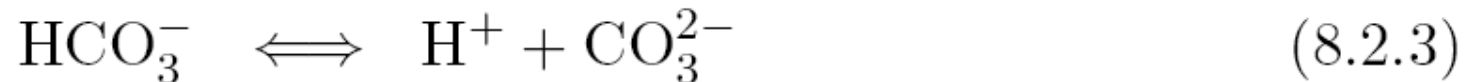
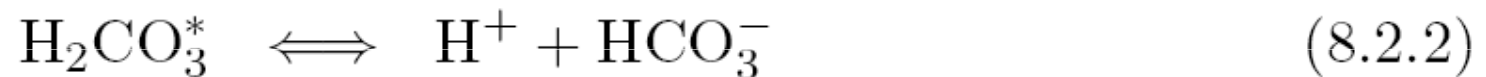
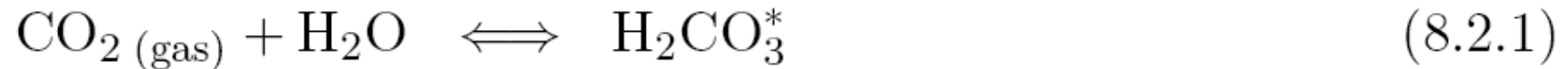


# CO<sub>2</sub> y Química Marina

El sistema de carbonatos

# Ecuaciones



CO<sub>2</sub> (gas) dióxido de carbono acuoso

HCO<sub>3</sub><sup>-</sup> bicarbonato

CO<sub>3</sub><sup>=</sup> carbonato

H<sub>2</sub>CO<sub>3</sub> el verdadero ácido carbónico (<0.3% CO<sub>2</sub>)

H<sub>2</sub>CO<sub>3</sub><sup>\*</sup> o (CO<sub>2</sub>)=(H<sub>2</sub>CO<sub>3</sub>)+(CO<sub>2</sub> (aq)) suma de las dos formas eléctricamente neutras, Químicamente no separables

## Constantes de equilibrio estequiometrico

$$K_0 = \frac{[\text{H}_2\text{CO}_3^*]}{p\text{CO}_2} \quad (8.2.4)$$

$$K_1 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3^*]} \quad (8.2.5)$$

$$K_2 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \quad (8.2.6)$$

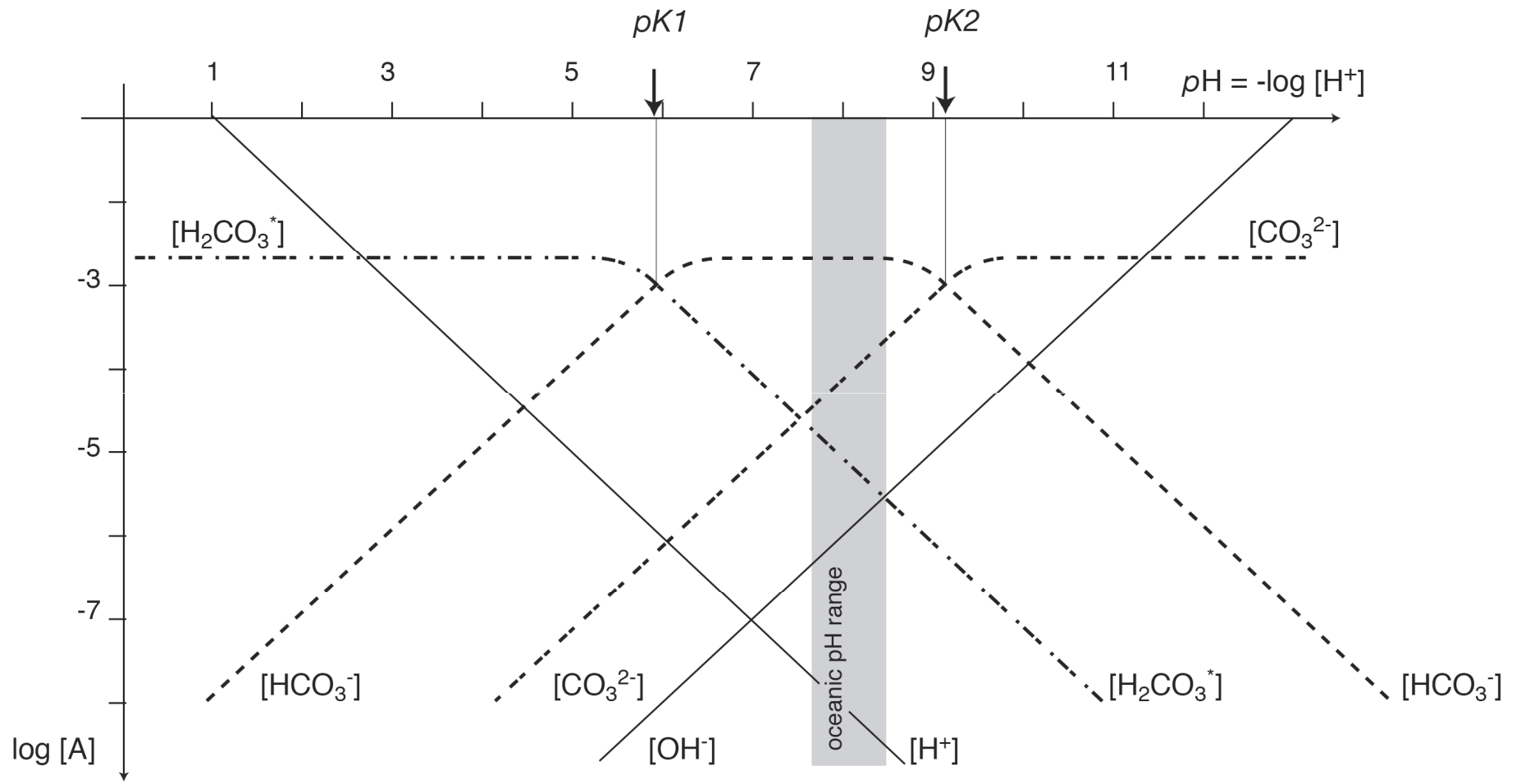
$(\text{CO}_2) = K_0(T, S) p\text{CO}_2$  Ley de Henry

$K_0, K_1, K_2$  dependen de la temperatura  $T$ , la presión  $P$  y la salinidad

# Carbono Inorganico disuelto y Alcalinidad

DIC

TA « I found at least 20 different definitions of alkalinity ! »  
« ...alkalinity, one of the most central but perhaps not  
the best understood concept in aquatic chemistry. »  
*Morel and Herin 1993*



$$\text{pH}_{\text{high school}} = -\log (\text{H}^+)$$

Diferentes escalas:

pHNBS: (IUPAC) serie de standard buffer  
solucion (no recomendada para el agua de mar)

Agua artificial :

pH<sub>f</sub> (free scale) freshwater (pure water)

pH<sub>T</sub> total scale (un medium con el ion sulfato)

pH<sub>sws</sub> sea water (artificial ) utilizadas por los  
quimicos marinos (diferencia entre ellas de 0.01)

Free scale pH 0.11 y 0.12 Unidades mas fuerte  
que la escala total y la sws

Accuracy in pH measuring  $\pm 0.002$  (Wedborg et  
al 1999) y DOE (1994) utilizada por Wolf

## 4 Ecuaciones 6 Incognitas

Ecuaciones: Equilibrio K1, K2  
Balance de Masa DIC  
Balance de Cargas CA o TA

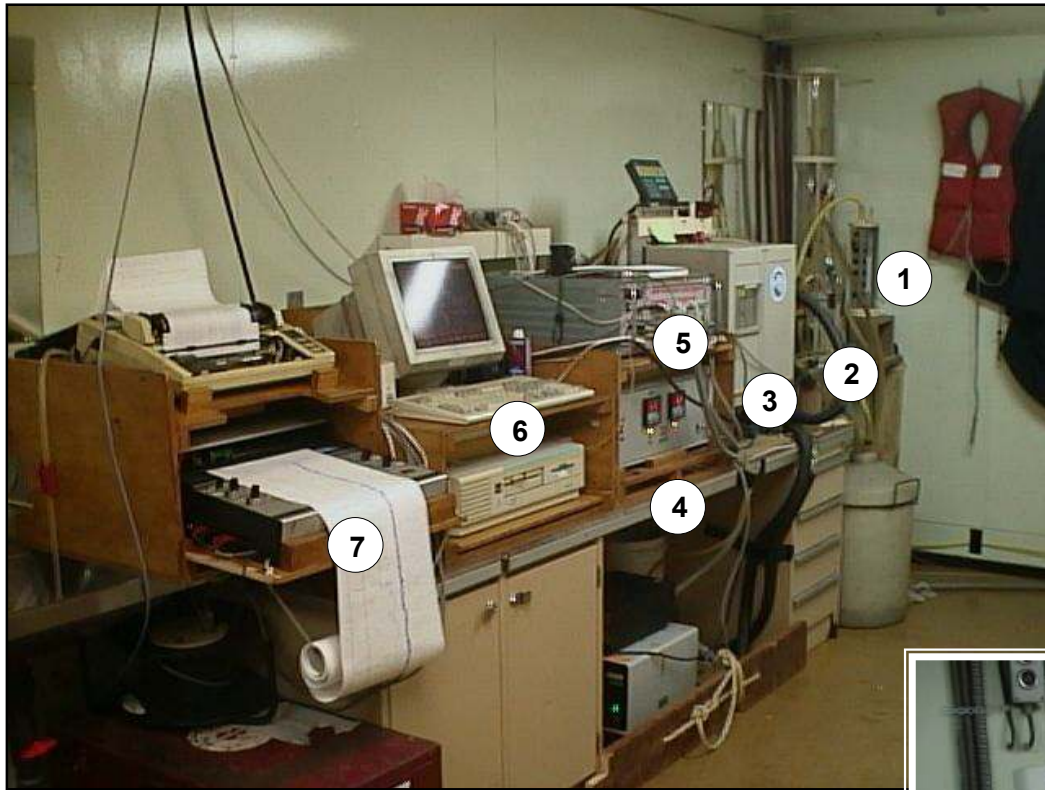
$$6? - 2 = 6 - 4$$

CO<sub>2</sub>, HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>=</sup>, H<sup>+</sup>, DIC CA

Medidas : CO<sub>2</sub>, H<sup>+</sup>, DIC, TA

Otras especies contribuyendo a TA deben ser incluidas  
(eg: Boron)

Solucion de las ecuaciones



- 1- CT Sea-bird SB-37
- 2- Equilibrador
- 3- Analizador IR
- 4- Sistema de enfriamiento
- 5- Interfase multicanal
- 6- PC

Medición de alcalinidad total (AT)  
y de carbono inorgánico disuelto (DIC).





# Ecuaciones utilizadas para calcular las constantes de equilibrio

Aproximacion

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

$$\text{Alk} = \text{CarbAlk}: \text{HCO}_3^- + 2\text{CO}_3^{2-}$$

$$\text{HCO}_3^- = ? \quad \text{CO}_3^{2-} = ? \quad (\text{se pueden calcular})$$

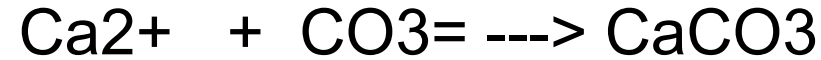
# Que hace variar la Alk ?

\*La diferencia de cargas entre cations y anions ( $f(S)$ ) --> Alk estrechamente relacionada a la salinidad

\*Cambios en la salinidad : precipitacion, evaporacion, aportes de agua dulce, formacion y fundimiento del hielo de mar --> cambios Alk

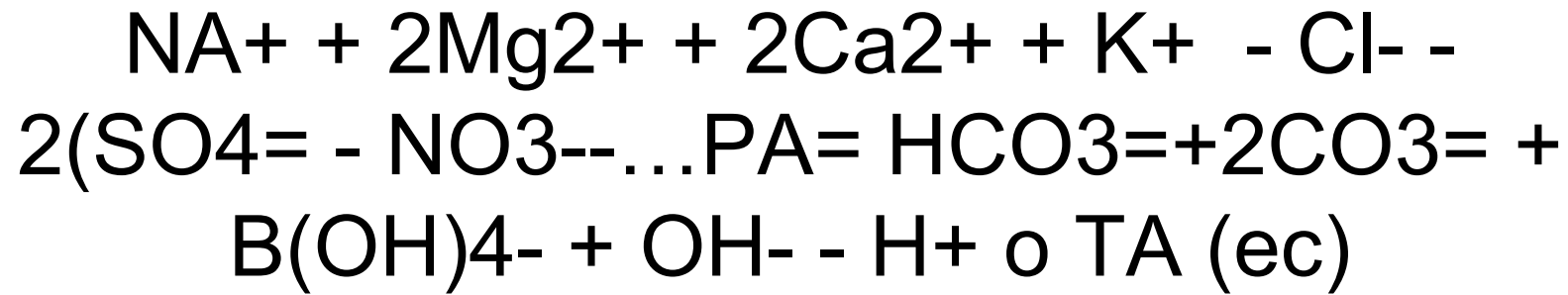
\*Precipitacion biologica de  $CaCO_3$  (cocolitoforidos, forameniferos, pteropodos, corales)

\*Disolucion de coquillas y esqueletos calcareos



Precipitation de una mol de  
CaCO<sub>3</sub> reduce DIC de 1 mol y  
TA de 2 moles

Notar que estas cargas son  
independientes de la fuente de  
carbono utilizado por los  
organismos para la calcificación



- Precipitación 1 mol  $\text{CaCO}_3$  Alk disminuye de 2 moles (term: 2 ( $\text{Ca}^{2+}$ ))
- Disolución de 1 mol  $\text{CaCO}_3$  : Alk aumenta de 2 moles (term 2  $\text{Ca}^{2+}$ )
- Toma de DIC (Algas) (Hyp: electroneutralidad del alga es asegurada por la toma paralela de  $\text{H}^+$  o el relargage de  $\text{OH}^-$  = Alk no cambia
- Toma de 1 mol Nitrato ( $\text{NO}_3^-$ ) = Alk aumenta de una mol (term:  $-\text{NO}_3^-$ ), coherente con las experiencias en laboratorio.
- Remineralización del alga Alk disminuye de una mol
- La toma de amonio o fosfatos necesita la definición de alcalinidad total

Factor de Revelle = La respuesta del oceano a la toma de CO2 atm

$$H = (H^+) \quad s = (CO_2)$$

$$dDIC = D_s ds + D_h dh$$

$$dTA = A_s ds + A_h dh$$

Hipotesis: la toma de CO2 de l'atmosfera no cambia la alcalinidad -->  $dTA = 0$

$dh/ds = -A_s A_h^{-1} > 0$  cuando CO2 aumenta pH disminuye

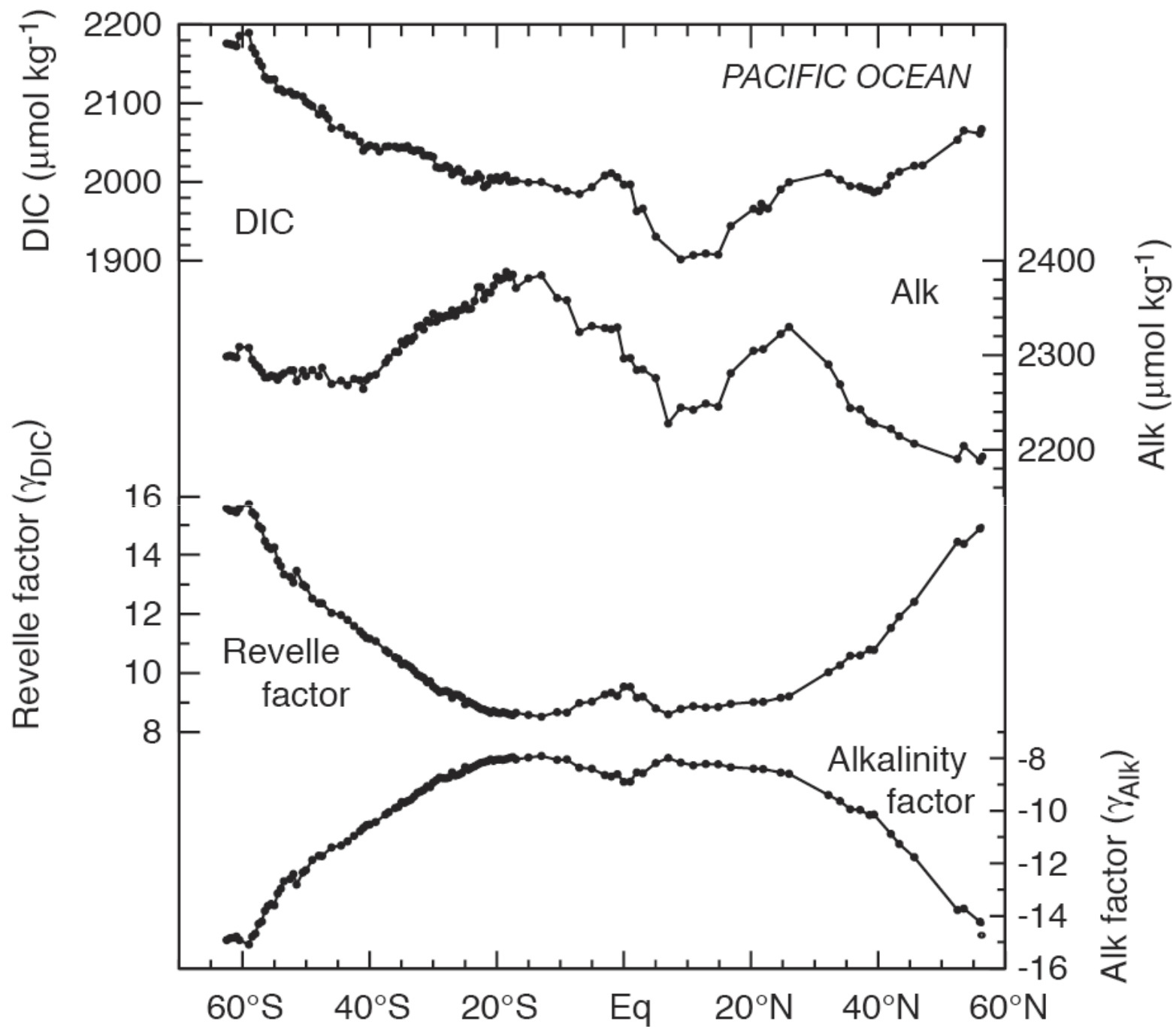
$dDIC : (D_s - dh A_s A_h^{-1}) > 0$  DIC aumenta y CO2 aumenta

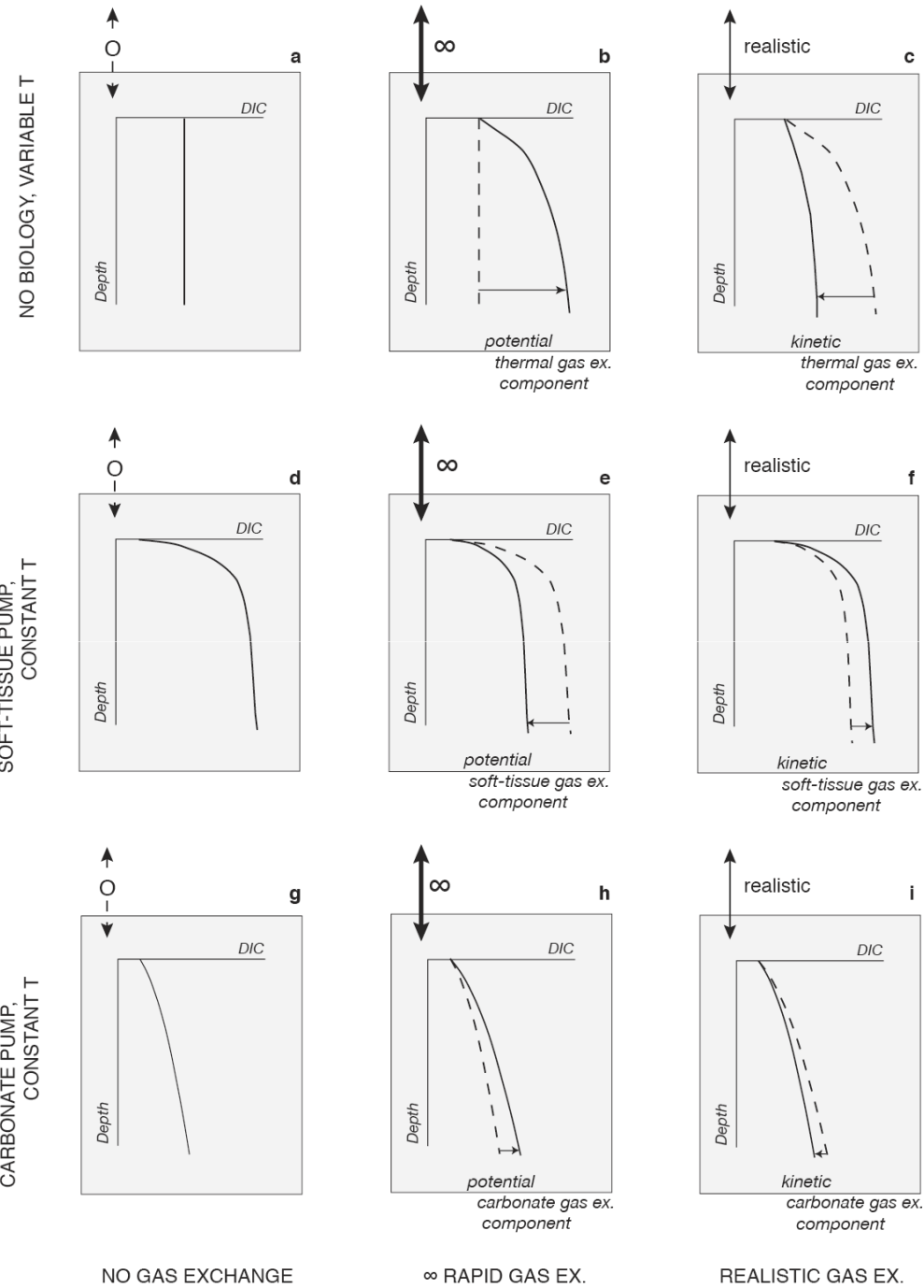
$$RF_0 = \frac{(d(CO_2)/(CO_2))}{(dDIC/dDIC)} \quad TA = \text{cte (Revelle 1909)}$$

$RF_0 = 8-15$  El aumento del DIC es solo 1/10 el aumento del CO2 disuelto

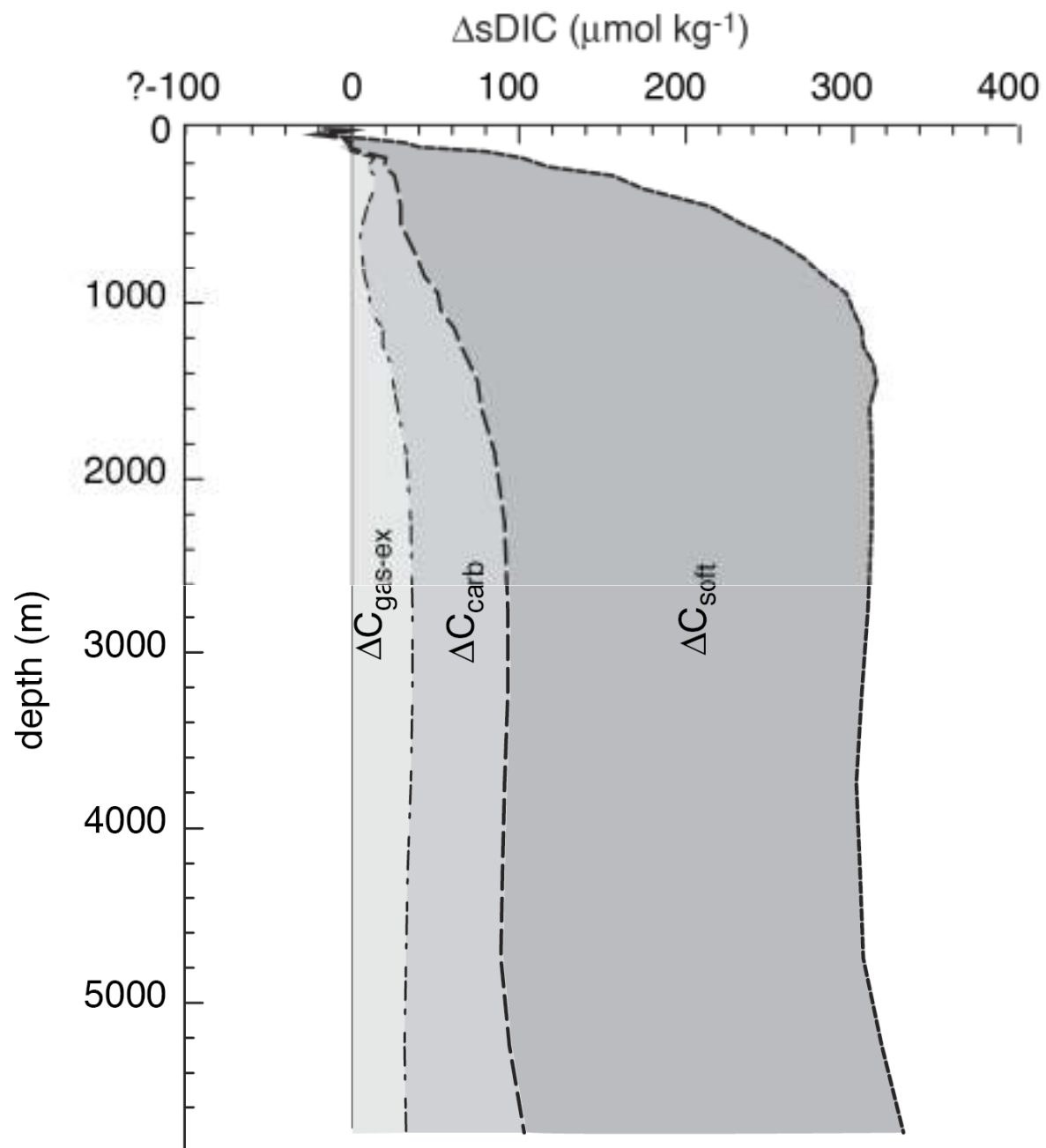


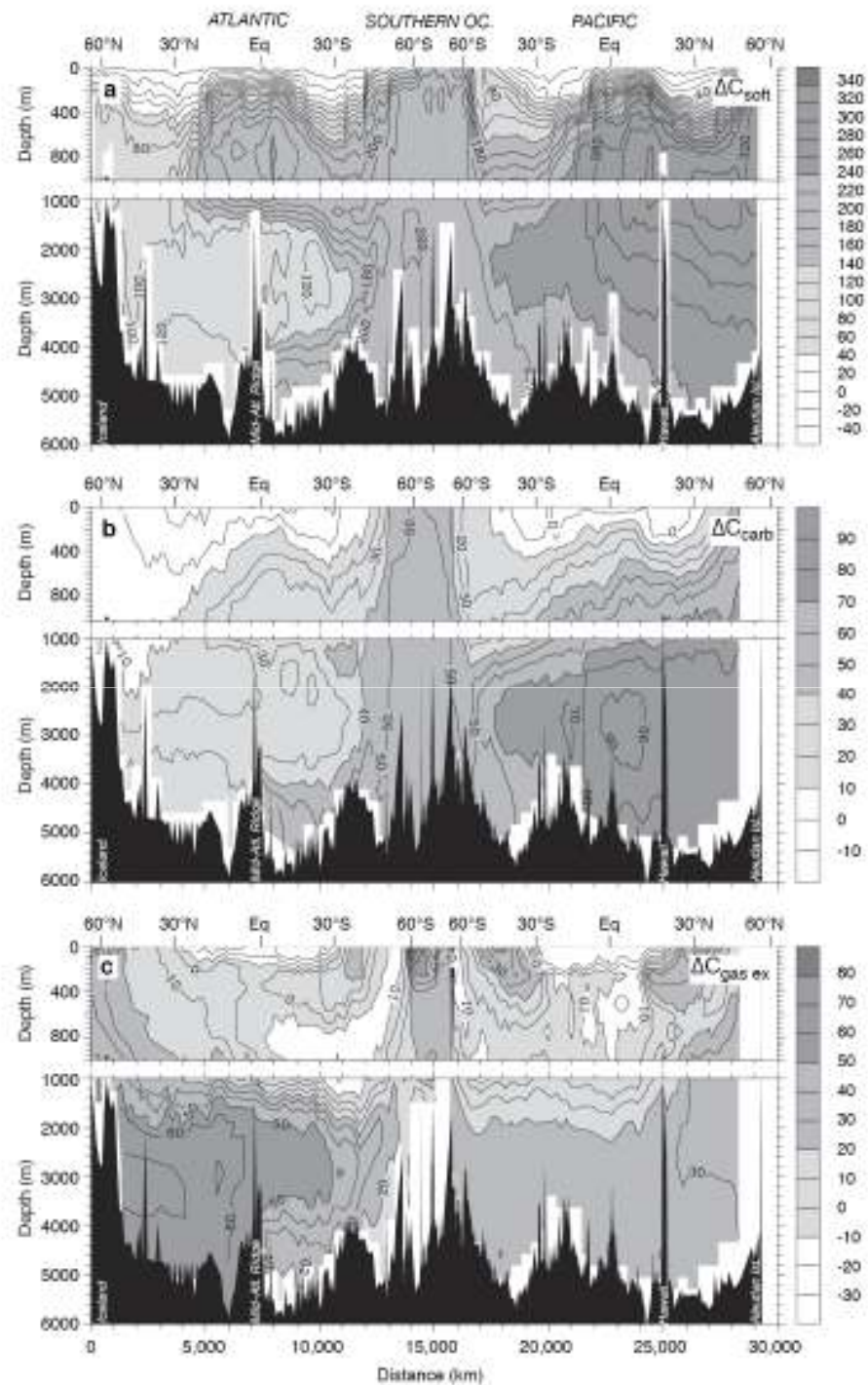
- \*  $\text{CaCO}_3$  produce  $\text{CO}_2$  (Correcto)
- \* Por cada mol de  $\text{CaCO}_3$  formada le  $\text{CO}_2$  en el agua aumenta de una mol (Falso, a causa del buffering : gran parte del  $\text{CO}_2$  es convertido en bicarbonato  $\rightarrow$  la ecuacion no esta completa
- \* TA y DIC son reducidos de 2 y de 1 unidad por cada unidad de  $\text{CaCO}_3$  formado
- Los organismos utilizan bicarbonato para la formacion de  $\text{CaCO}_3$ . Esto puede ser correcto, seguro que la alcalinidad de los carbonatos es consumida

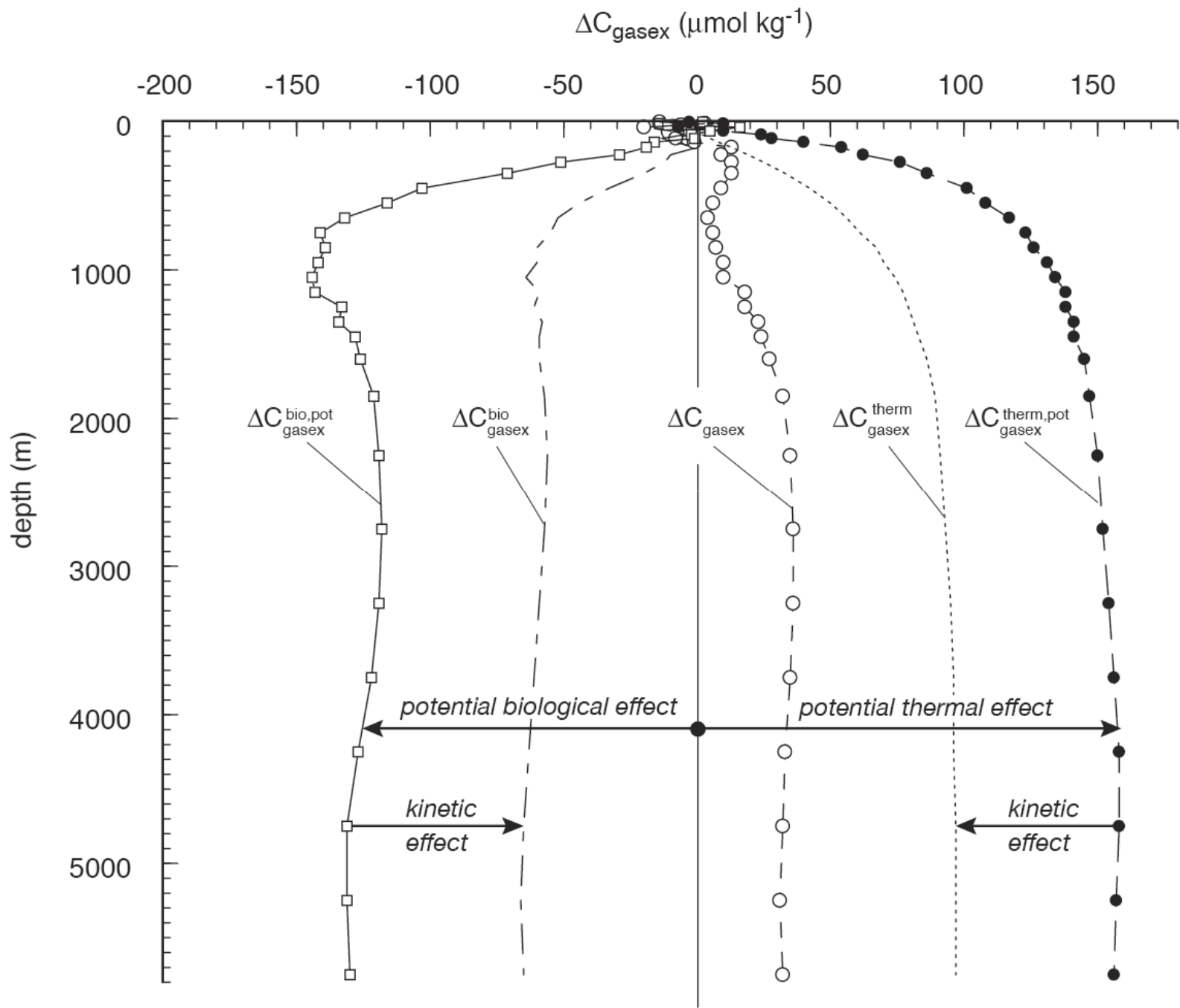




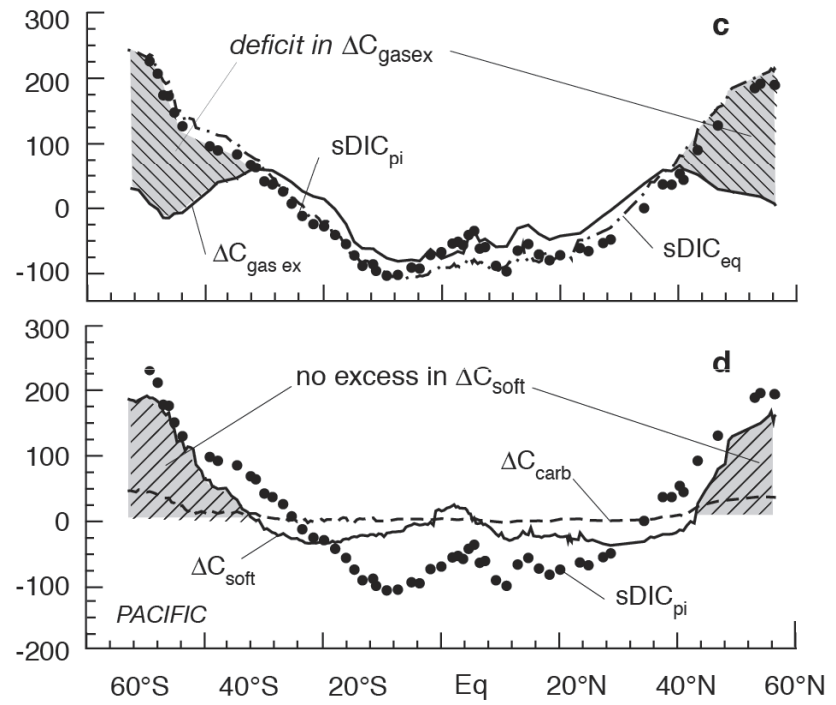
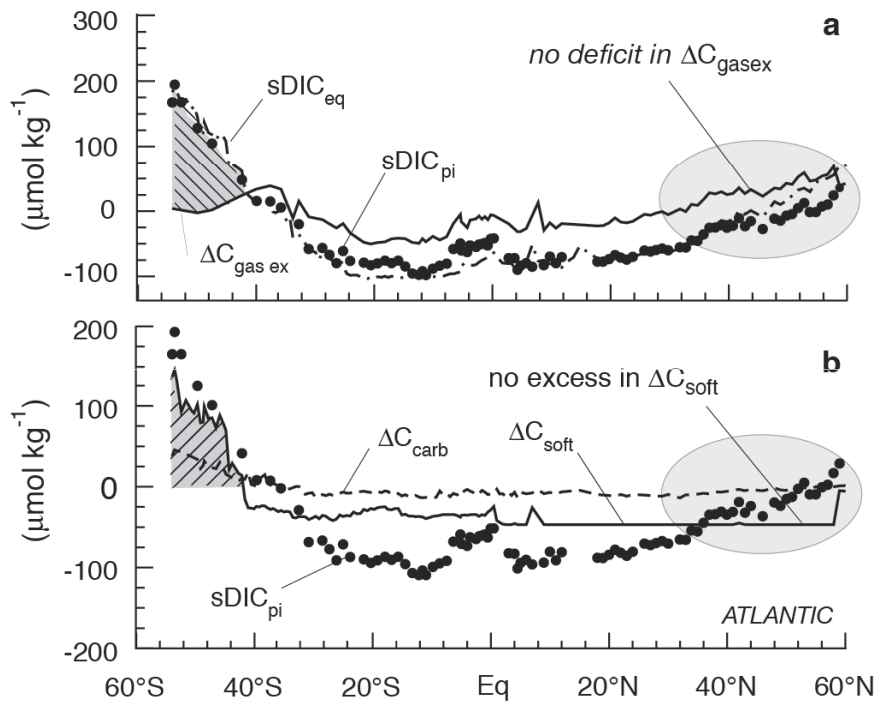








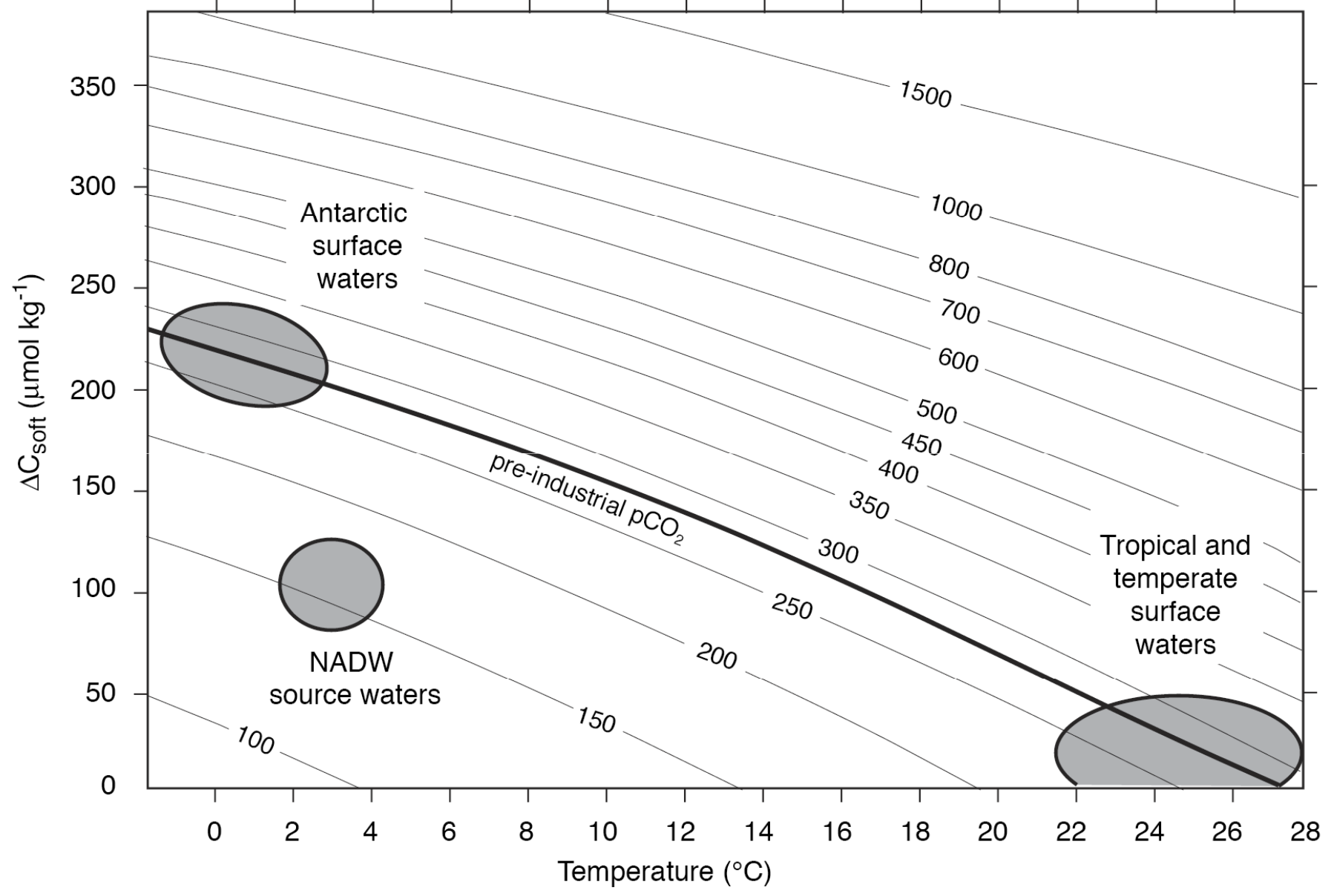
	(1)	(2)	(3)	(4)	(5)
	deep water	move to surface	warm up	formation of organic matter	formation of CaCO <sub>3</sub>
Pressure (atm)	400	1	1	1	1
Temp (°C)	1.8	1.8	23	23	23
PO <sub>4</sub> (μmol kg <sup>-1</sup> )	2.2	2.2	2.2	0	0
<i>DIC</i> (μmol kg <sup>-1</sup> )	2298	2298	2298	2058	1994
<i>Alk</i> (μmol kg <sup>-1</sup> )	2400	2400	2400	2433	2305
<i>p</i> CO <sub>2</sub> (μatm)		510	1220	293	348

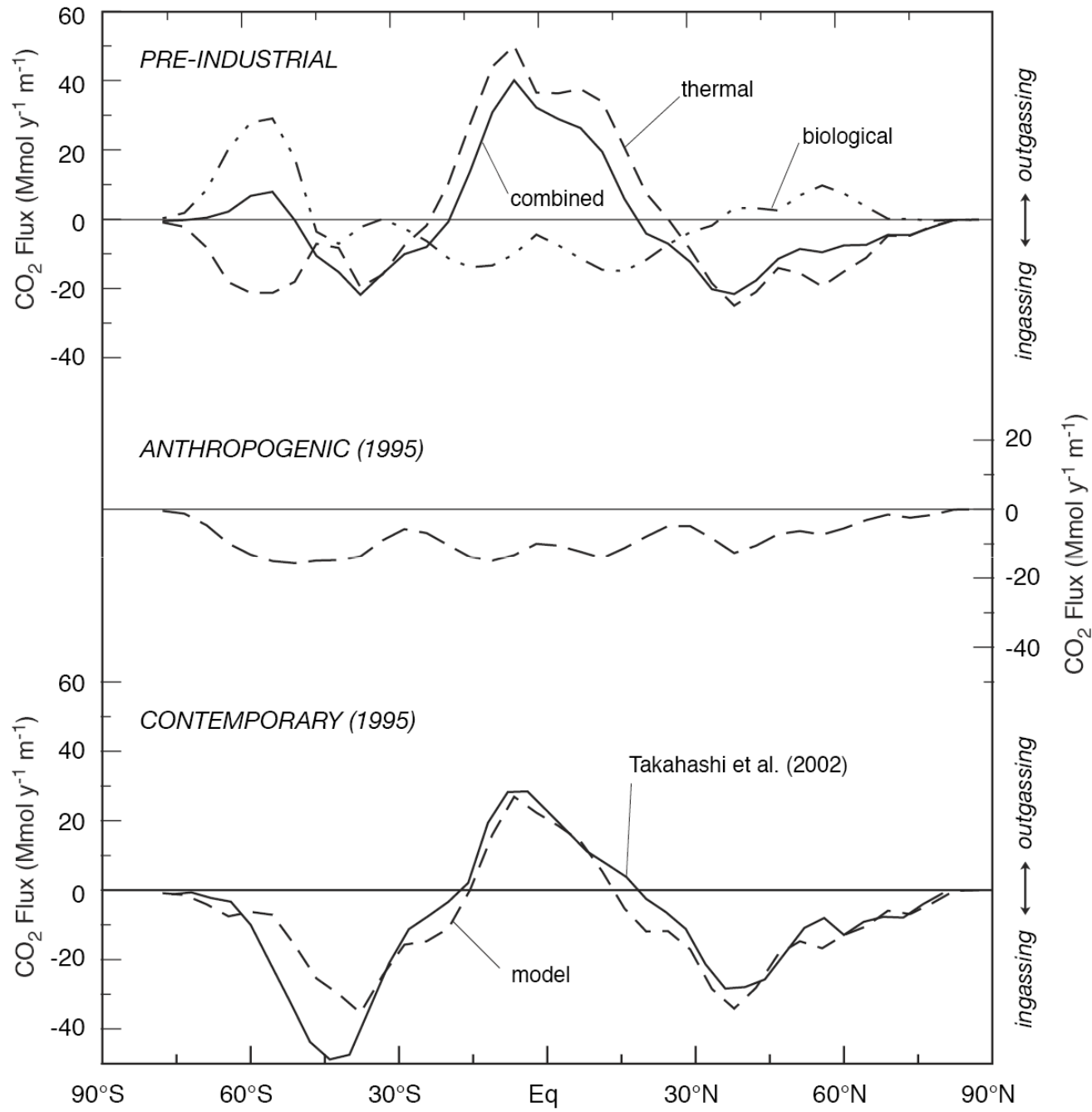


---

	Mineralization of org. matter	Dissolution of CaCO <sub>3</sub>
$\Delta DIC$ (mol/mol)	+1	+1
$\Delta \text{Alk}$ (mol/mol)	-0.14	+2
$\Delta [\text{CO}_3^{2-}]$ (mol/mol)	-1.14	+1
$\Delta [\text{HCO}_3^-]$ (mol/mol)	+2.14	0

---







Tiempo de puesta en equilibrio para el intercambio de CO<sub>2</sub> entre el oceano y la atmosfera

CO<sub>2</sub> = 240d

O<sub>2</sub> = 12d

## EL Ultimo LGM CO2

LGM 18000Y CO2 = 100ppmv mas bajo  
que el de 1800 (pre-industrial 280)

Puede este cambio ser debido al cambio de  
temperatura de superficie ?

Temperatura 1K mas baja

Salinidad 3% mas alta(sea level 100m mas bajo)

Hipotesis : DIC y TA 3% mas altos de 3% (oversimplificacion)

## CO2 Futuras emisiones y cambio en el pH

En la atmosfera CO2 preindustrial 280ppmv

1997 CO2 atm= 364 ppmv

2100 700 (Escenario IS92a,  
IPCC; 1995)

CaCO2 solubilidad estoquiometrica

$$K_{sp}^* = (Ca^{2+})_{sat} \times (CO_3^{2-})_{sat}$$

$$\Omega = \frac{(Ca^{2+})_{sw} \times (CO_3^{2-})_{sw}}{K_{sp}^* (insitu\ T, S\ y\ presion)}$$

> 1 supersaturacion  
< 1

undersaturacion

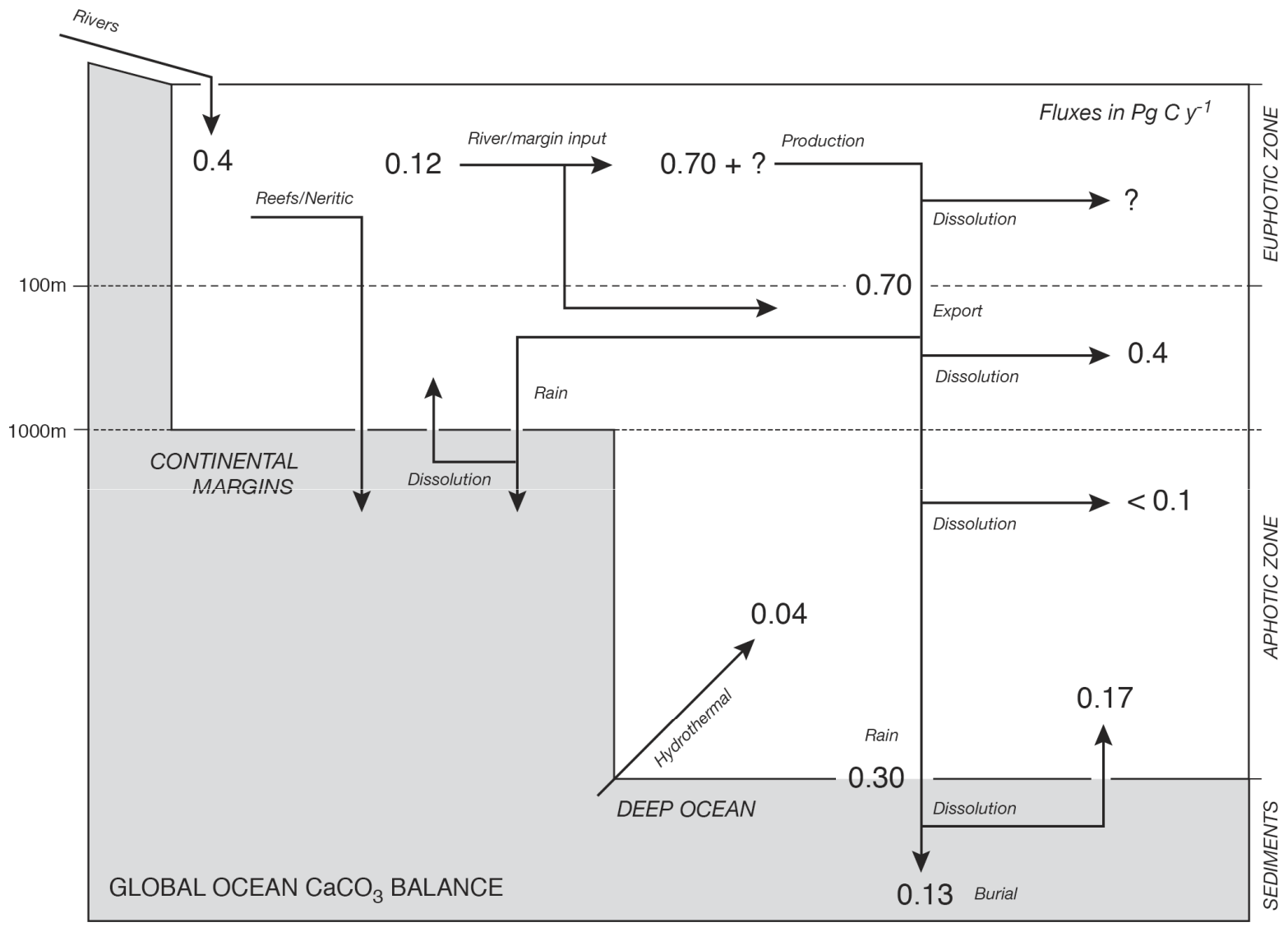
Variaciones de Ca<sup>2+</sup> son muy bajas, omega es controlado por CO<sub>3</sub><sup>2-</sup>

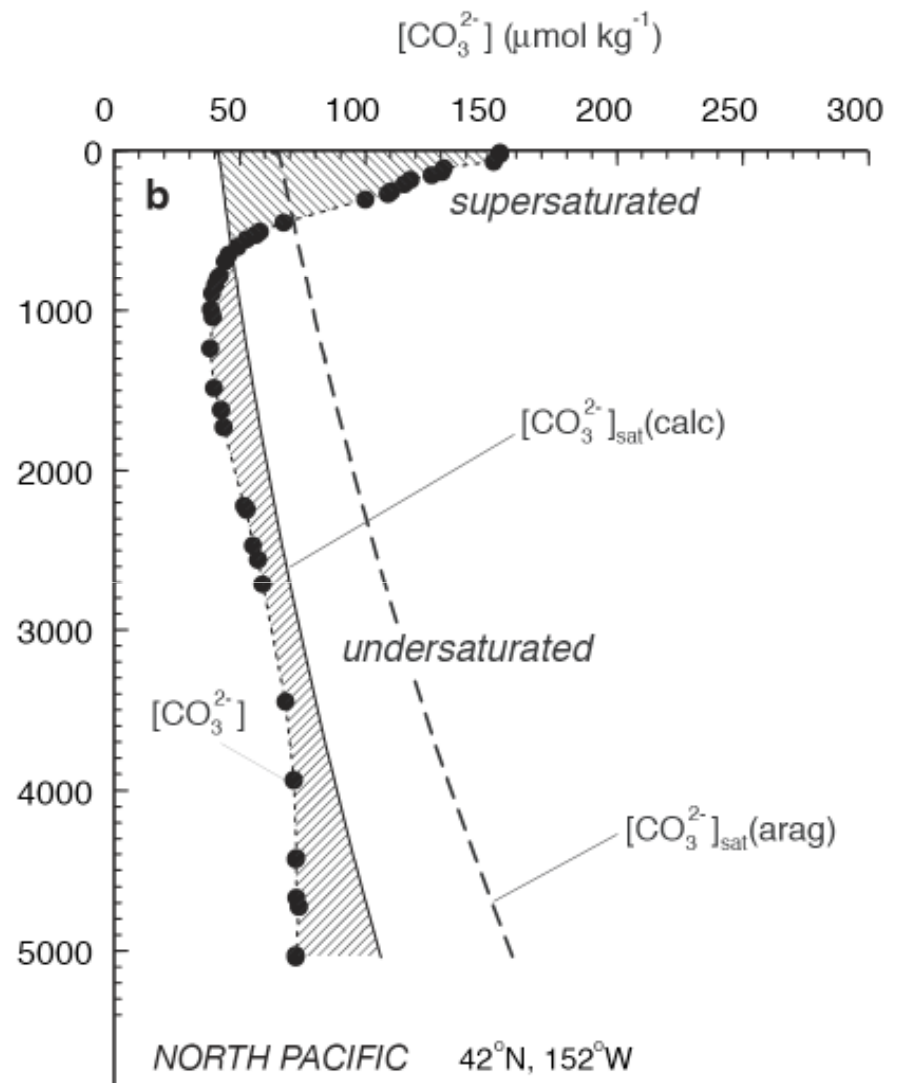
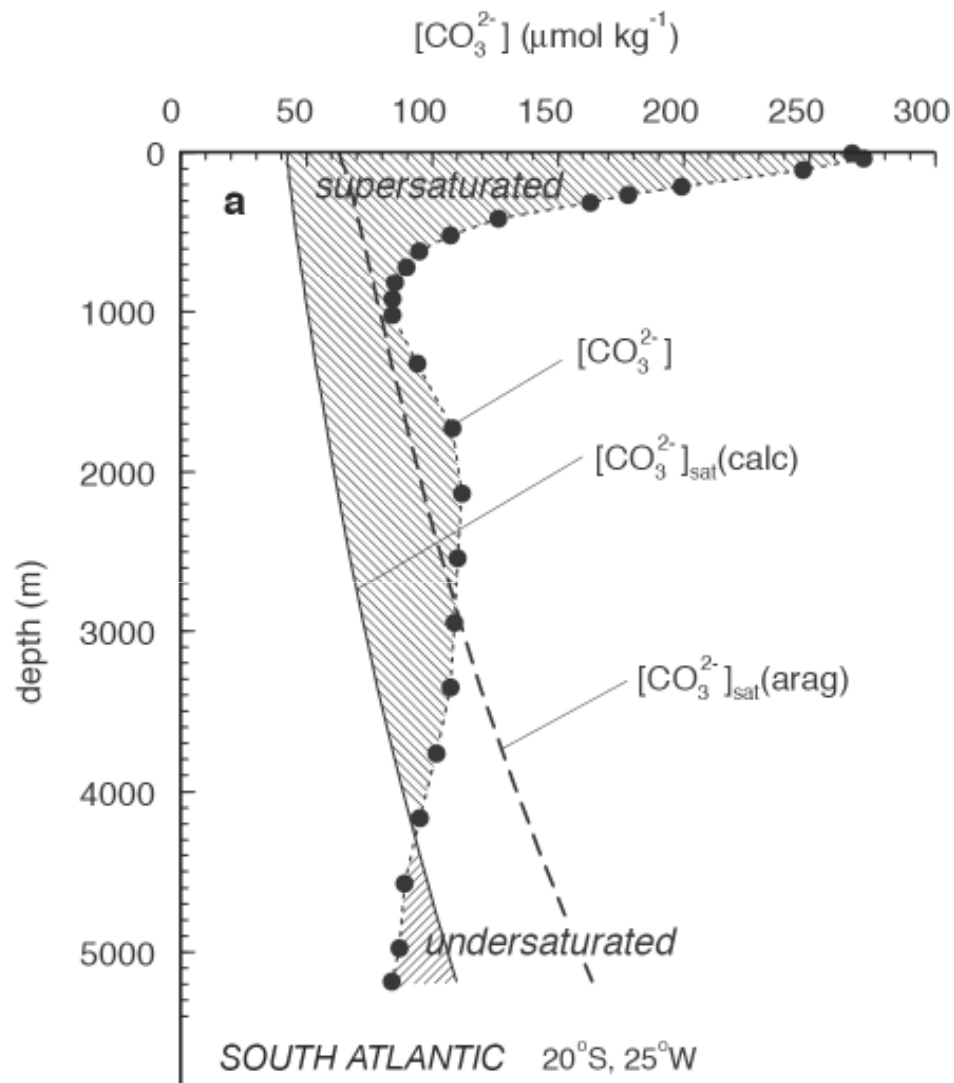
Reduccion de CaCO<sub>3</sub> ----> 6 a 32 GtC antes del

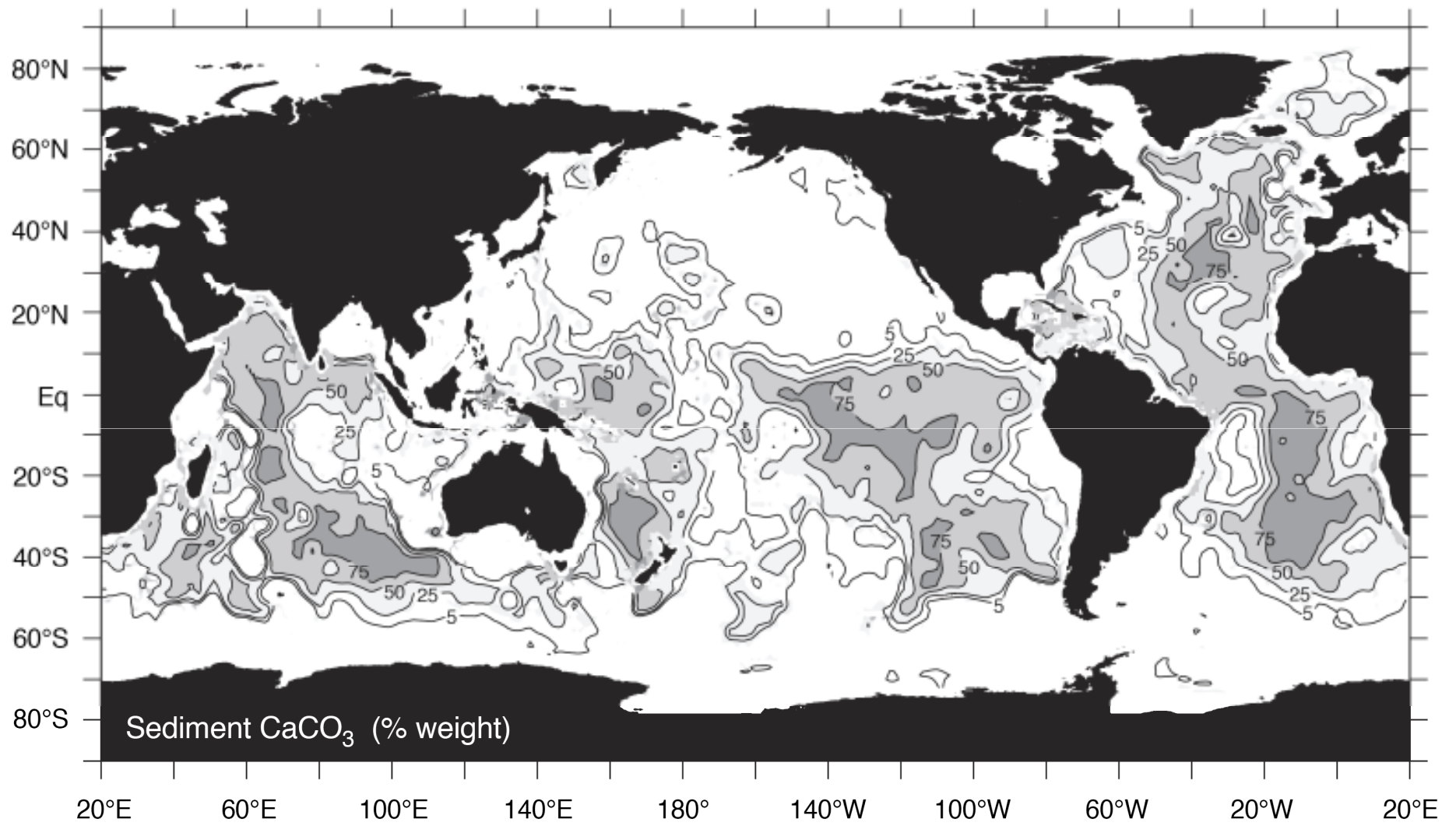
Table 9.3.4: Saturation concentration of  $\text{CO}_3^{2-}$  as a function of temperature and pressure for a salinity of 35.

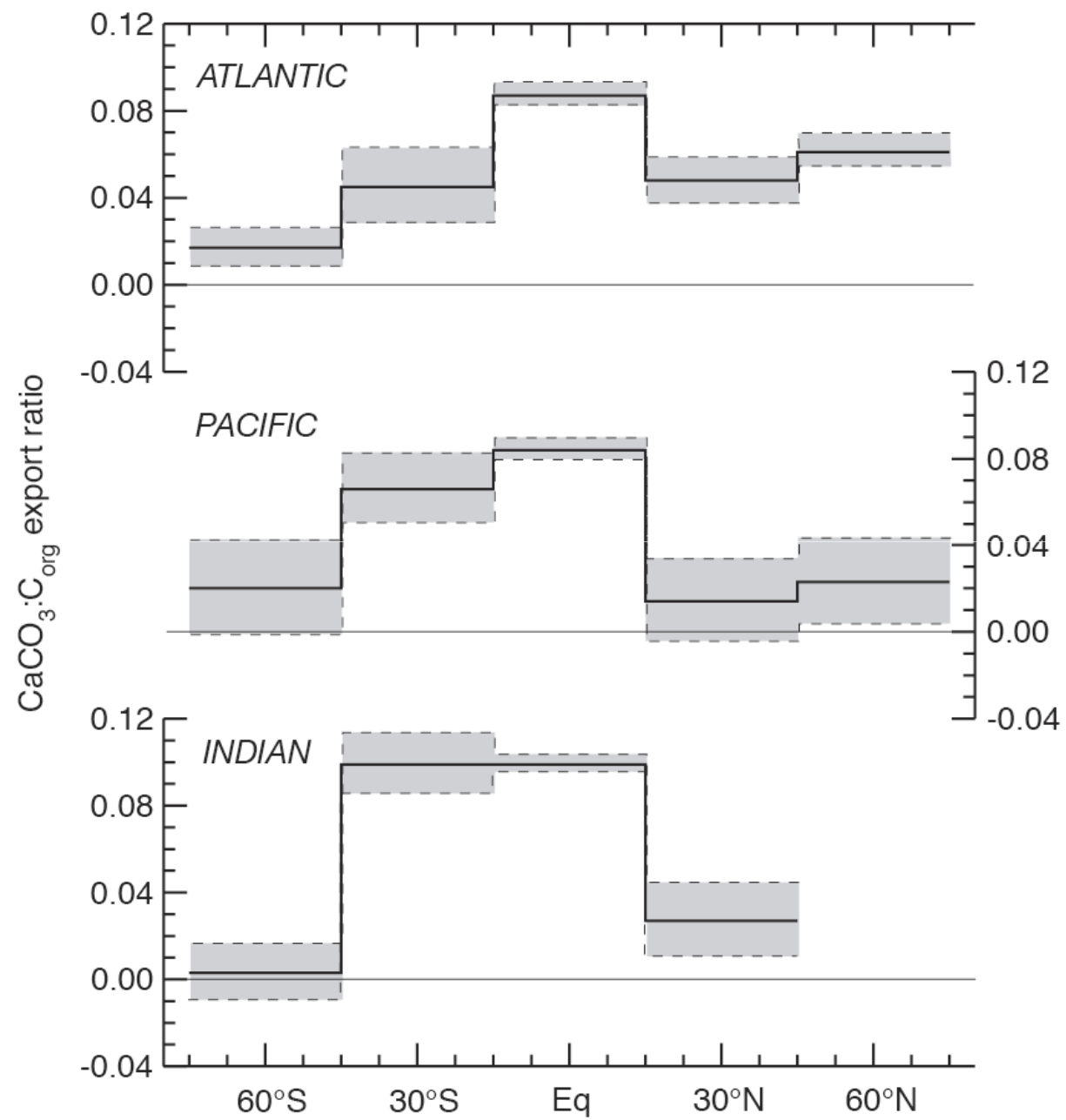
Temp.	surface (0 dbar)		thermocline (1000 dbar)		deep ocean (6000 dbar)	
	$[\text{CO}_3^{2-}]_{sat}$ calcite	$[\text{CO}_3^{2-}]_{sat}$ aragonite	$[\text{CO}_3^{2-}]_{sat}$ calcite	$[\text{CO}_3^{2-}]_{sat}$ aragonite	$[\text{CO}_3^{2-}]_{sat}$ calcite	$[\text{CO}_3^{2-}]_{sat}$ aragonite
$^{\circ}\text{C}$	$\mu\text{mol kg}^{-1}$	$\mu\text{mol kg}^{-1}$	$\mu\text{mol kg}^{-1}$	$\mu\text{mol kg}^{-1}$	$\mu\text{mol kg}^{-1}$	$\mu\text{mol kg}^{-1}$
0.00	41.6	66.3	50.7	79.8	124.2	183.7
2.00	41.7	66.3	50.6	79.4	121.5	179.5
4.00	41.8	66.3	50.5	79.1	119.0	175.5
6.00	41.8	66.2	50.3	78.7	116.6	171.7
8.00	41.9	66.1	50.2	78.3	114.4	168.1
10.00	41.9	65.9	50.0	77.8	112.4	164.6
12.00	41.9	65.7	49.9	77.3	110.5	161.3
14.00	41.9	65.4	49.7	76.7	108.7	158.1
16.00	41.8	65.0	49.5	76.1	107.0	155.1
18.00	41.8	64.7	49.3	75.5	105.4	152.1
20.00	41.7	64.2	49.1	74.8	103.9	149.3
22.00	41.6	63.7	48.9	74.0	102.5	146.6
24.00	41.5	63.2	48.7	73.3	101.2	143.9
26.00	41.4	62.6	48.4	72.5	99.9	141.3
28.00	41.2	62.0	48.2	71.6	98.7	138.9
30.00	41.0	61.3	47.9	70.8	97.6	136.4

The solubility products at 1 atm pressure are from *Mucci* [1983]. The pressure dependence is after *Millero* [1983]. The calcium concentration was assumed to be  $0.01028 \mu\text{mol kg}^{-1}$ .

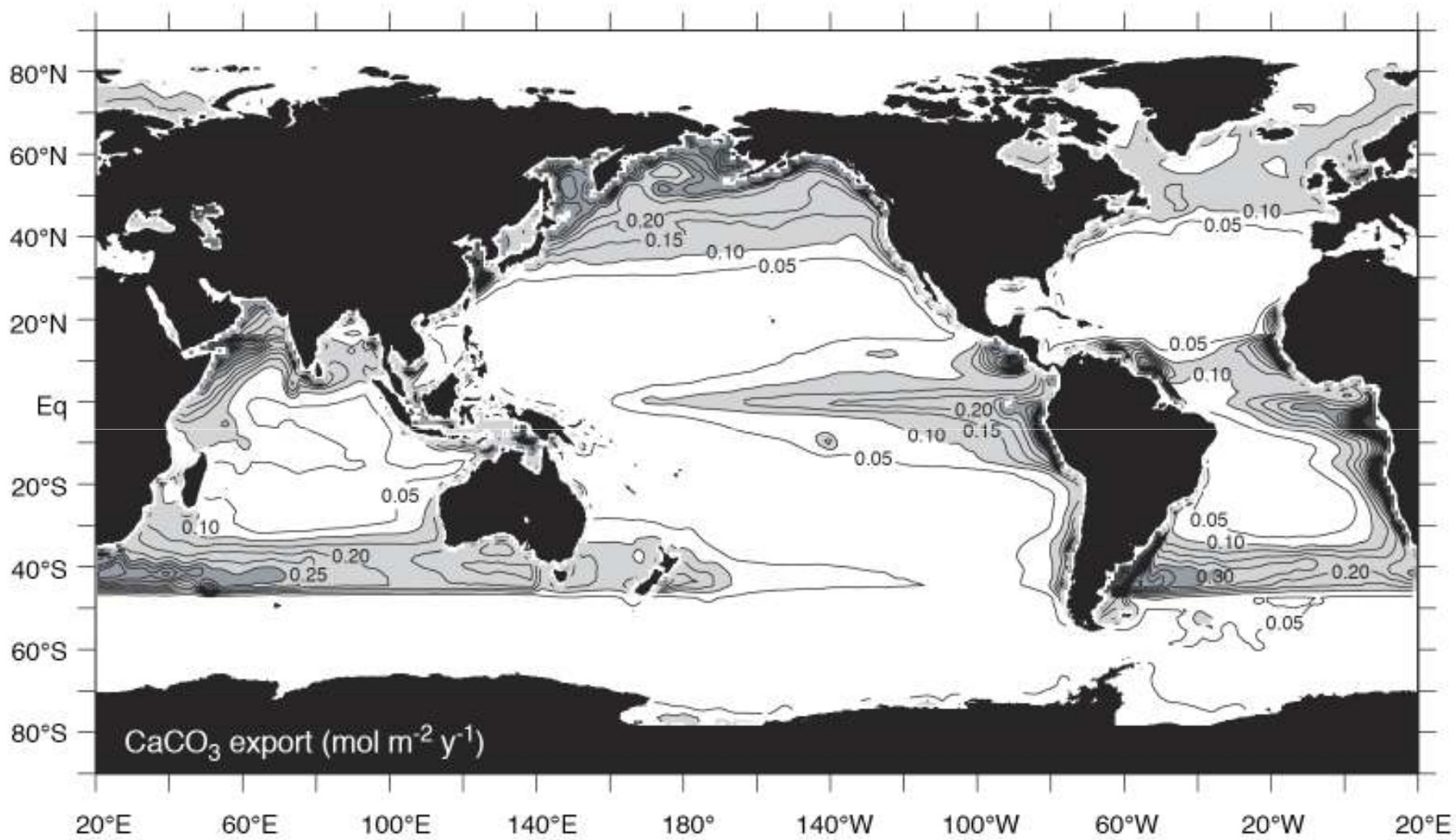


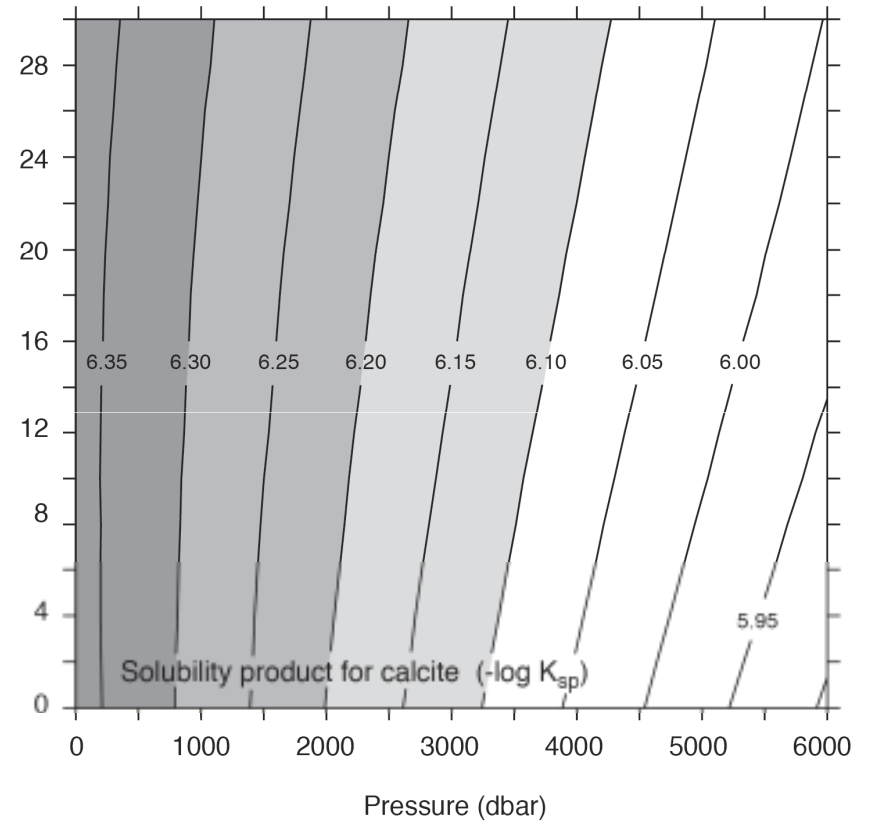
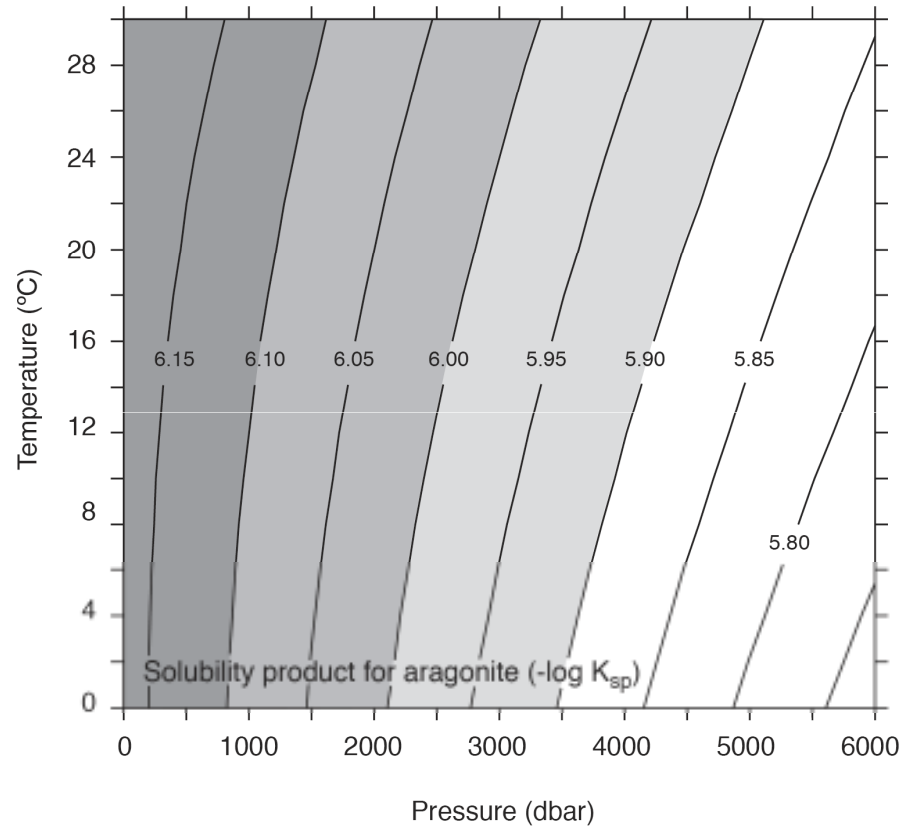




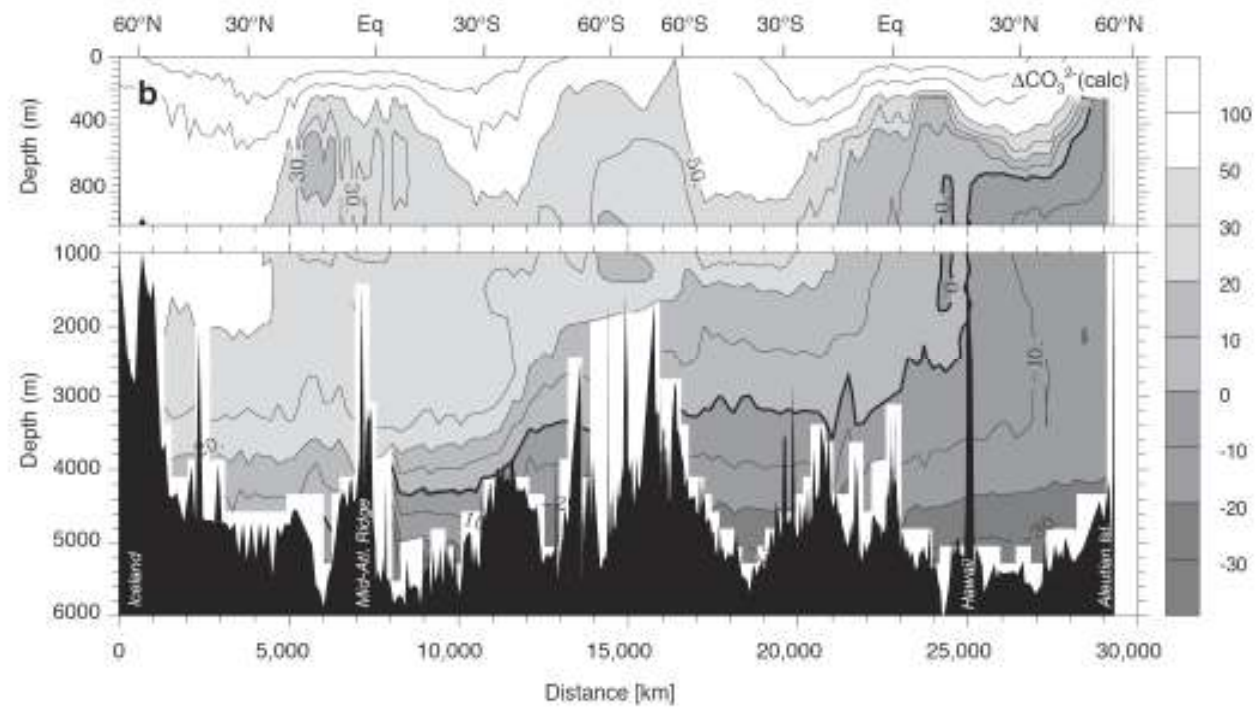
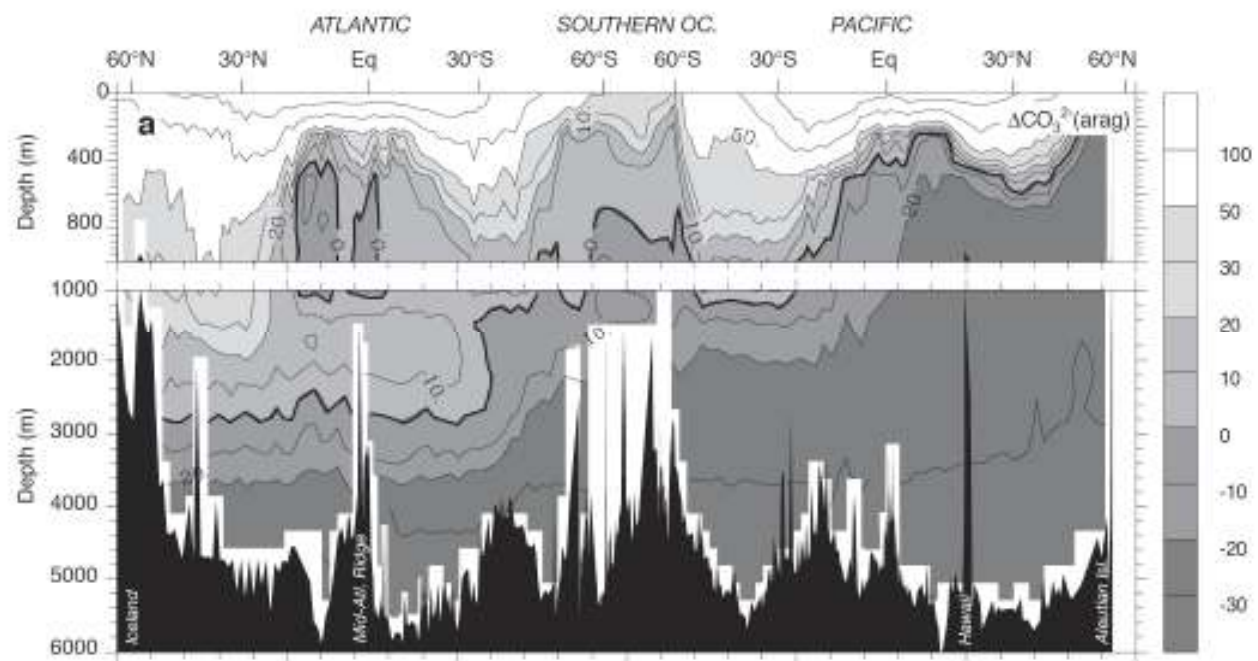


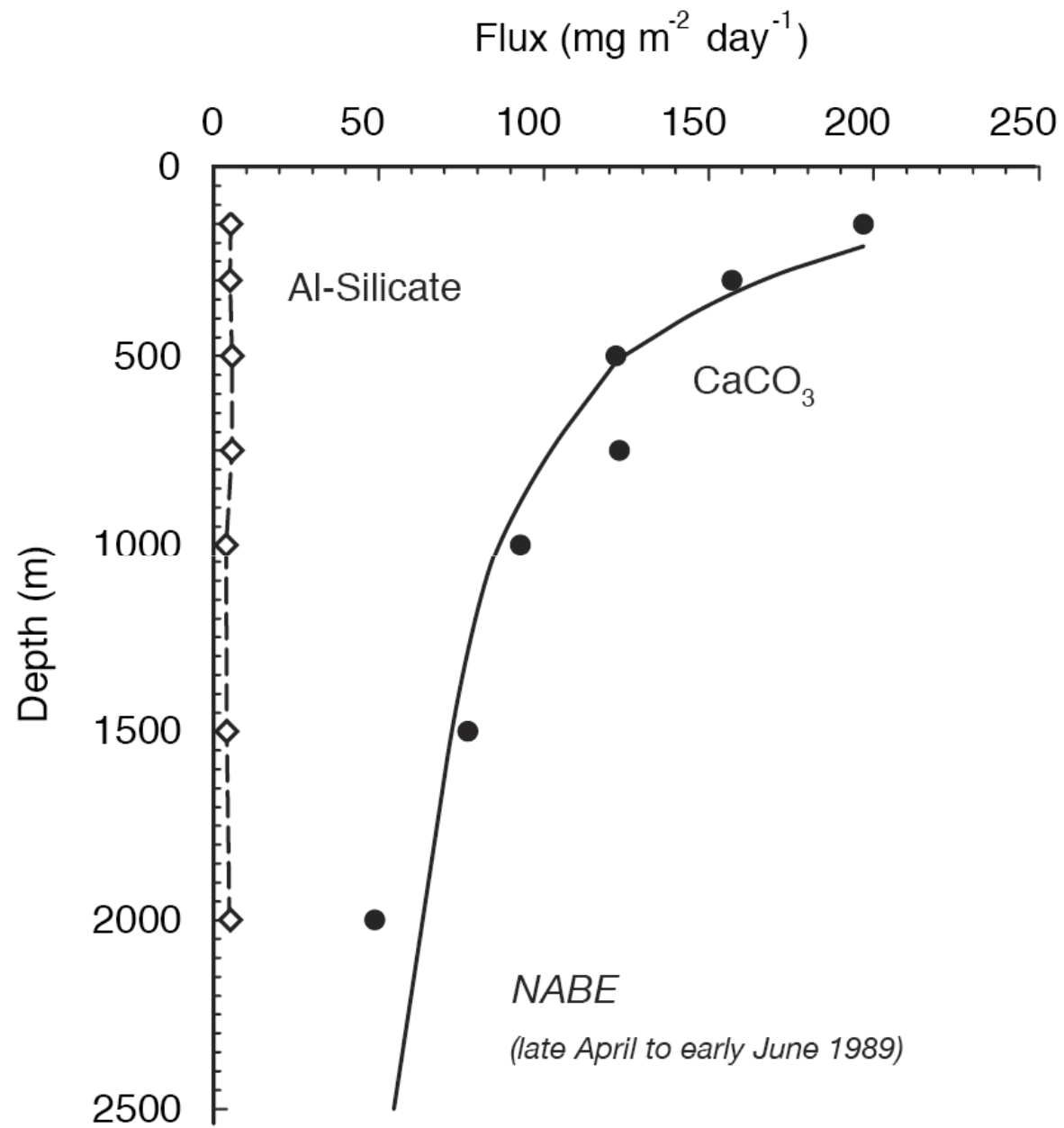


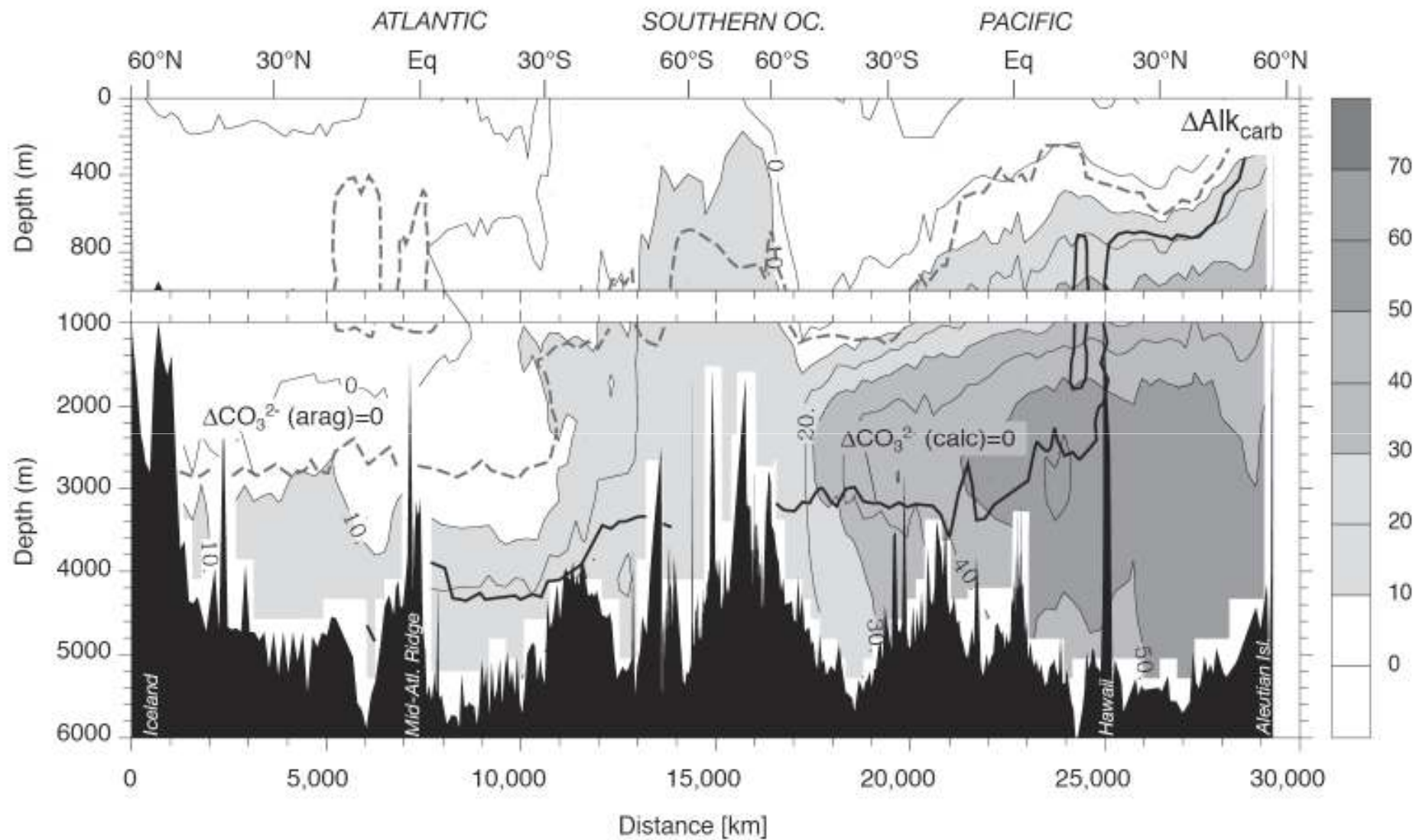


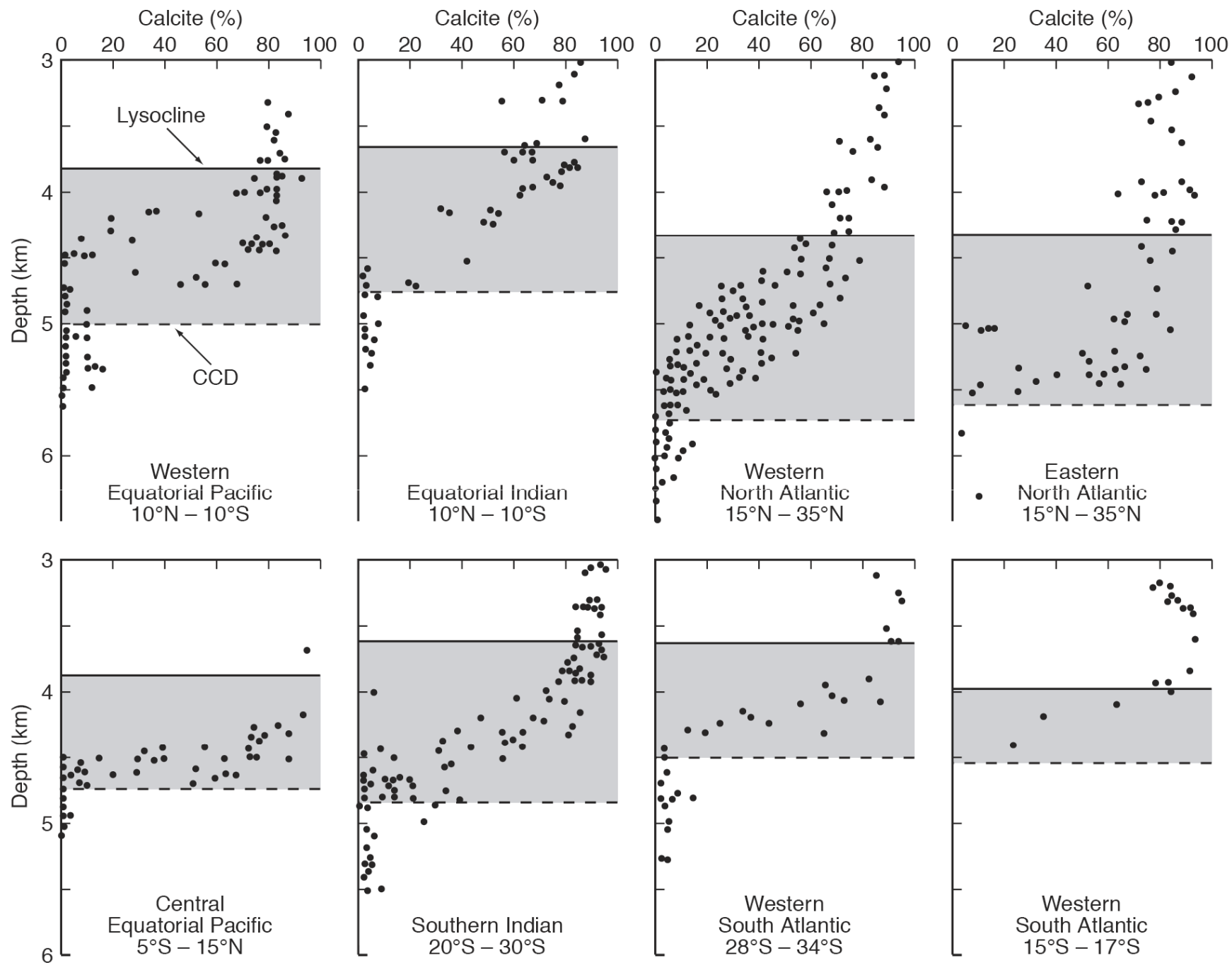


	(1) surface water	(2) move to intermed. water <sup>a</sup>	(3) move to deep water <sup>b</sup>
<i>DIC</i> ( $\mu\text{mol kg}^{-1}$ ) <sup>c</sup>	2026	2246	2346
Alk ( $\mu\text{mol kg}^{-1}$ ) <sup>c</sup>	2308	2320	2413
[CO <sub>3</sub> <sup>2-</sup> ] ( $\mu\text{mol kg}^{-1}$ ) <sup>d</sup>	202	80	80
[HCO <sub>3</sub> <sup>-</sup> ] ( $\mu\text{mol kg}^{-1}$ ) <sup>d</sup>	1812	2123	2220





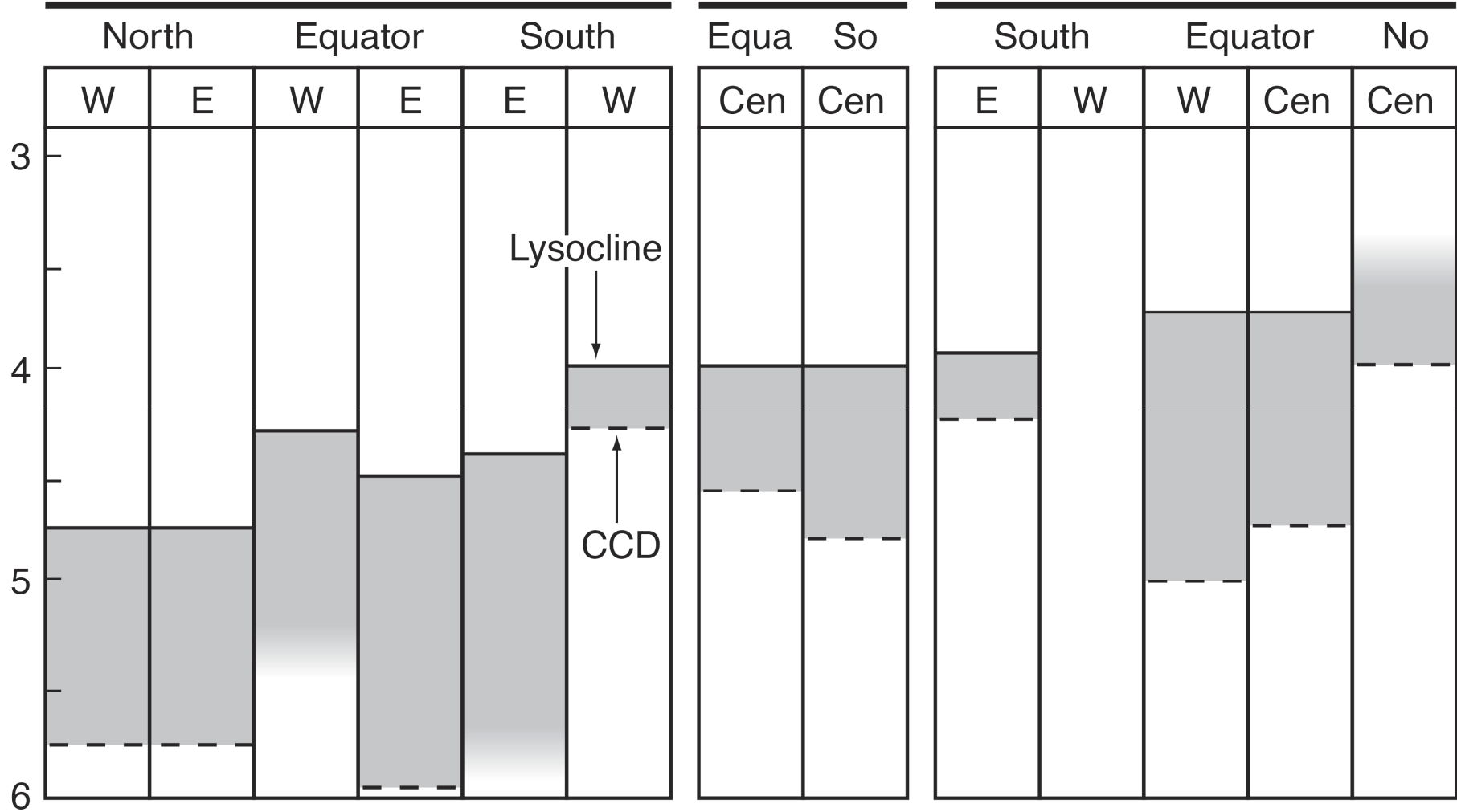




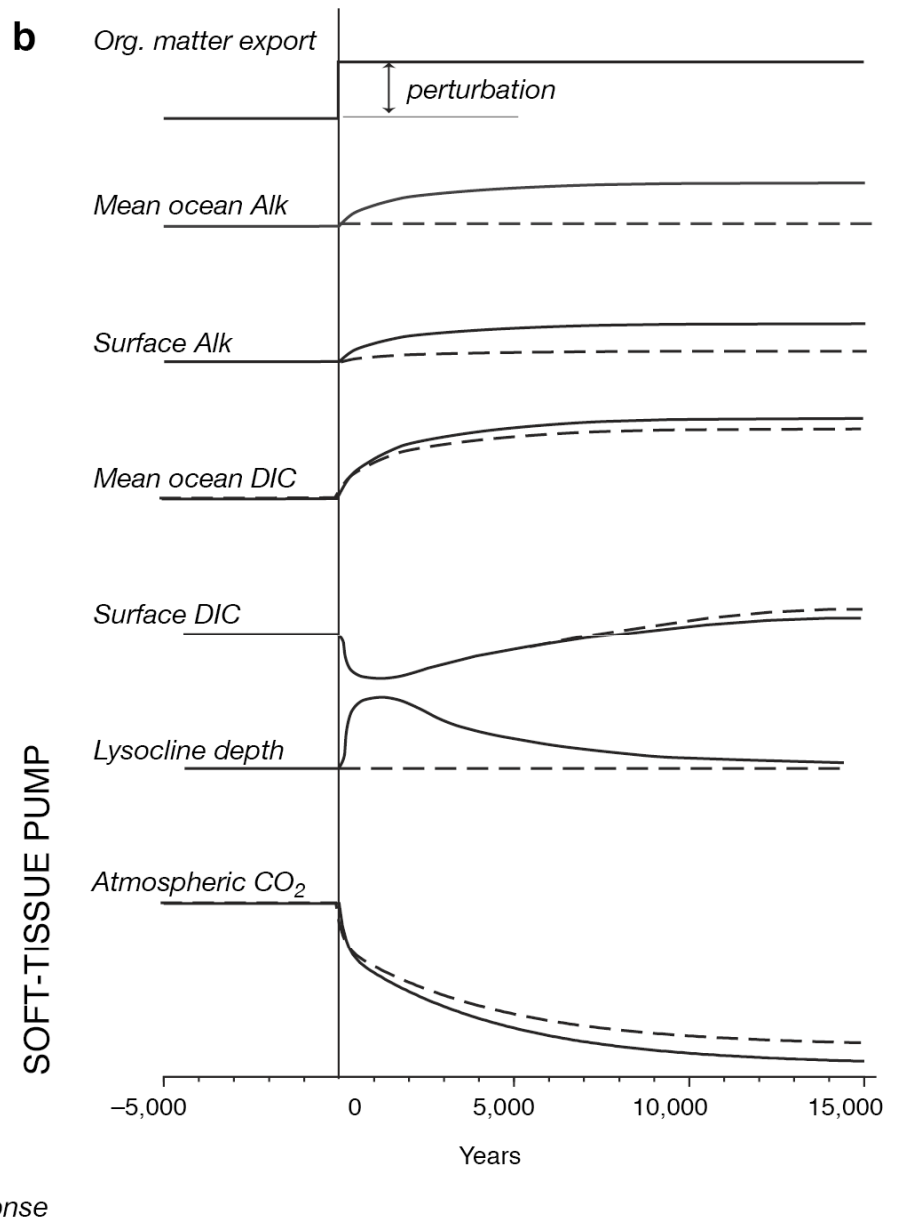
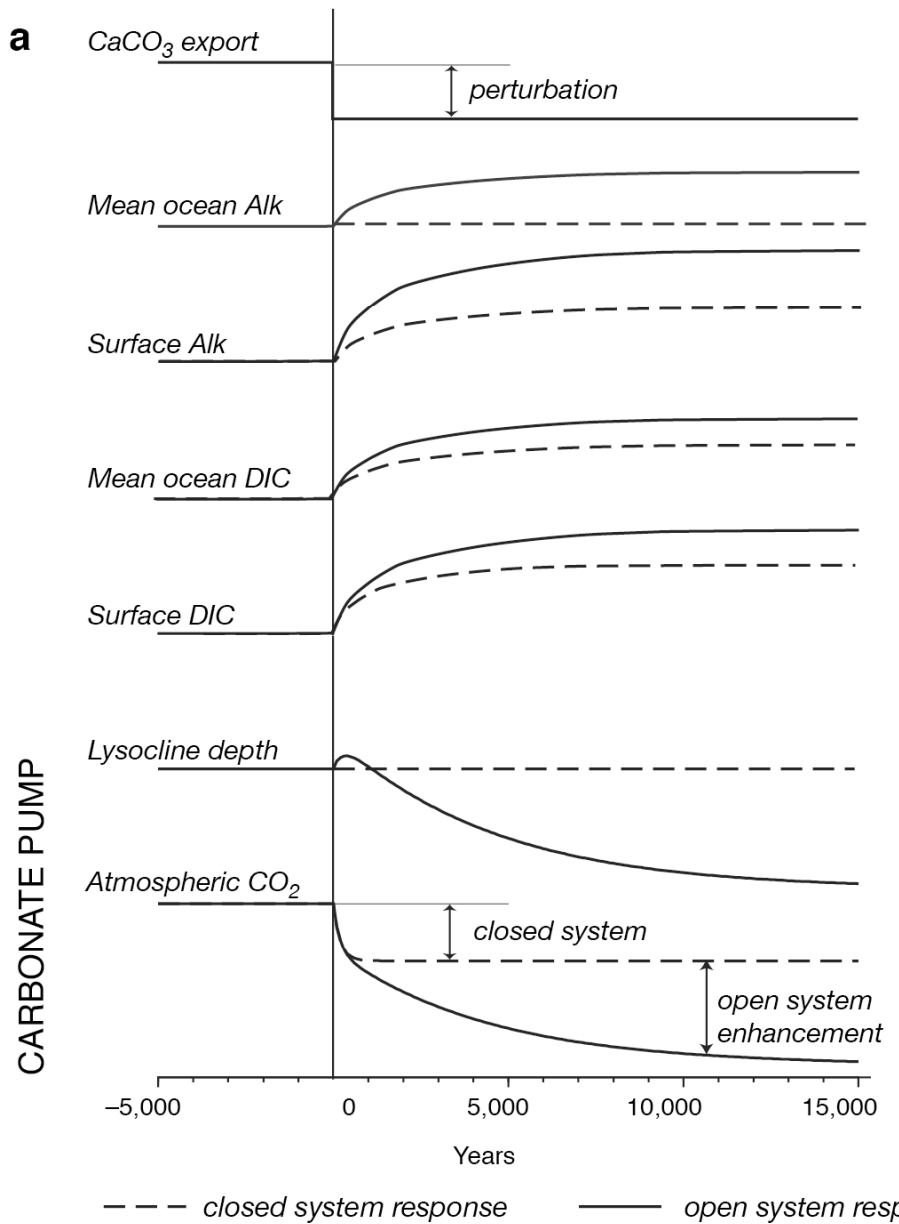
### Atlantic

### Indian

### Pacific



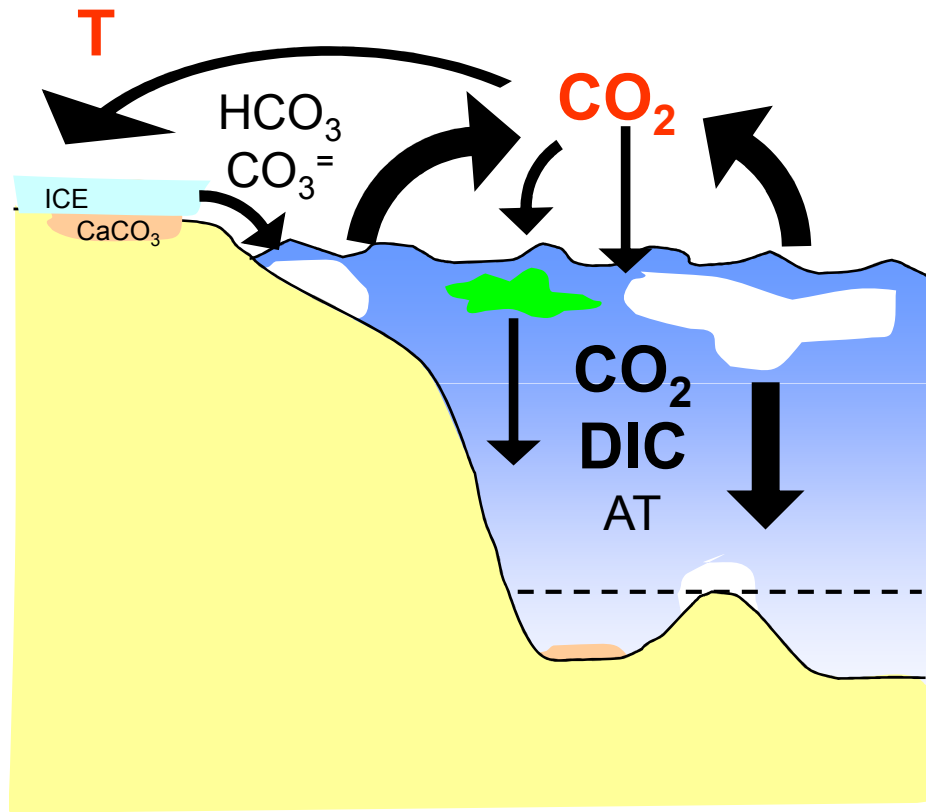




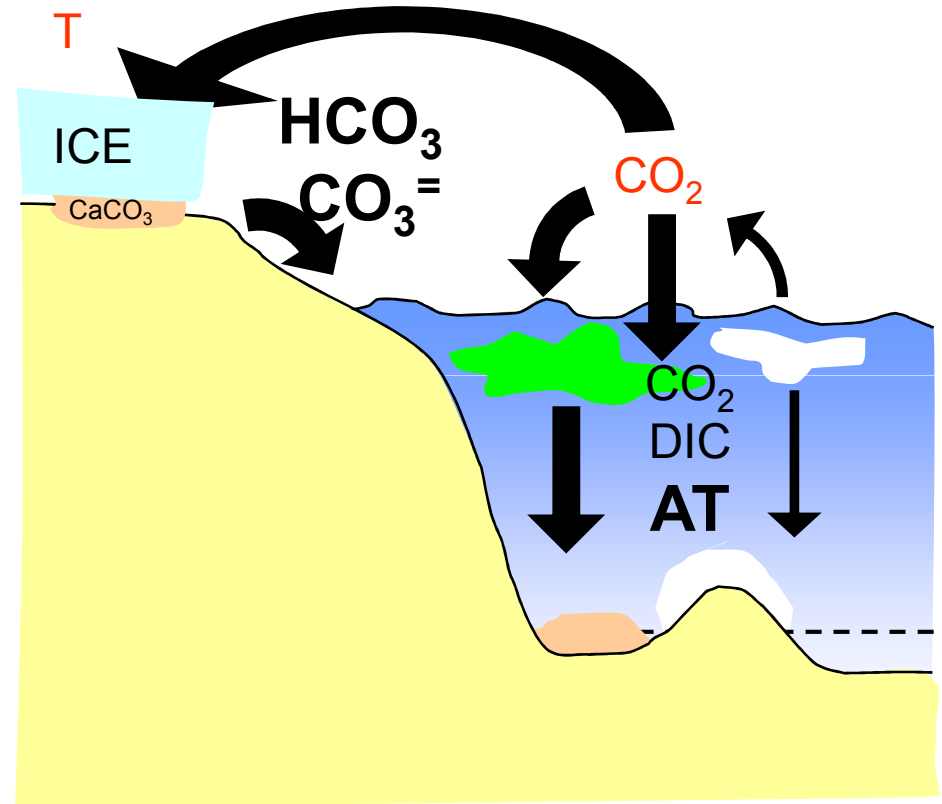
## Deep ocean organic carbon and CaCO<sub>3</sub> budget

	Organic carbon	CaCO <sub>3</sub>	Org C: CaCO <sub>3</sub>
	Pg C yr <sup>-1</sup>	Pg C yr <sup>-1</sup>	
Flux across 1000 m	0.87	0.70	1.2
Burial in sediments	-0.02	-0.13	0.2
Remineralization/dissolution	-0.85	-0.57	1.5

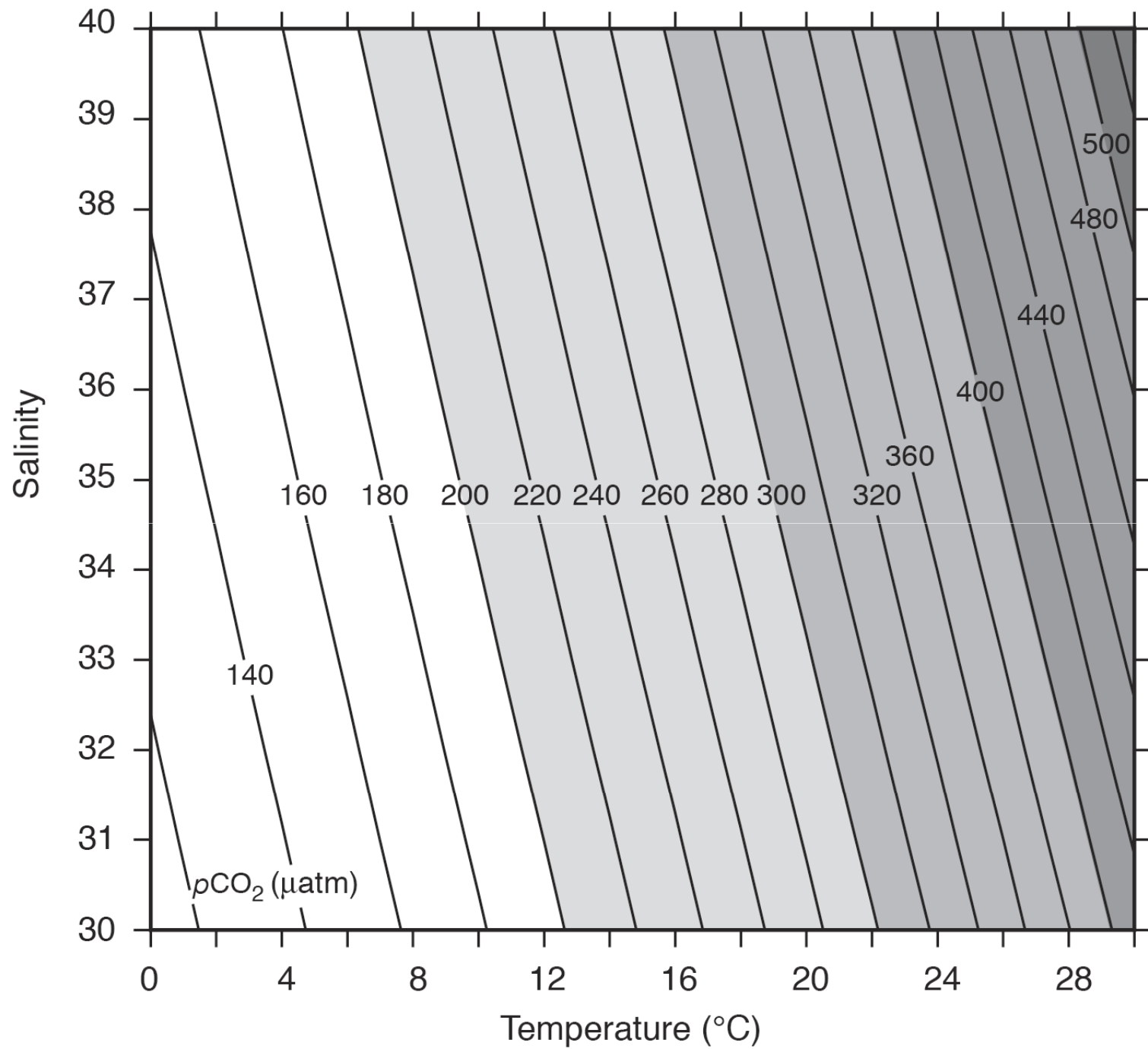
# CO<sub>2</sub> absorption by Ocean driving by Calcification

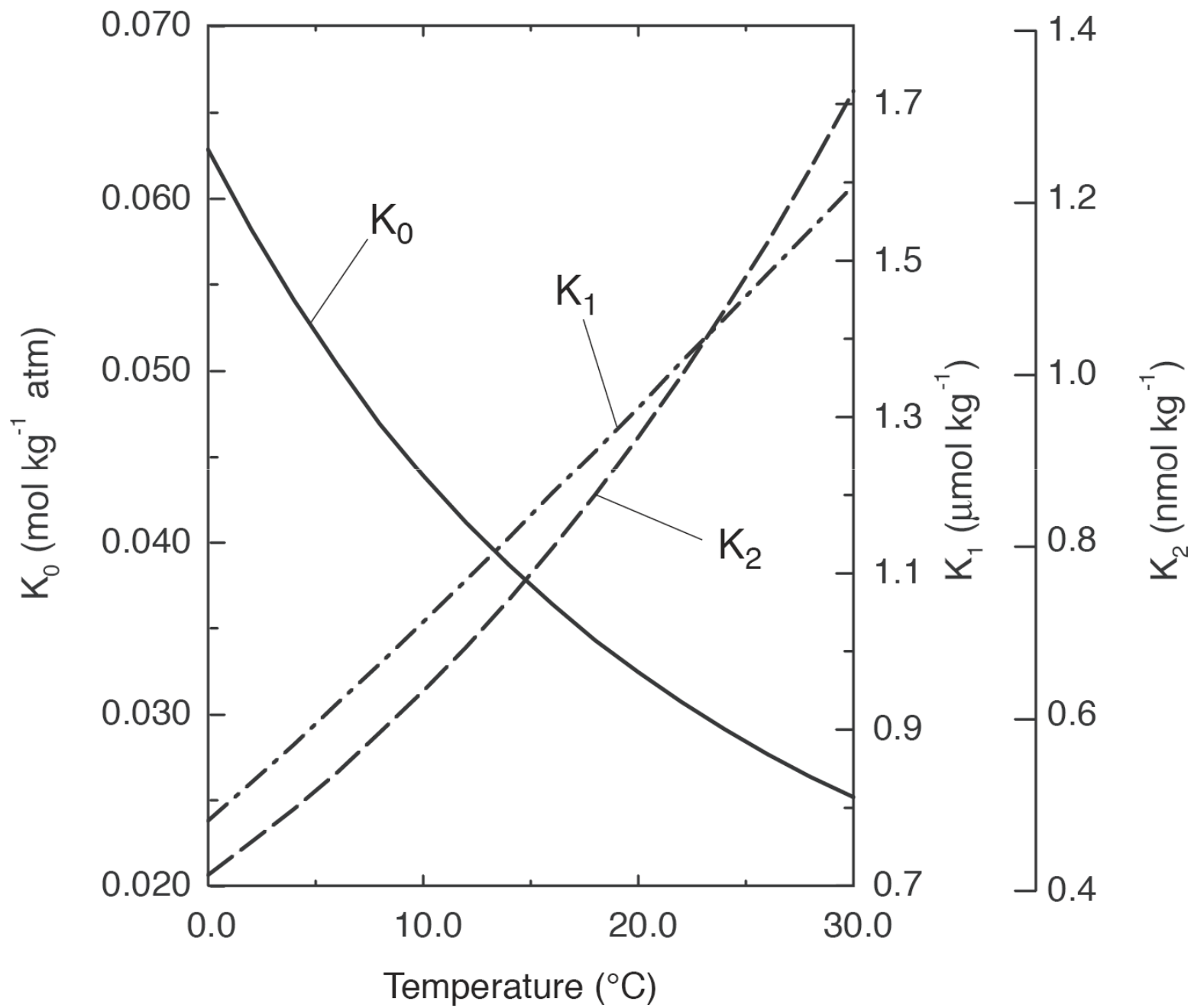


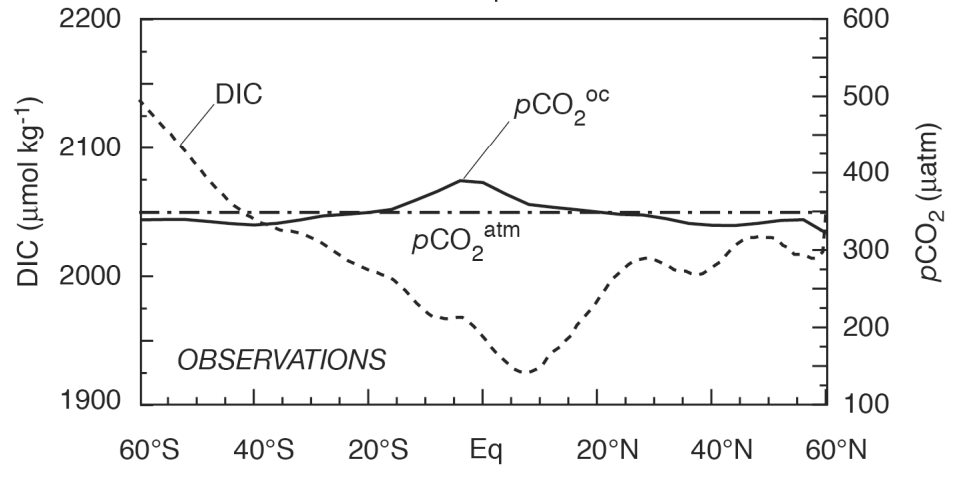
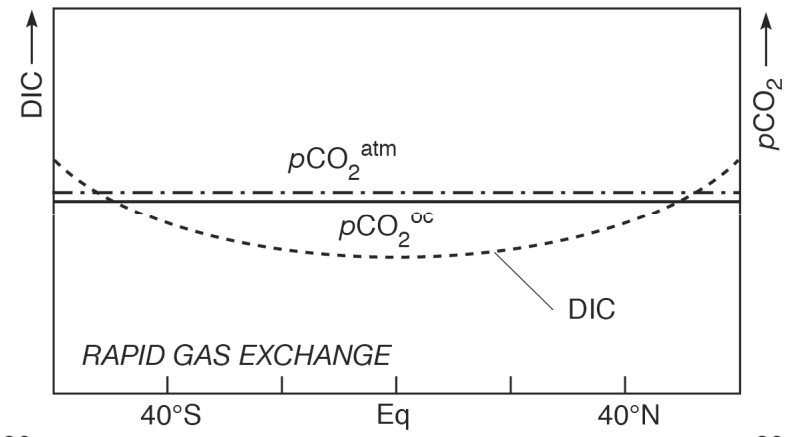
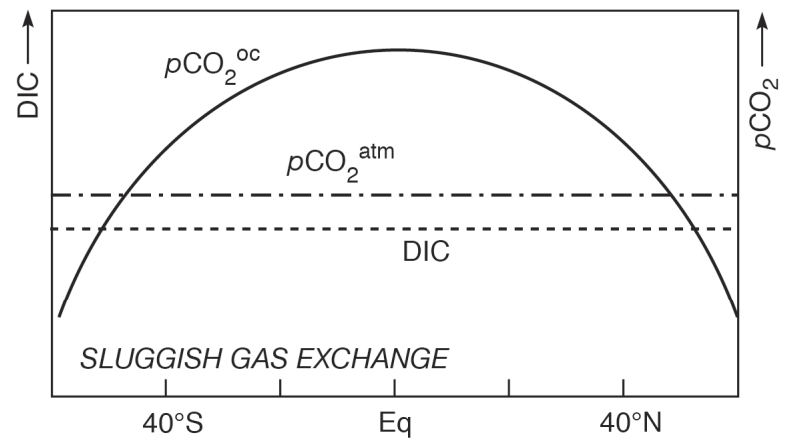
Interglacial

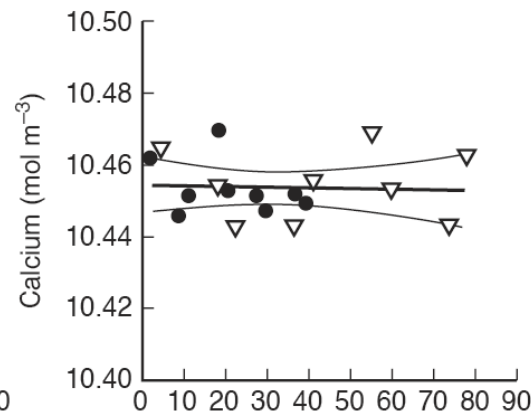
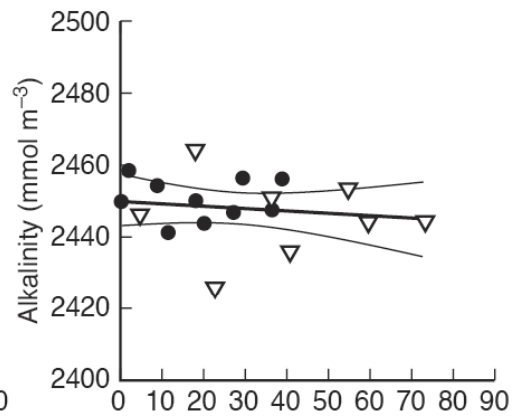
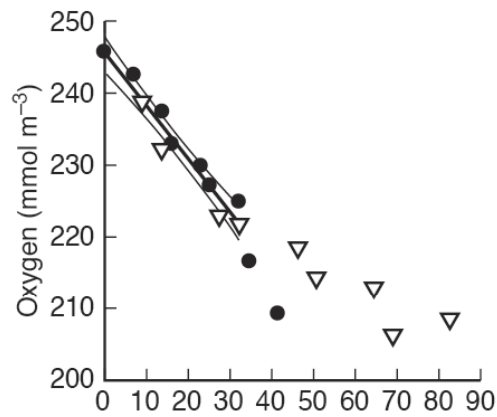


glacial



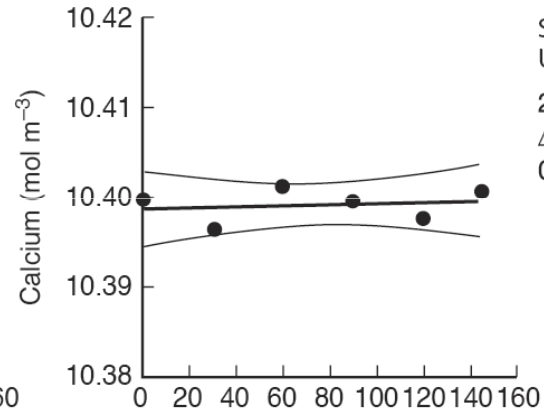
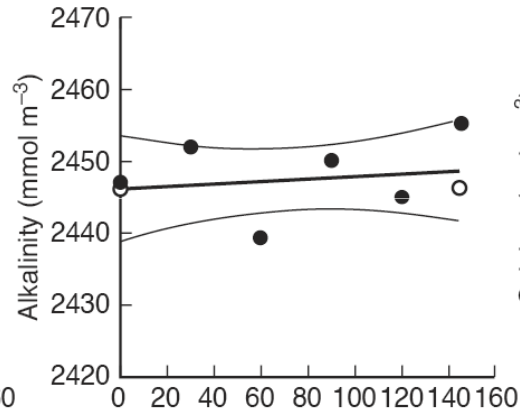
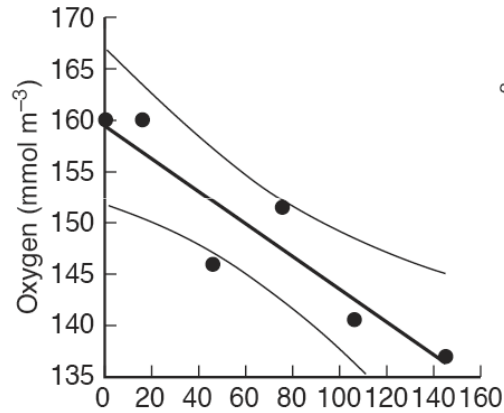




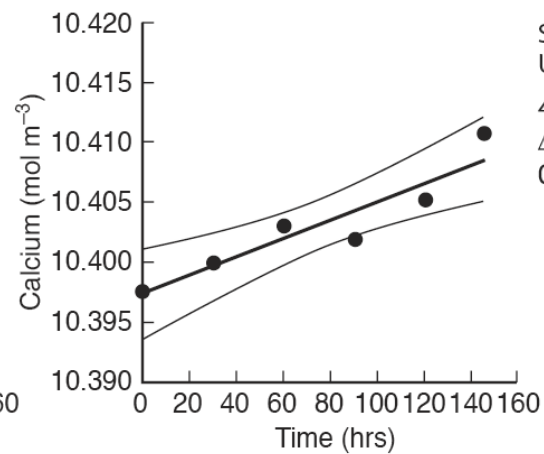
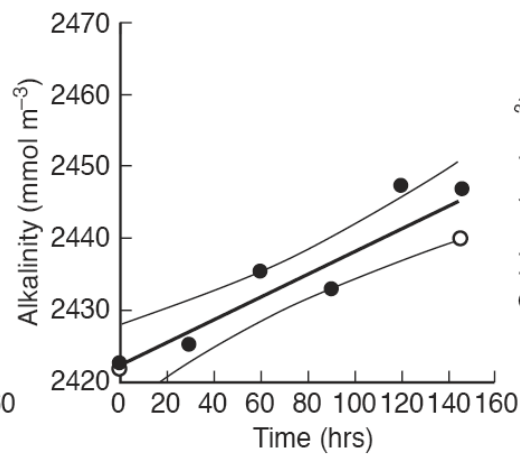
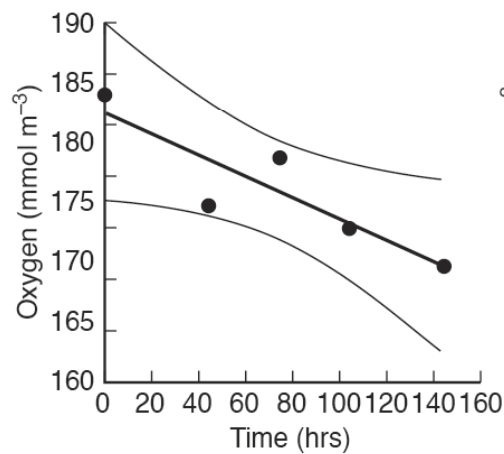


**Characteristics**

Supersaturated  
 3110 m  
 $\Delta\text{CO}_3 = 27 \mu\text{mol kg}^{-1}$   
 18°N/21°W



Slightly  
 Undersaturated  
 2972 m  
 $\Delta\text{CO}_3 = -6 \mu\text{mol kg}^{-1}$   
 0°S/160°E



Strongly  
 Undersaturated  
 4439 m  
 $\Delta\text{CO}_3 = -37 \mu\text{mol kg}^{-1}$   
 0°S/162°E

