Paraphrasing Stanley: many of the environmental changes affecting the Earth are ultimately caused by chemical changes.

- e.g.: surface temperature is controlled in part by the concentration of atmospheric CO\textsubscript{2}.
- Transition from a reducing to an oxidizing atmosphere. This made higher life possible. The Earth is not a static place.
- Changes such as these reflect changes in the manner and rates at which elements cycle between reservoirs. As it turns out, cycling of oxygen and carbon are closely linked. Let's examine this chemical cycling in more detail.

Some Definitions
Reservoir

- Mass of material that is potentially subject to a common set of chemical interactions.
  - Reservoirs may have distinct, sharp boundaries:
    - Example: the oceans, the atmosphere
  - Alternatively, a reservoir may be dispersed throughout some region of the Earth.
    - Example: "sedimentary organic carbon"
      - sediments are dispersed throughout the crust, and organic carbon is dispersed through those sediments. However, all sedimentary organic carbon is formed through burial of the remains of organisms, and is subject to oxidation and conversion to CO$_2$ upon erosion.
    - Sometimes speak of a reservoir of a single element, or a single form of an element.

Flux

- A flux represents a flow of material from one reservoir to another.
  - This may reflect physical movement of the material.
    - e.g.: subduction zone volcanism is a mantle-to-crust flux.
  - Alternatively, it may represent only a chemical change.
    - Organic carbon may be oxidized to carbonate and remain in the same place. Hence a flux may simply be a chemical reaction.
  - A flux may involve both physical movement and chemical reaction.

- The flux into a reservoir (or the reservoir from which the flux comes) is called a source; the flux out is called a sink.
**Steady-State**

- For most geochemical reservoirs, there is a constant flow of material both to and from that reservoir.
- If the flow out is greater than the flow in, the mass of the reservoir will decrease and visa versa.
- If the flux in and the flux out are equal, the mass of the reservoir will not change. In this case, it is said to be *steady-state*.

**Residence Time**

- For a steady-state reservoir, we may define a residence time, which is the average time a molecule or atom (or any other unit) of the substance spends in that reservoir. The residence time can be calculated as:

\[
\tau = \frac{M_e}{dM_e/dt}
\]

- \( \tau \) is the residence time, \( M_e \) is the mass of the element in the reservoir, \( dM_e/dt \) is the flux into or out of the reservoir.
- In English, the residence time is the mass of substance in the reservoir divided by the flux into that reservoir.
The Oceans

- The oceans play a key role in life, geochemical cycling, and climate. They also illustrate these concepts of geochemical cycling and demonstrate the intricate link between life and the physical world.

The Oceans as a Geochemical System

- Why the Sea is Salty
  - Lavoisier: Oceans are “the rinsings of the Earth”
  - Ocean salt is a bi-product of weathering on the continents

\[
\text{Igneous Rock} + \text{Water} = \text{Sedimentary Rock (Clays)} + \text{Seawater}
\]
\[
2\text{NaAlSi}_3\text{O}_8 + 3\text{H}_2\text{O} = \text{Al}_2\text{Si}_2\text{O}_8(\text{OH})_4 + 4\text{SiO}_2 + 2\text{Na}^+ + 2\text{OH}^-
\]

- Elements such as Cl, S, etc. are not accounted for by weathering. These volatile elements are the products of volcanic degassing rather than weathering.
Seawater Composition

- Seawater has on average 34.8‰ (parts per thousand) dissolved solids.
- The dissolved solid content of seawater is called its salinity. Salinity varies only because of dilution (by addition of rain or river water) and concentration (resulting from evaporation or freezing).
  - Chlorinity (which is the total of F, Cl, Br, and I) is another measure of the salt content. Average chlorinity is 19.2‰.
- Salinity is important because it, along with temperature, control density, and hence vertical motion of water.

Principal Salts in the Ocean

<table>
<thead>
<tr>
<th>Anion</th>
<th>% at Cl = 19‰</th>
<th>% dissolved solids</th>
<th>Cation</th>
<th>% at Cl = 19‰</th>
<th>% dissolved solids</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>18.98</td>
<td>55.05</td>
<td>Na</td>
<td>10.57</td>
<td>30.61</td>
</tr>
<tr>
<td>SO₄</td>
<td>2.65</td>
<td>7.68</td>
<td>Mg</td>
<td>1.27</td>
<td>3.89</td>
</tr>
<tr>
<td>HCO₃</td>
<td>0.14</td>
<td>0.41</td>
<td>Ca</td>
<td>0.40</td>
<td>1.16</td>
</tr>
<tr>
<td>Br</td>
<td>0.065</td>
<td>0.19</td>
<td>K</td>
<td>0.38</td>
<td>1.1</td>
</tr>
<tr>
<td>H₂BO₄</td>
<td>0.026</td>
<td>0.07</td>
<td>Sr</td>
<td>0.008</td>
<td>0.03</td>
</tr>
<tr>
<td>F</td>
<td>0.001</td>
<td>0.003</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- These salts (with the exception of bicarbonate) are present in constant proportions.
- Such elements are said to be conservative.
- Constant concentration a result of:
  - high abundance
  - unreactivity of these elements
The Global Carbon Cycle

- The concentration of CO$_2$ in the atmosphere exerts a major control on terrestrial climate and likely has throughout Earth’s history.
- Atmospheric CO$_2$ is, however, only one of many carbon reservoirs on Earth through which carbon cycles. It is changes in the distribution of carbon between these reservoirs that affects climate.
- Major carbon reservoirs in the Earth:
  - Oceans, Biosphere (& soil) Atmosphere: 44.25 Tt (teratons)
  - Mantle 1.5 x $10^8$ Tt
  - Carbonate Sediments: 5.2 x $10^7$ Tt
  - Sedimentary Organic Carbon: 1.1 x $10^7$ Tt.

Carbonate in Solution

- Weathering of silicates effectively takes carbon from the atmosphere/ocean/biosphere reservoir and transfers it to the carbonate reservoir.
- CO$_2$ dissolves in water to form carbonic acid:
  - CO$_2$ + H$_2$O = H$_2$CO$_3$
- Carbonic acid can then dissociate to form bicarbonate ion:
  - H$_2$CO$_3$ = H$^+$ + HCO$_3^-$
- Bicarbonate can then dissociate to form carbonate ion:
  - HCO$_3^-$ = H$^+$ + CO$_3^{2-}$
- Which of these three forms predominates depends on pH. Most natural solutions are near neutral and bicarbonate ion dominates (carbonate ion dominates in alkaline solutions such as alkali lakes, carbonic acid dominates in acidic solutions).
**CO₂ and Ocean pH**

- The two dissociation reactions:
  \[
  \text{H}_2\text{CO}_3 = \text{H}^+ + \text{HCO}_3^- \\
  \text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{2-}
  \]
  both affect and are affected by pH.
- Carbonate thus acts as a buffer on ocean pH.
- In addition, ocean pH depends on the amount of dissolved CO₂:
  - Because of respiration, ocean pH decreases with depth from about 8.1 to 7.6.
  - Because of the anthropogenic increase in atmospheric CO₂, ocean pH is decreasing, and has already decreased by nearly 0.1 unit.
  - If we can determine the ocean pH in the past, we can determine atmospheric CO₂ in the past.

**Biology and CO₂**

- Photosynthesis converts CO₂ to organic carbon and thus removes CO₂ from the atmosphere.
- Most of this organic matter is quickly (years to hundreds of years) oxidized through respiration to CO₂ (the oceans are a little different, as we shall see).
- Nevertheless, photosynthesis produces a net change in atmospheric CO₂ when
  - There is a net change in the biomass - there is currently nearly as much carbon in the living biosphere as CO₂ in the atmosphere.
  - Organic matter is buried in sediment without being oxidized.
    - (Sediment contains 0.3-0.5% organic matter; recoverable fossil fuels represent only a small fraction of sedimentary organic matter).
Weathering and atmospheric CO$_2$

- Weathering of Ca- and Mg-bearing silicate rocks (which is most rocks) effectively removes CO$_2$ from the atmosphere and sequesters it as carbonate sediment.
- CO$_2$ dissolves in rain and dissociates:
  - CO$_2$ + H$_2$O = H$_2$CO$_3$
  - H$_2$CO$_3$ = H$^+$ + HCO$_3^-$
- This acidity is available for rock weathering:
  - 2H$^+$ + H$_2$O + CaAl$_2$Si$_2$O$_8$ = Ca$^{2+}$ + Al$_2$Si$_2$O$_5$(OH)$_4$
  - Calcium then combines with carbonate in the ocean and precipitates as calcite:
    - Ca$^{2+}$ + HCO$_3^-$ = CaCO$_3$ + H$^+$
- The flux is small, however, so this is important only on long time scales (>10$^7$ years).

Ocean Thermal Structure

- Characterized by warm mixed surface layer (100-200 meters deep), a thermocline to about 1000 m, and nearly constant temperature below that.
- Thermocline may partly break down in winter in temperate latitudes and is not present in high latitudes.
- Resulting density stratification inhibits vertical exchange.
Two box model of the oceans.

- Exchange between the 2 boxes is limited to *upwelling*, *downwelling*, and sinking particles.
- Since light only penetrates ~100 m depth, all photosynthesis occurs in surface layer.
- All atmospheric exchange and atmospheric and riverine inputs occur in surface layer. Only in this zone can changes in Temperature and Salinity occur. Hence, temperature and salinity are said to be *conservative*.
- The surface water is only 3.5% of total ocean.

The Biological Pump

- Photosynthesis restricted to upper 100m, but respiration occurs throughout the water column.
- Consequences of the the distribution of photosynthesis and respiration in the ocean:
  - Falling organic particles results in the transport of carbon from surface to deep water, where it is oxidized to $\text{CO}_2$.
  - This process is called the *biological pump*.
  - The biological pump enhances transport of $\text{CO}_2$ from atmosphere and ocean and effectively removes (sequesters) a large amount of $\text{CO}_2$ from climate system (There is currently 50 times as much $\text{CO}_2$ in deep ocean water as in the atmosphere). Without it, atmospheric $\text{CO}_2$ levels would be double what they are.
**Nutrients and Their Distribution**

- **Definition:** elements essential to life.

- In addition to H, C, and O, P and N (most "plants" can utilized only "fixed" nitrogen: NO, N₂O, and NH₃) are the most important. Photosynthetic organisms take up dissolved inorganic nutrients to meet their needs.

- **The oceans are oligotrophic** – biological productivity is limited by the availability of nutrients.

- Phytoplankton use essentially all available fixed N and P in surface water, resulting in strong surface depletion. These nutrients are released to solution when organic matter is oxidized in deep water.

**Micro-Nutrients**

- Other elements show similar “nutrient” type profiles.
  - Si used by diatoms (principal photosynthetic organism in oceans) to build shells and is strongly depleted in surface water.
  - Other surface-depleted nutrients include Mn, Fe, Cu, Zn, V, Cr, Ni, Se, and I.

- In addition, biota take up a number of elements incidentally: e.g., Sc, Ge, As, Pd, Ag, Cd, Ba.

- Other elements (B, Na, Mg, S, Cl, K, Ca, Mo, F and Br) are utilized, but no vertical variation results because only a small fraction of the amount available is used.
Nutrient Distribution and Biological Productivity

- The ocean circulation pattern results in horizontal gradients in nutrient abundances. Deep water continually accumulates nutrients, thus “old” deep water, e.g., Pacific, is nutrient-rich, “young” deep water, e.g., Atlantic, is nutrient poor.
- Nutrient availability, together with light, limit biological productivity in surface water.
  - Productivity is high where upwelling returns deep water to surface.
  - In some regions, notably equatorial Pacific, in the Subarctic and Antarctic, it appears availability of Fe limits productivity.

Ocean Circulation and Climate

- Ocean circulation can be divided into two parts:
  - The wind-driven surface circulation
  - The deep or thermohaline circulation, which is driven by density differences (controlled by temperature and salinity).
- Ocean circulation affects climate in two ways:
  - Indirectly, but redistributing nutrients and changing the efficiency of the biological pump.
  - By transporting heat.
    - Water has a very high heat capacity, meaning ocean currents transport enormous amounts of heat.
    - Heat capacities:
      - Water 4.2 J/g-K
      - Air 1 J/g-K
      - Iron 0.4 J/g-K
      - Rock 0.7 J/g-K
Deep Ocean Circulation

- Because the ocean is usually thermally and therefore density stratified, water cannot freely move up and down.
- Water moves downward (oceanographers say deep water is *formed*) only in restricted areas, mainly near the poles.
- Two main areas of deep water formation are the Weddell Sea (Antarctica) - where Antarctic Bottom Water (AABW) is formed, and the far North Atlantic, where North Atlantic Deep Water (NADW) is formed.

Deep Water Circulation in the Atlantic
North Atlantic Deep Water and Climate

- NADW forms in winter as the cold atmosphere cools surface water, causing it to sink. It then circulates southward, eventually mixing with AABW, and not returning to the surface for 1000 years.
- Heat given up by the water warms the air, keeping Europe and the North Atlantic region warmer than it would otherwise be.