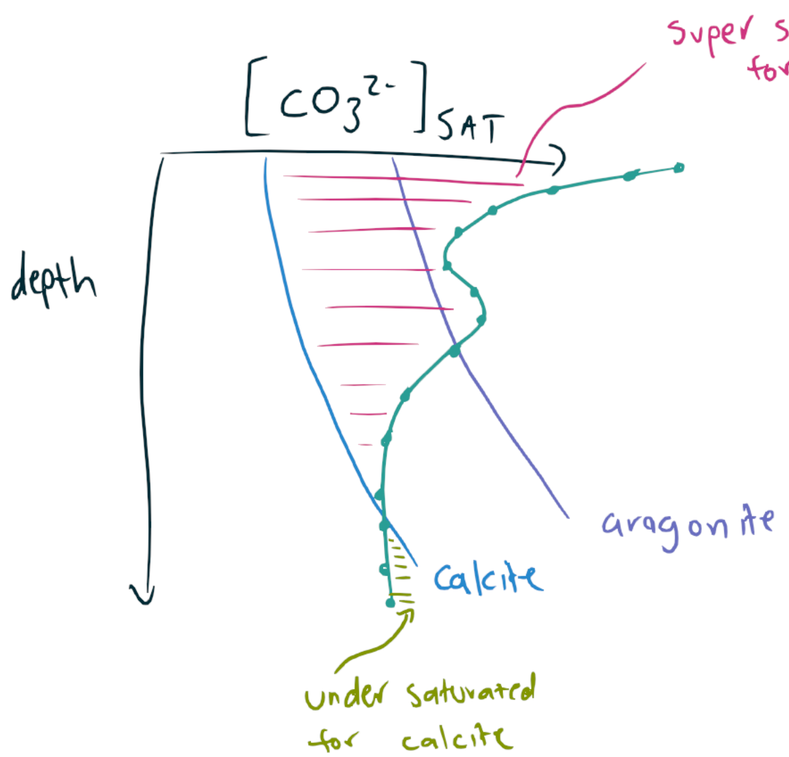
$K_{sp} = [Ca^{2+}]_{SW} [CO_3^{2-}]_{SAT}$



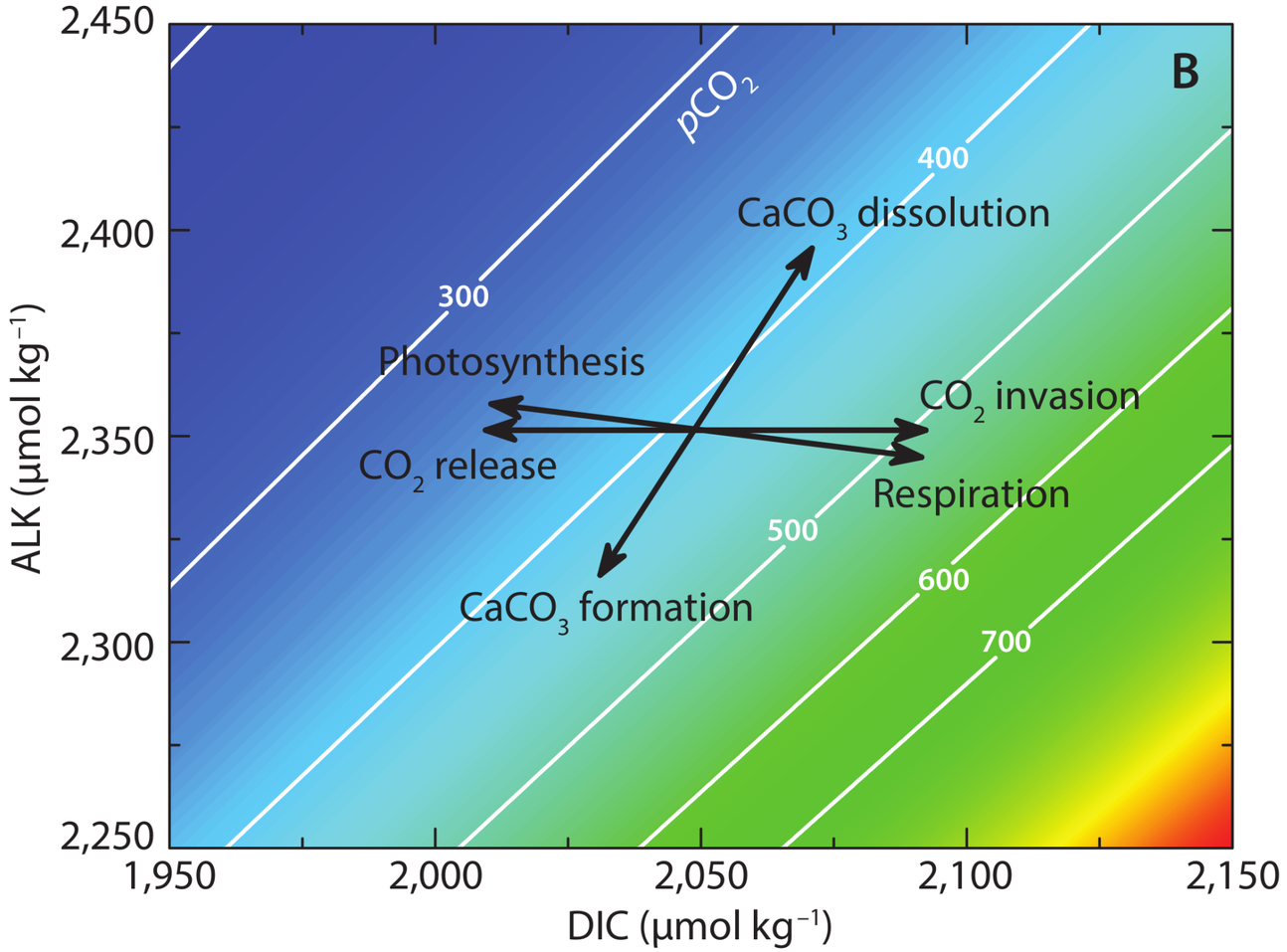
What do you think ocean looks like?

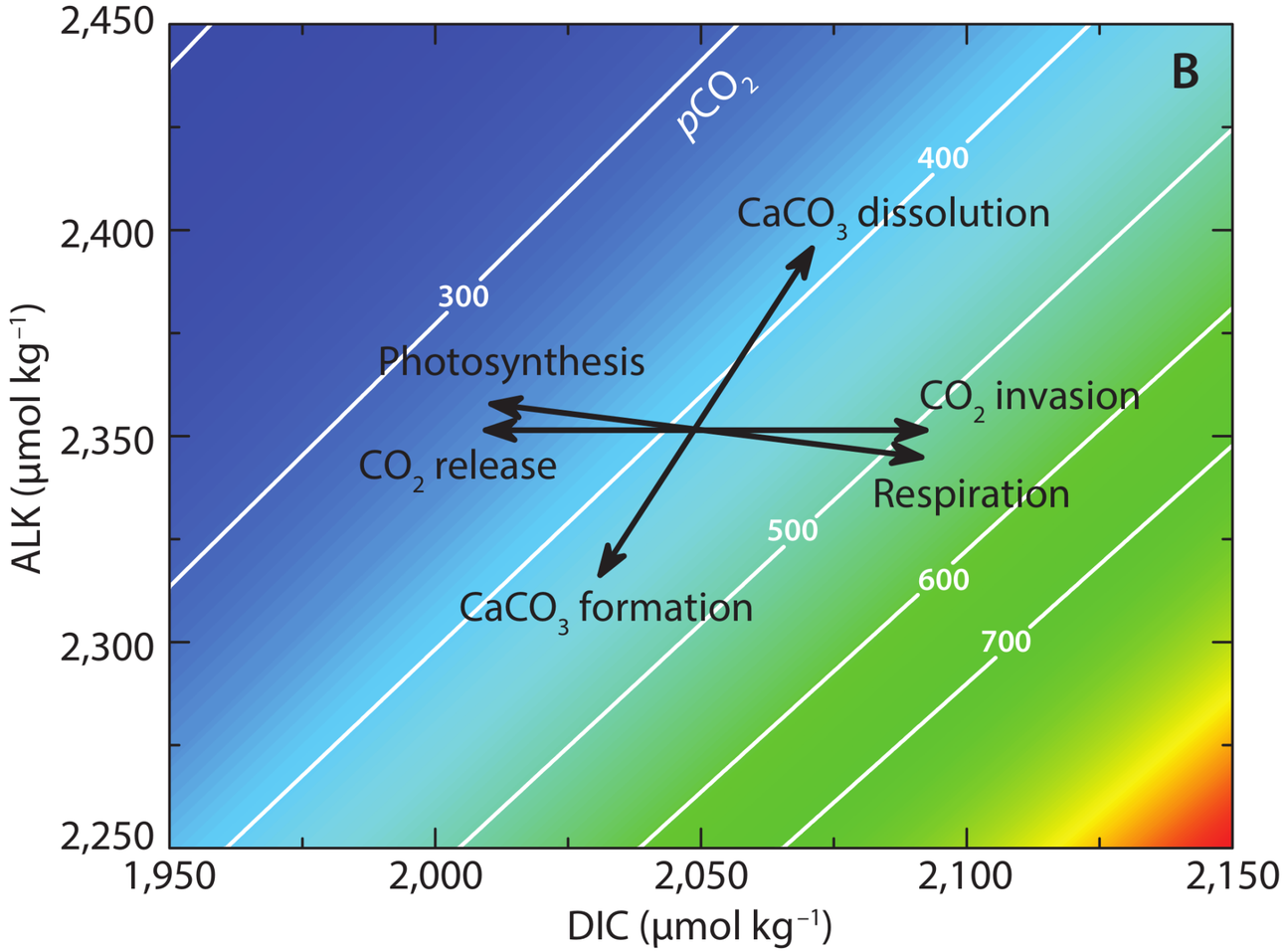



[CO3 2-] (µmol kg-1)
0
50
100
150
200
250
300
0
1000
2000
3000
4000
5000
depth (m)
a
supersaturated
[CO3 2-]
[CO3 2-]sat(calc)
[CO3 2-]sat(arag)
undersaturated
SOUTH ATLANTIC 20°S, 25°W

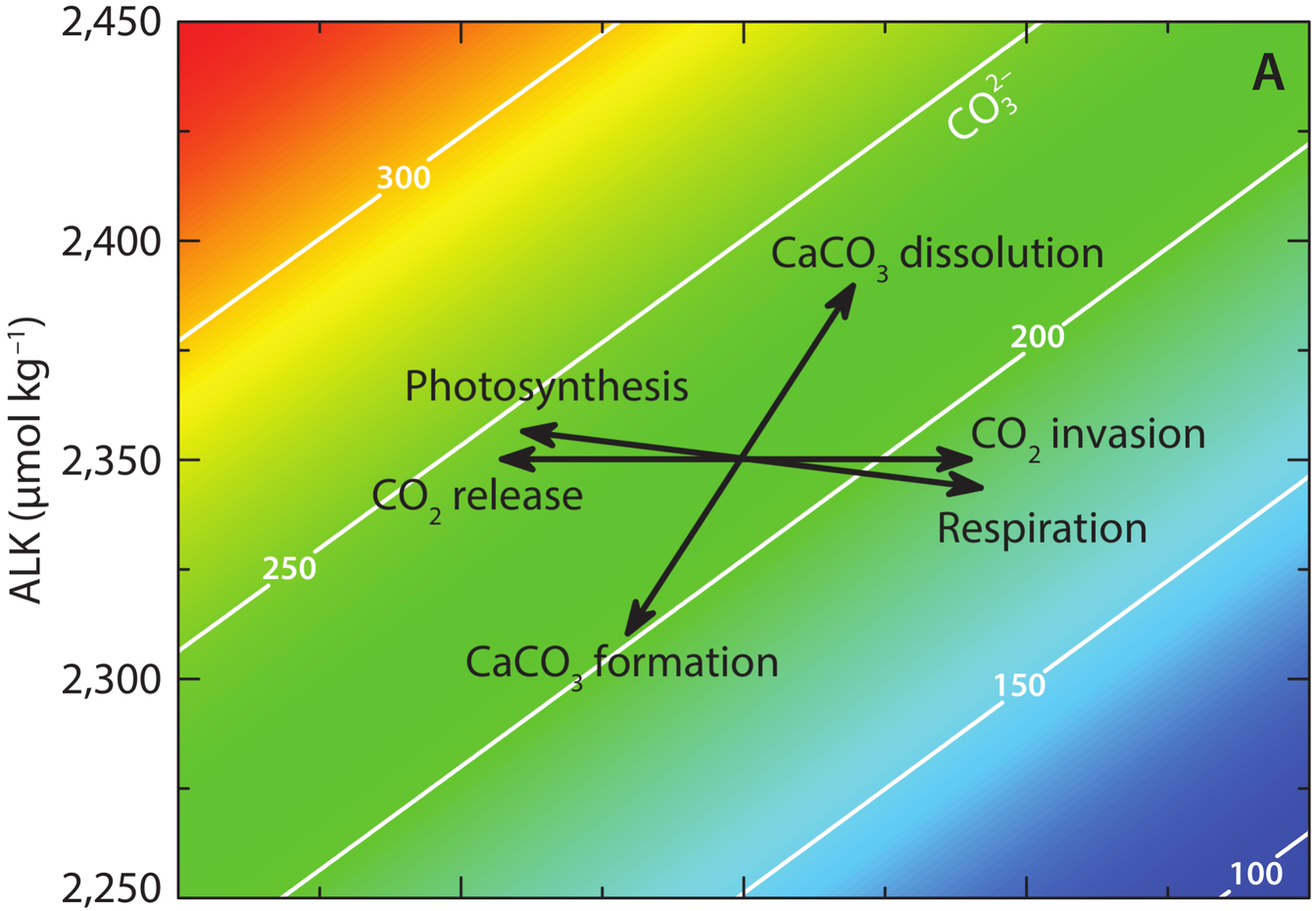


why is $[CO_3^{2-}]$ highest where $\Omega \gg 1$ and lowest where $\Omega \ll 1$?

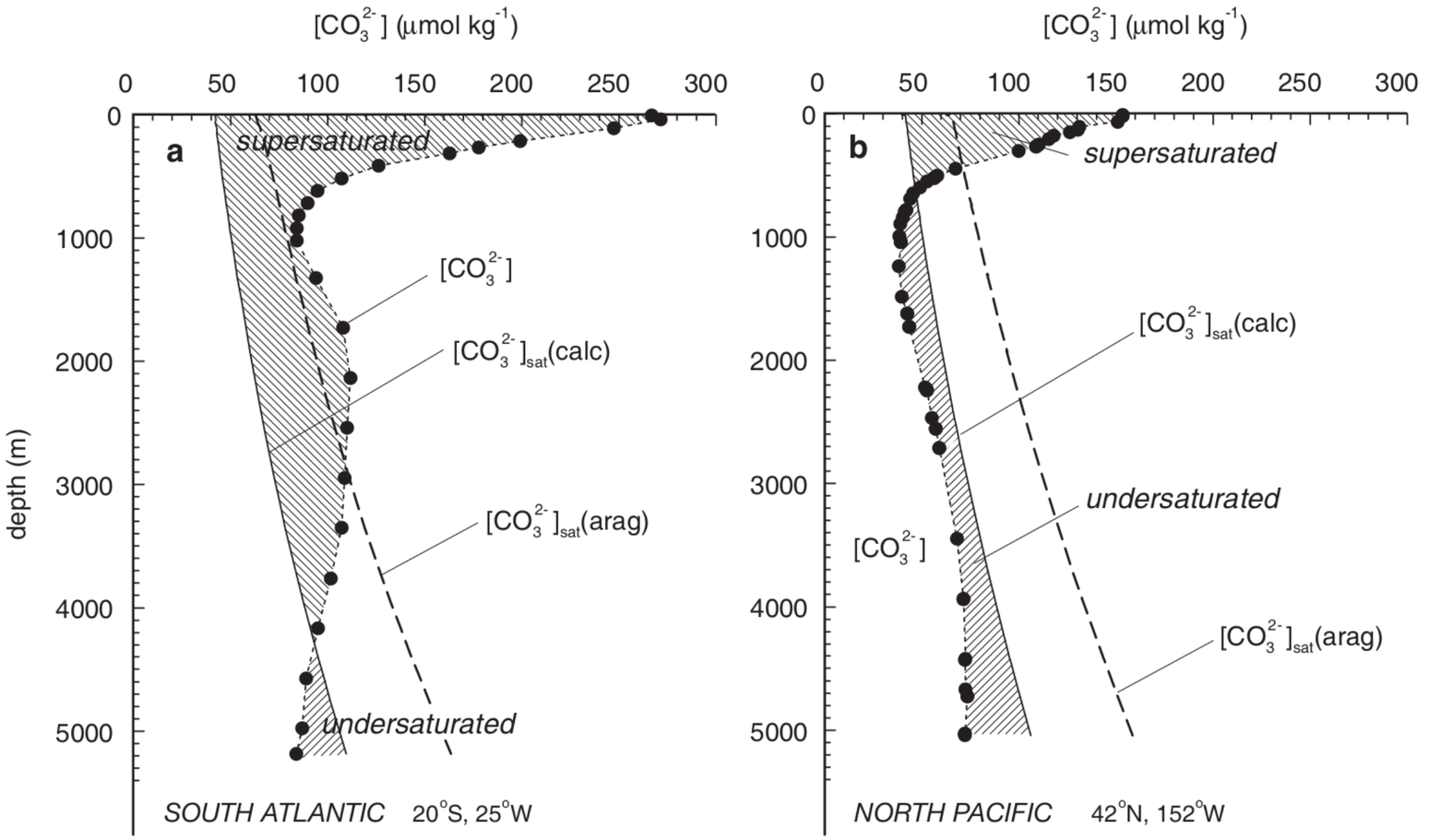

B
pCO_2
300
400
500
600
700
$CaCO_3$ dissolution
Photosynthesis
CO_2 invasion
CO_2 release
Respiration
$CaCO_3$ formation
2,450
2,400
2,350
2,300
2,250
ALK (µmol kg^{-1})
1,950
2,000
2,050
2,100
2,150
DIC (µmol kg^{-1})

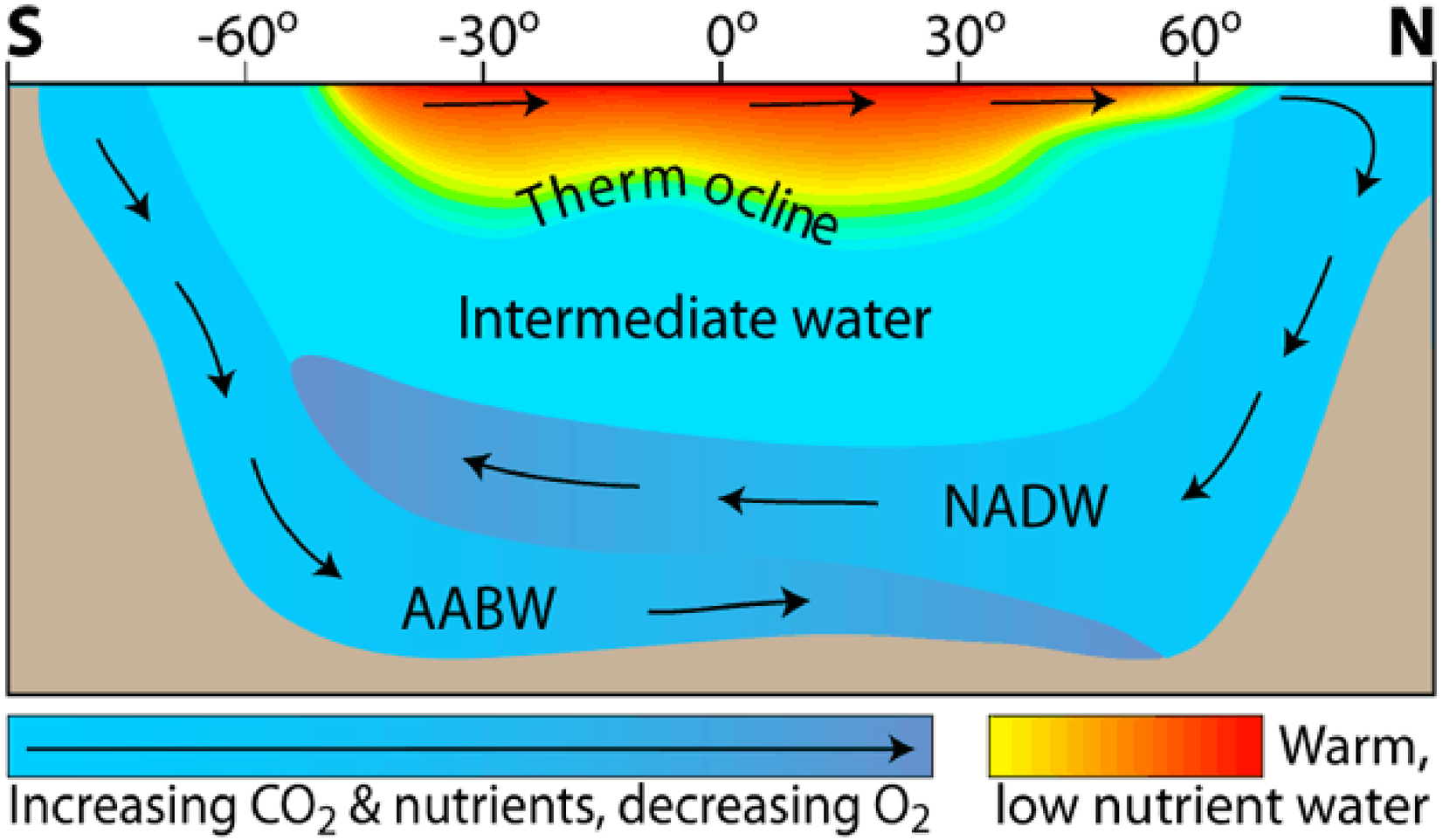


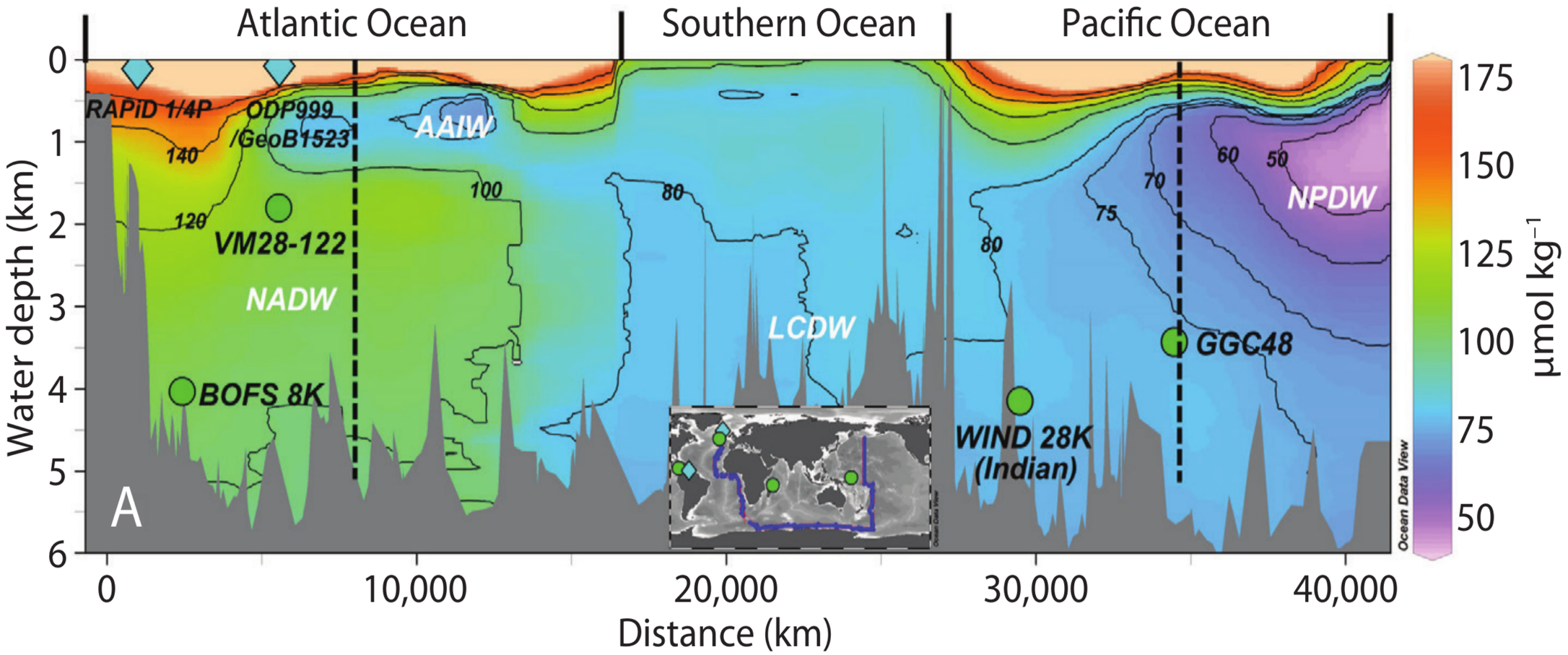
Recall that $[CO_3^{2-}] \approx$ ALK-DIC

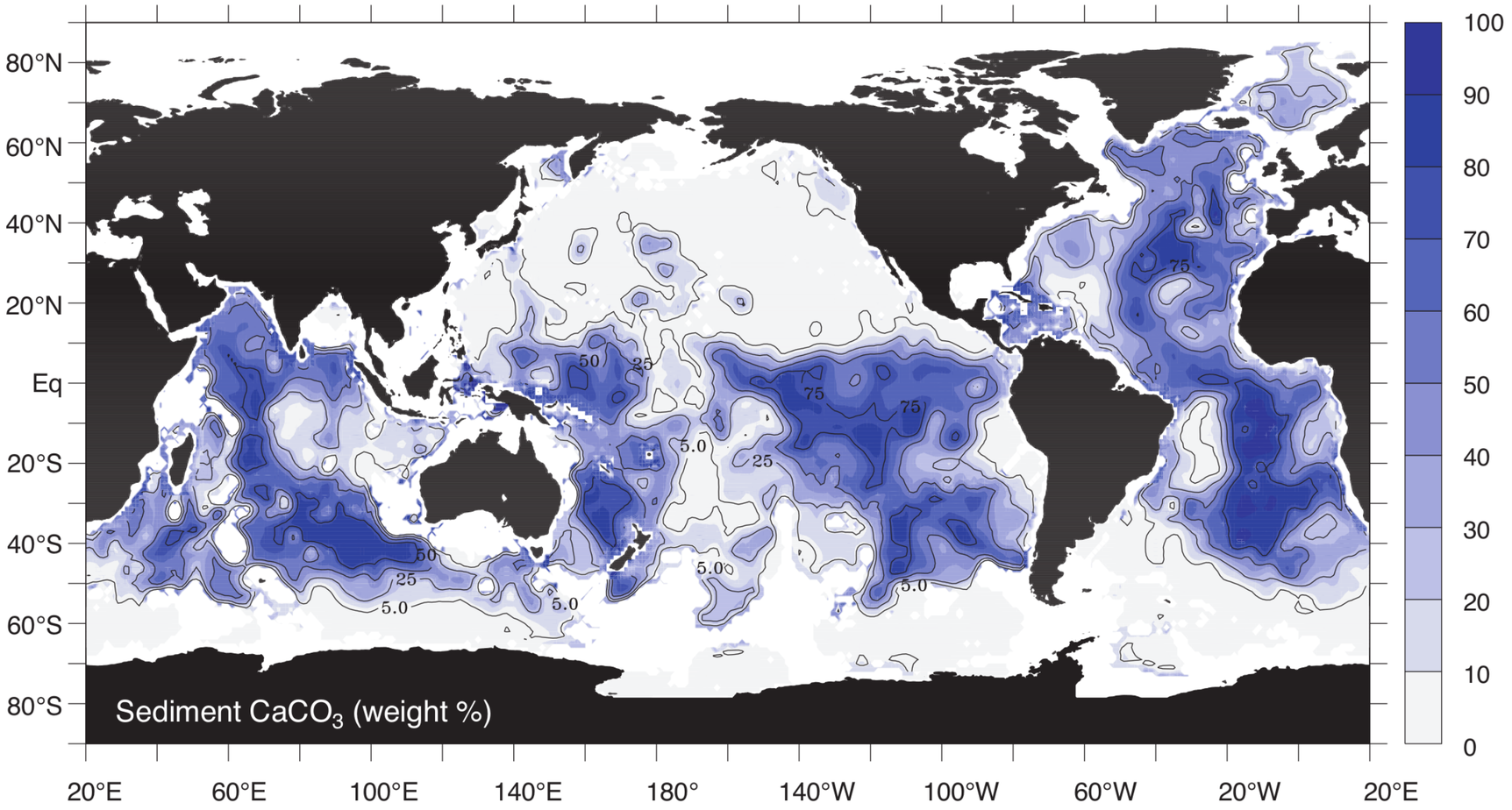


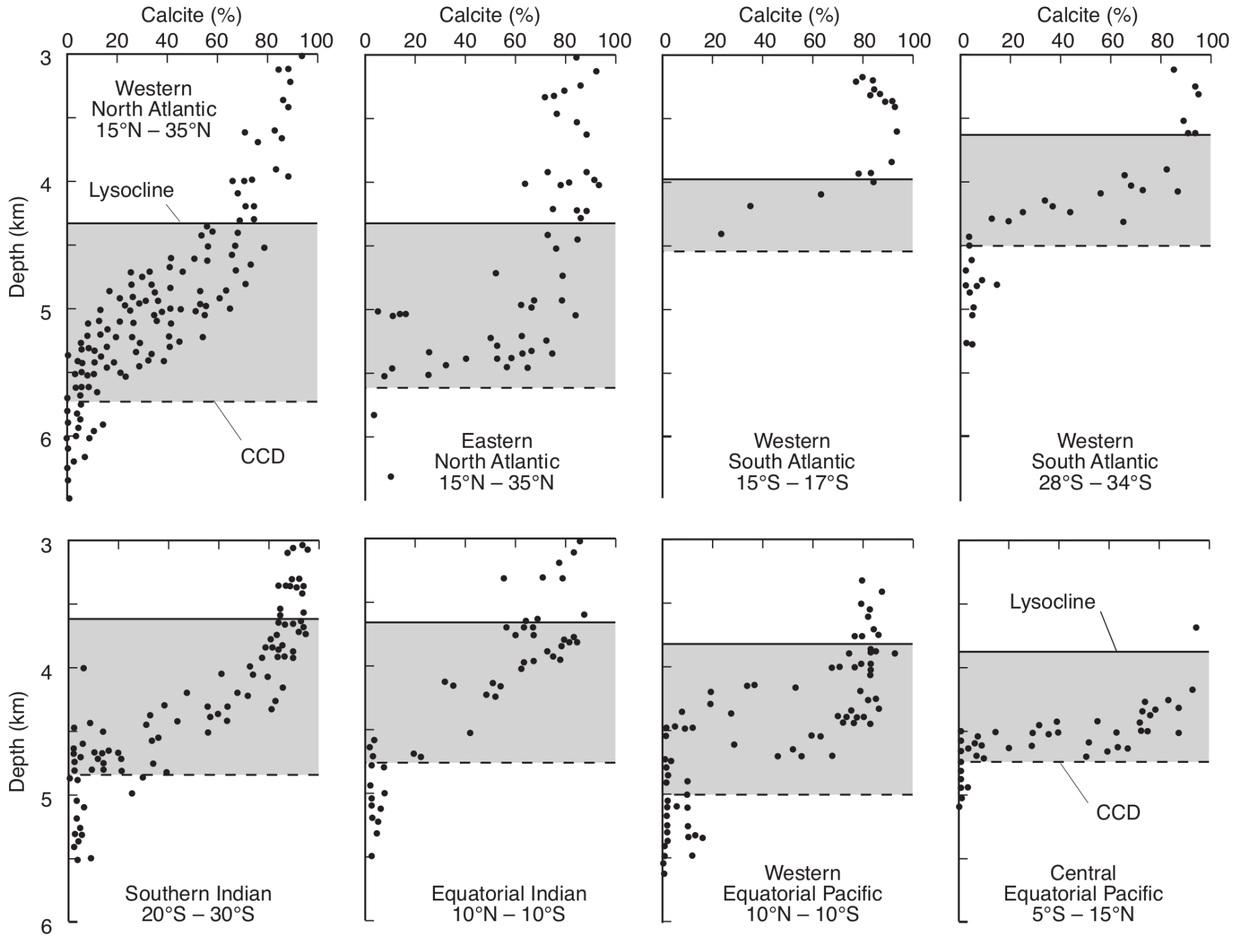
Recall that $[CO_3^{2-}] \approx$ ALK-DIC


[CO3 2-] (μmol kg-1)
0
50
100
150
200
250
300
0
1000
2000
3000
4000
5000
depth (m)
a
supersaturated
[CO3 2-]
[CO3 2-]sat(calc)
[CO3 2-]sat(arag)
undersaturated
SOUTH ATLANTIC 20°S, 25°W
b
supersaturated
[CO3 2-]sat(calc)
undersaturated
[CO3 2-]
[CO3 2-]sat(arag)
NORTH PACIFIC 42°N, 152°W

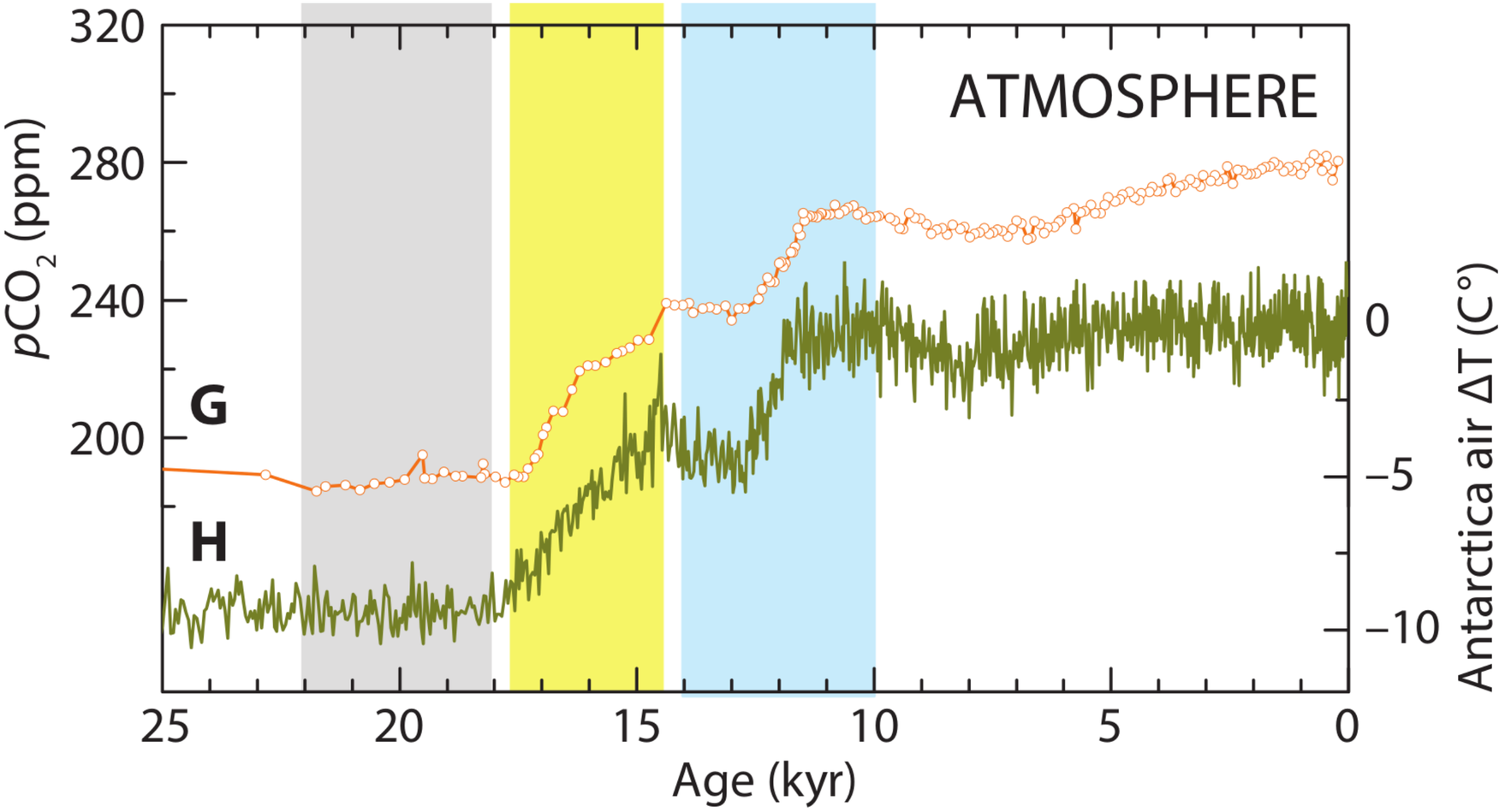

S
-60°
-30°
0°
30°
60°
N
Therm ocline
Intermediate water
NADW
AABW
Increasing CO_2 & nutrients, decreasing O_2
Warm,
low nutrient water

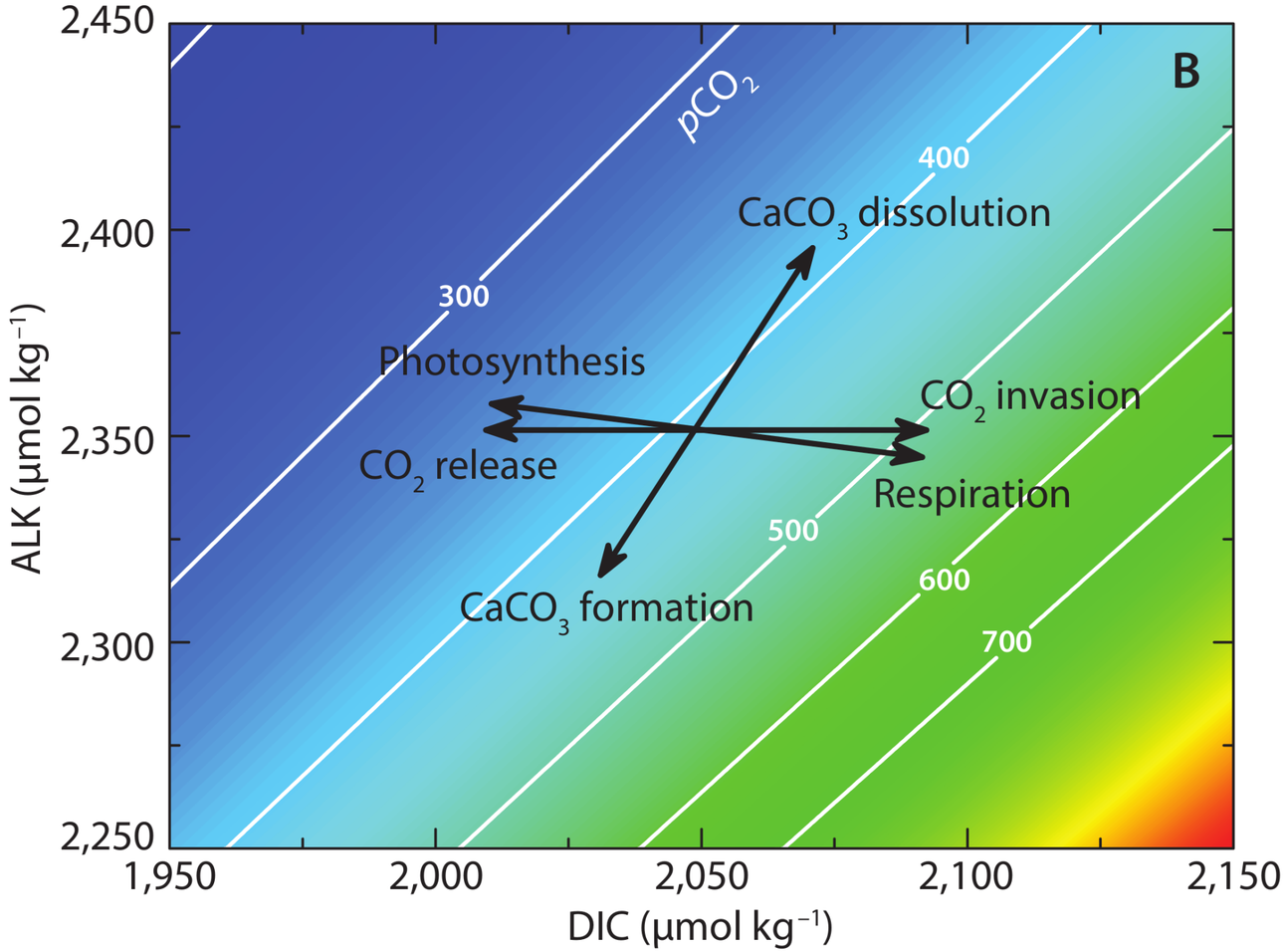

Atlantic Ocean
Southern Ocean
Pacific Ocean
RAPID 1/4P
ODP999
/GeoB1523
AAIW
140
120
100
80
70
75
80
60
50
NPDW
VM28-122
NADW
LCDW
GGC48
BOFS 8K
WIND 28K
(Indian)
A
Water depth (km)
0
1
2
3
4
5
6
0
10,000
20,000
30,000
40,000
Distance (km)
175
150
125
100
75
50
µmol kg⁻¹
Ocean Data View

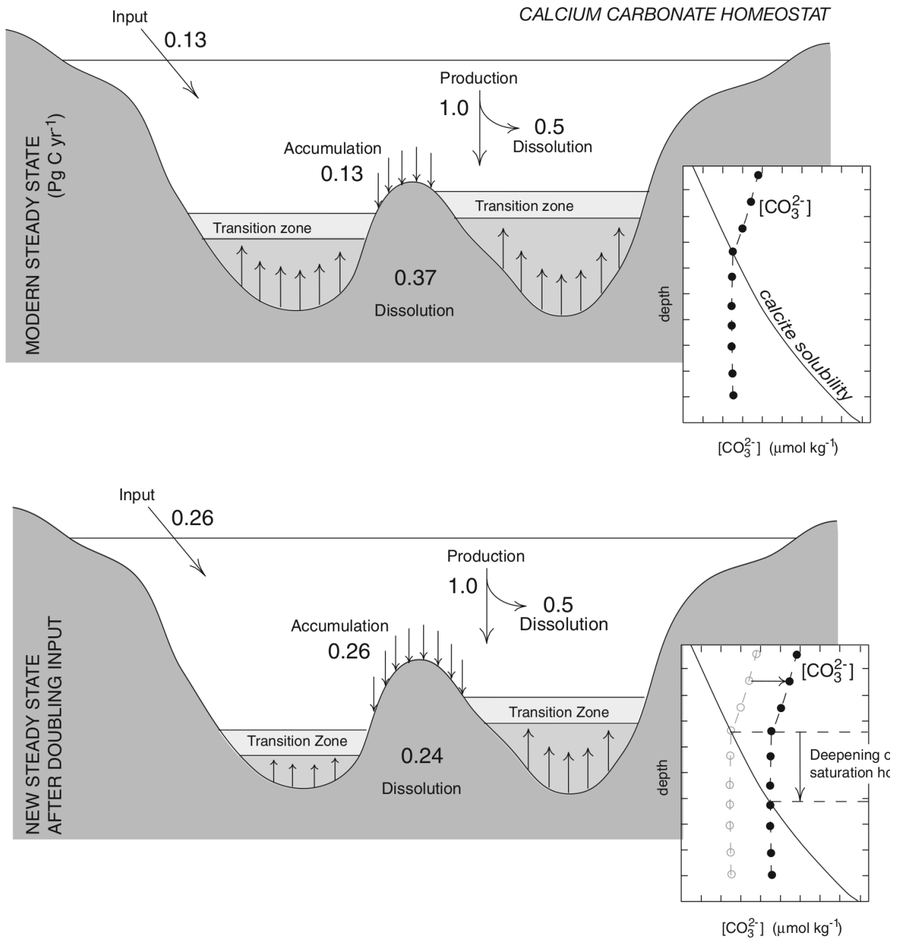

80°N
60°N
40°N
20°N
Eq
20°S
40°S
60°S
80°S
20°E
60°E
100°E
140°E
180°
140°W
100°W
60°W
20°W
20°E
100
90
80
70
60
50
40
30
20
10
0
Sediment CaCO3 (weight %)
50
25
5.0
75



What do you think controls the thickness of the grey region?


ATMOSPHERE
320
280
240
200
pCO2 (ppm)
G
H
25
20
15
10
5
0
Age (kyr)
0
−5
−10
Antarctica air ΔT (C°)


B
pCO_2
300
400
500
600
700
$CaCO_3$ dissolution
Photosynthesis
CO_2 invasion
CO_2 release
Respiration
$CaCO_3$ formation
2,450
2,400
2,350
2,300
2,250
ALK (µmol kg^{-1})
1,950
2,000
2,050
2,100
2,150
DIC (µmol kg^{-1})


CALCIUM CARBONATE HOMEOSTAT
Input
0.13
Production
1.0
0.5
Dissolution
Accumulation
0.13
Transition zone
Transition zone
0.37
Dissolution
MODERN STEADY STATE
(Pg C yr-1)
depth
[CO32-]
calcite solubility
[CO32-] (µmol kg-1)
Input
0.26
Production
1.0
0.5
Dissolution
Accumulation
0.26
Transition Zone
Transition Zone
0.24
Dissolution
NEW STEADY STATE
AFTER DOUBLING INPUT
depth
[CO32-]
Deepening o
saturation ho
[CO32-] (µmol kg-1)