The ocean profiles of PO₄, dissolved inorganic carbon (DIC or ΣCO₂), 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. DIC < Alk and ΔDIC > ΔAlk
5. Profile of pH is similar in shape to O₂.
6. Profile of PCO₂ (not shown) mirrors O₂.

Fig 13-1
Representative values of alkalinity, $\Sigma CO_2$, $CO_3^{2-}$ 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

<table>
<thead>
<tr>
<th></th>
<th>$x10^{-3}$</th>
<th>$x10^{-6}$</th>
<th>$PH$</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>ALK</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Surface waters</td>
<td>2.300</td>
<td>1.950</td>
<td>2.42</td>
<td>8.3</td>
</tr>
<tr>
<td>North Atlantic</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Deep water</td>
<td>2.350</td>
<td>2.190</td>
<td>1.09</td>
<td>8.03</td>
</tr>
<tr>
<td>Antarctic</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Deep water</td>
<td>2.390</td>
<td>2.280</td>
<td>0.84</td>
<td>7.89</td>
</tr>
<tr>
<td>North Pacific</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Deep water</td>
<td>2.420</td>
<td>2.370</td>
<td>0.57</td>
<td>7.71</td>
</tr>
</tbody>
</table>

$CO_3^{2-}$ 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 and 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.

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

\[ \text{Alk} \approx C_T \alpha_1 + 2 C_T \alpha_2 \]

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

Rearranging, we can calculate pH from Alk and C_T.

\[ (H^+) = \left\{ -K_1' (\text{Alk}-C_T) + [(K_1')^2 (\text{Alk}-C_T)^2 - 4 \text{Alk} K_1' K_2' (\text{Alk} - 2C_T)]^{1/2} \right\} / 2 \text{Alk} \]
What controls the alkalinity and DIC of deep ocean waters? The answer is respiration of organic matter and dissolution of CaCO₃.

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.**

<table>
<thead>
<tr>
<th>Material</th>
<th>P</th>
<th>N</th>
<th>C</th>
<th>Ca</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soft parts</td>
<td>1</td>
<td>15</td>
<td>105</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Hard parts</td>
<td>0</td>
<td>0</td>
<td>26</td>
<td>26</td>
<td>SD</td>
</tr>
<tr>
<td>Composite</td>
<td>1</td>
<td>15</td>
<td>131</td>
<td>26</td>
<td>SD</td>
</tr>
</tbody>
</table>

\[
\frac{\text{Org C}}{\text{CaCO}_3} \approx \frac{105}{26} \approx \frac{4}{1}
\]

**Impact of this material dissolving**

\[
\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad \Delta \text{DIC} = 1 \quad \Delta \text{ALK} = 0
\]
\[
\text{CaCO}_3 \rightarrow \text{Ca}^{2+} + \text{CO}_3^{2-} \quad \Delta \text{DIC} = 1 \quad \Delta \text{ALK} = 2
\]

\[
\begin{array}{ccc}
\text{DIC} & \text{CaCO}_3 & \text{Org C} \\
\Delta \text{DIC} & 1 & 4 \\
\Delta \text{Ca} & 1 & 0 \\
\Delta \text{ALK} & 2 & 0
\end{array}
\]

**Consequences**

1. \( \frac{\Delta \text{ALK}}{\Delta \text{DIC}} = \frac{2}{5} = 0.40 \) (DIC changes more than Alk)
2. \( (\Delta \text{ALK} - \Delta \text{DIC}) = \Delta \text{CO}_3^{2-} = 2 - 5 = -3 \) (\( \text{CO}_3^{2-} \) decreases)
3. \( \text{H}_2\text{CO}_3 \leq \text{H}^+ + \text{HCO}_3^- \leq \text{2H}^+ + \text{CO}_3^{2-} \)
   \( \text{CO}_3^{2-} \downarrow \text{H}^+ \uparrow \text{pH} \downarrow \)
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:

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

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 µEq kg⁻¹ while total CO₂ increases from 2200 to 2375 µM kg⁻¹. On average what is the relative contributions of CaCO₃ dissolution and organic matter respiration for producing these changes.

2. The precipitation and dissolution of CaCO₃ is one of the important solubility reactions in seawater. The reaction can be written as: \( \text{CaCO}_3(s) = \text{Ca}^{2+} + \text{CO}_3^{2-} \)

   a) Calculate \( \Delta G_r^\circ \) for this reaction given the following \( \Delta G_f^\circ \) species:

<table>
<thead>
<tr>
<th>species</th>
<th>( \Delta G_f^\circ )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CaCO}_3(s) )</td>
<td>-1128.79 kJ mol⁻¹</td>
</tr>
<tr>
<td>( \text{Ca}^{2+} )</td>
<td>-553.58</td>
</tr>
<tr>
<td>( \text{CO}_3^{2-} )</td>
<td>-527.81</td>
</tr>
</tbody>
</table>

   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 \( \text{CO}_3^{2-} \)?

   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 CaCO₃ represents a sink for anthropogenic CO₂.

   a. Explain the qualitative effect of CaCO₃ formation in reefs (skeletogenesis) on alkalinity and \( \Sigma \text{CO}_2 \)

   b. The expression for \( P_{\text{CO}_2} \) in terms of \( \text{alkalinity} \) and \( \Sigma \text{CO}_2 \) 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 CO₂)

   You may find it useful to plug demonstration numbers into this equation for comparison purposes. A typical surface value for \( \Sigma \text{CO}_2 \) is 2.0 mM and for Alk is 2.2 meq/l. What value of \( P_{\text{CO}_2} \) is this water in equilibrium with and how would it change if about 0.1 mM of \( \Sigma \text{CO}_2 \) was removed to form reef material.

   \( K' = 4.5 \times 10^4 \text{ mmol/l-atm.} \)
References: