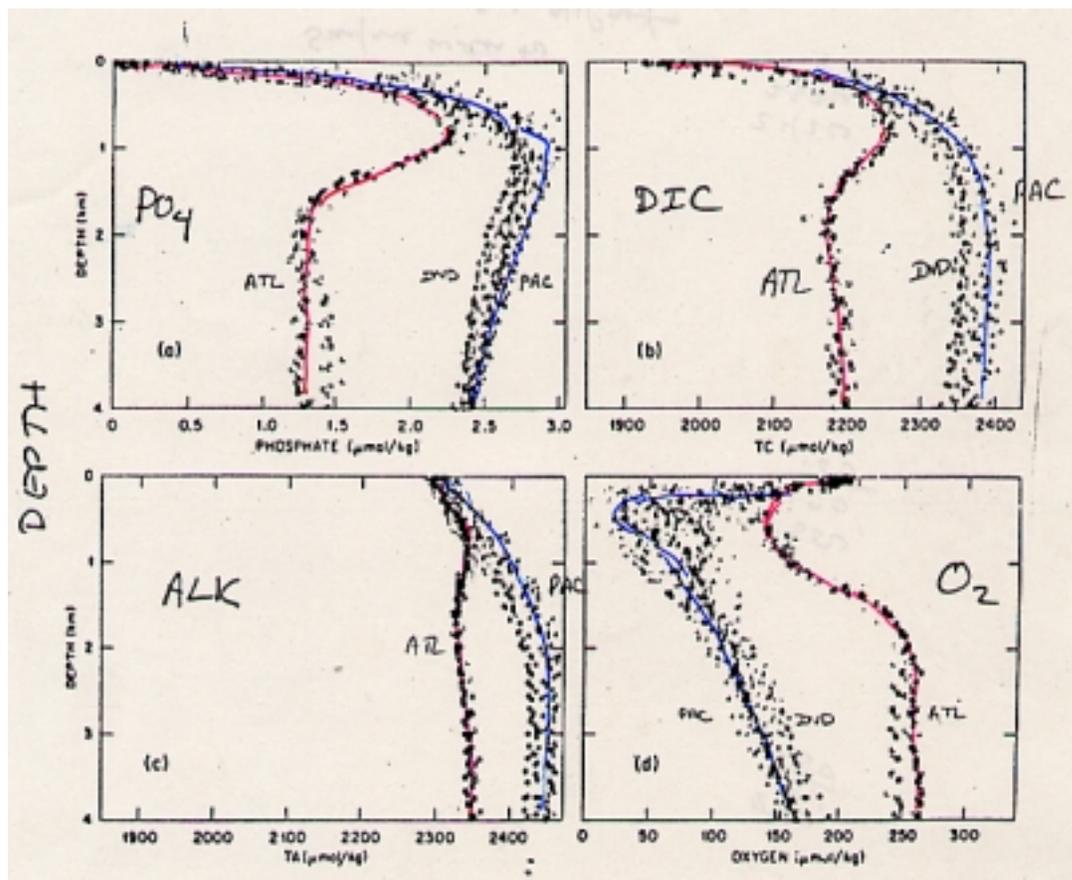


The ocean profiles of PO_4 , dissolved inorganic carbon (DIC or ΣCO_2), alkalinity and oxygen in the Atlantic, Indian and Pacific Oceans are shown below.

The main features are:

1. uniform surface values
2. increase with depth
3. Deep ocean values increase from the Atlantic to the Pacific
4. $\text{DIC} < \text{Alk}$ and $\Delta\text{DIC} > \Delta\text{Alk}$
5. Profile of pH is similar in shape to O_2 .
6. Profile of PCO_2 (not shown) mirrors O_2 .

Fig 13-1



Representative values of alkalinity, ΣCO_2 , CO_3^{2-} and pH for the surface ocean and deep Atlantic, Antarctic and Pacific are shown below (Table 13-1). Note that CO_3^{2-} decreases from the Atlantic to the Pacific by a factor of four. Because CO_3^{2-} is lower in the Pacific we expect CaCO_3 to be more soluble and for there to be less CaCO_3 preserved in the sediments. This is generally true.

Table 13-1

	$\times 10^{-3}$		$\times 10^{-6}$	
	ALK	ΣCO_2	CO_3^{2-}	pH in situ
SURFACE WATERS	2.300	1.950	242	8.3
NORTH ATLANTIC DEEP WATER	2.350	2.190	109	8.03
ANTARCTIC DEEP WATER	2.390	2.280	84	7.89
NORTH PACIFIC DEEP WATER	2.420	2.370	67	7.71

↑

CO_3^{2-} DECREASES FROM ATLANTIC TO PACIFIC.
WHAT ARE THE IMPLICATIONS?

What controls the pH of seawater? The long term controls on alkalinity and DIC and the weathering (sources) and burial (sinks) of silicate and carbonate rocks. We showed that internal variations of pH in the ocean are controlled by internal variations in DIC and alkalinity which are controlled by photosynthesis, respiration and CaCO₃ dissolution and precipitation.

pH is controlled by alkalinity and DIC and can be calculated from these two parameters as shown below.

$$\text{Alk} \approx \text{HCO}_3^- + 2 \text{CO}_3^{2-}$$

$$\text{Alk} \approx C_T \alpha_1 + 2 C_T \alpha_2$$

$$\text{Alk} = C_T (\text{H}^+ K_1' + 2 K_1' K_2') / (\text{H}^2 + \text{H} K_1' + K_1' K_2')$$

Rearranging, we can calculate pH from Alk and C_T.

$$(\text{H}^+) = \left\{ -K_1' (\text{Alk} - C_T) + [(K_1')^2 (\text{Alk} - C_T)^2 - 4 \text{Alk} K_1' K_2' (\text{Alk} - C_T)] \right\} / 2 \text{Alk}$$

What controls the alkalinity and DIC of deep ocean waters?

The answer is respiration of organic matter and dissolution of CaCO_3 .

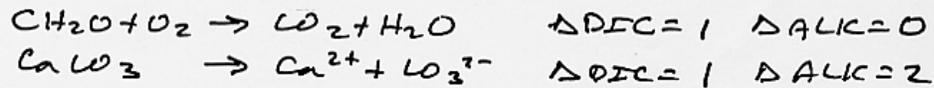
Example: What changes in deep ocean DIC and Alk do we predict if typical sediment trap particles respire and dissolve.

ASSUME THE FOLLOWING AVERAGE ELEMENTAL COMPOSITION OF PARTICULATE MATERIAL, FROM DEEP SEDIMENT TRAPS.

	P	N	C	Ca	Si
SOFT PARTS	1	15	105	0	0
HARD PARTS	0	0	26	26	50
COMPOSITE	1	15	131	26	50

$$\frac{\text{ORG C}}{\text{CaCO}_3} \sim \frac{105}{26} \sim \frac{4}{1}$$

IMPACT OF THIS MATERIAL DISSOLVING



	1 MOL CaCO_3	4 MOL ORG C	COMPOSITE
ΔDIC	1	4	5
ΔCa	1	0	1
ΔALK	2	0	2

CONSEQUENCES

- 1) $\frac{\Delta \text{ALK}}{\Delta \text{DIC}} = \frac{2}{5} = 0.40$ * DIC CHANGES MORE THAN ALK
- 2) $(\Delta \text{ALK} - \Delta \text{DIC}) \sim \Delta \text{CO}_3^{2-} = 2 - 5 = -3$
* $\{\text{CO}_3^{2-} \text{ DECREASES}\}$
- 3) $\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \rightleftharpoons 2\text{H}^+ + \text{CO}_3^{2-}$
 $\text{CO}_3^{2-} \downarrow \quad \text{H}^+ \uparrow \quad \text{pH} \downarrow$

Examine the trends in Alk and DIV in the world's oceans (Borecker and Peng, 1982)

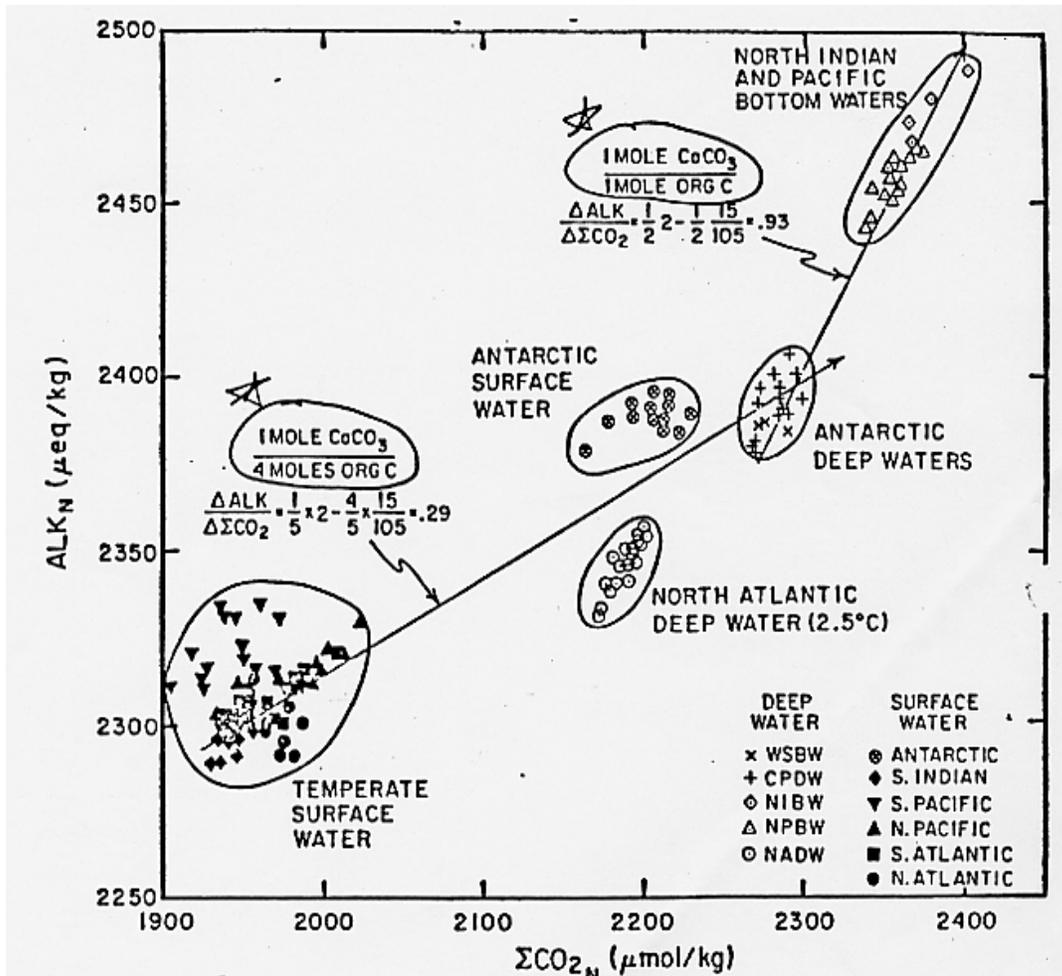
In **Fig 13-2** we show alkalinity and DIC (normalized to S = 35) in different major parts of the ocean.

The expected slope is:

$$\Delta \text{alk} / \Delta \text{DIC} = 2 \Delta \text{CaCO}_3 / (\Delta \text{CaCO}_3 + \Delta \text{Org C}) - 15/105 \Delta \text{Org C} / (\text{CaCO}_3 + \Delta \text{Org C})$$

This last term is a correction for NO₃ remineralization during respiration.

Fig 13-2



Problems:

1. Going from the deep North Atlantic to the deep North Pacific, alkalinity increases in seawater from 2350 to 2475 $\mu\text{Eq kg}^{-1}$ while total CO_2 increases from 2200 to 2375 $\mu\text{M kg}^{-1}$. On average what is the relative contributions of CaCO_3 dissolution and organic matter respiration for producing these changes.

2. The precipitation and dissolution of CaCO_3 is one of the important solubility reactions in seawater. The reaction can be written as: $\text{CaCO}_3(\text{s}) = \text{Ca}^{2+} + \text{CO}_3^{2-}$

a) Calculate ΔG_f° for this reaction given the following ΔG_f°

species	ΔG_f°
$\text{CaCO}_3(\text{s})$	-1128.79 kJ mol^{-1}
Ca^{2+}	-553.58
CO_3^{2-}	-527.81

b) Calculate the equilibrium constant for this solubility reaction at 25°C . Remember $R = 8.314 \times 10^{-3} \text{ kJ deg}^{-1} \text{ mol}^{-1}$

c) If surface seawater has an alkalinity = $2.300 \times 10^{-3} \text{ eq l}^{-1}$ and total $\text{CO}_2 = 1.950 \times 10^{-3} \text{ mol l}^{-1}$, what is the approximate concentration of CO_3^{2-} ?

d) Using the information given above if this surface seawater was in equilibrium with Calcite, what would be the total concentration of Ca?

e) Write the relation for the apparent equilibrium constant (K')

f) Under what conditions would K and K' be equal?

3. Carbonate system controls

The popular press (and a few scientists) claim that the health of coral reefs is crucial to humanity because reef CaCO_3 represents a sink for anthropogenic CO_2 .

a. Explain the qualitative effect of CaCO_3 formation in reefs (skeletalogenesis) on alkalinity and ΣCO_2

b. The expression for P_{CO_2} in terms of alkalinity and ΣCO_2 is:

$$P_{\text{CO}_2} = \frac{(2 \Sigma\text{CO}_2 - \text{Alk})^2}{K' (\text{Alk} - \Sigma\text{CO}_2)}$$

Use this expression to support or refute this idea (e.g. that reefs are a sink for CO_2)

You may find it useful to plug demonstration numbers into this equation for comparison purposes. A typical surface value for ΣCO_2 is 2.0 mM and for Alk is 2.2 meq/l. What value of P_{CO_2} is this water in equilibrium with and how would it change if about 0.1 mM of ΣCO_2 was removed to form reef material.

$$K' = 4.5 \times 10^4 \text{ mmol/l-atm.}$$

References: