The relative distribution of the three major species of dissolved inorganic carbon in water as a function of pH. Note that at pH of seawater (~8.1), approximately 95% of the inorganic carbon is in the form of bicarbonate anion.
Carbon Cycle Fluxes and $\delta^{13}C$ Values

**Fluxes in Gigatons of Carbon/Year**

- **Atmosphere**: 778 (-7‰)
  - Surface Ocean: 600 (1‰) (100 flux)
  - Dissolved bicarbonate deep ocean: 36,000 (0‰) (35 flux, 36 transformation)
  - Marine carbonate sediments: 2,500 (0‰) (0.3 flux, 0.5 transformation)
  - Carbonate rocks: 60,000,000 (0-1‰) (0.2 flux)
  - Fossil Fuels: 5,000 (-25‰) (5 flux)
  - Land biota: 1,600 (-25‰) (62 flux)
  - Terrestrial soils: 1,600 (-25‰) (122 flux)
  - Organic C in sediments/rocks: 15,000,000 (-25‰) (60 flux)
  - Atmosphere: 778 (-7‰) (60 flux)
  - Mantle: 324,000,000 (-5‰) (0.05 flux)
  - Continental Crust: 7,000,000 (-5‰) (0.05 flux)

- **Deep Ocean**: 36,000 (0‰)

**Debates**:
- Near-surface water temperatures
- Ice cover extent
- Harsh living conditions

**Summary**
- Earth's carbon cycle is complex and involves a multitude of processes and interactions.
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Redox reactions

**Concepts:** thermodynamic basis of microbial growth, sources of energy for microbial growth, utilization of natural chemical and light gradients, chemical profiles in aquatic environments and sediments, microbial processes and redox evolution of the environment, prediction of metabolisms supported by different environments, the influence of pH and environmental redox state on the formation of minerals

**Reading:** Brock Biology of Microorganisms, Morel and Hering, Aquatic chemistry, Oremland et al. The microbial arsenic cycle in Mono Lake, California (2004), Lavik et al. (2009), Dolfing et al. (2008)
Fig. 1. (A) Sampling stations overlaid on a Google Earth image highlighting the area of the intrusion. Blue plus, red diamond, and white triangle symbols indicate sampling stations for the 18 August–2 September, 7–17 September, and 22 September–4 October 2010 expeditions, respectively. The yellow and green boundaries indicate the extent of the contouring bounds as determined from the extent of DO and fluorescence anomalies and bathymetric restrictions. (B) Contour plot within the yellow boundary of the vertically integrated DO anomaly at each station using data from the 18 August September 2010 expedition. Units are moles DO m⁻². (C) Profiles of DO [43, Sea-Bird Electronics Incorporated (Bellevue, WA); red line calibrated Winkler titrations] and fluorescence [UV AquaTracka (emission = 360 Cheslea Technologies Group (West Molesey, UK); black line] at station PC (26.7098°N, 90.6286°W). The green circles represent Winkler titration samples. CTD indicates conductivity, temperature, and depth.

(Kessler et al., 2011)
Acid-mine drainage

$\text{H}_2\text{S} + 2 \text{O}_2 \rightarrow \text{H}_2\text{SO}_4$

$2 \text{H}_2\text{S} + \text{O}_2 \rightarrow 2 \text{S}^\circ + 2 \text{H}_2\text{O}$

$2 \text{S}^\circ + 3 \text{O}_2 + 2 \text{H}_2\text{O} \rightarrow 2 \text{H}_2\text{SO}_4$

$\text{Na}_2\text{S}_2\text{O}_3 + 2 \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4$

$4 \text{Na}_2\text{S}_2\text{O}_3 + \text{O}_2 + 2 \text{H}_2\text{O} \rightarrow 2 \text{Na}_2\text{S}_4\text{O}_6 + 4 \text{NaOH}$

$2 \text{Na}_2\text{S}_4\text{O}_6 + 7 \text{O}_2 + 6 \text{H}_2\text{O} \rightarrow 2 \text{Na}_2\text{SO}_4 + 6 \text{H}_2\text{SO}_4$

$2 \text{KSCN} + 4 \text{O}_2 + 4 \text{H}_2\text{O} \rightarrow (\text{NH}_4)_2\text{SO}_4 + \text{K}_2\text{SO}_4 + 2 \text{CO}_2$

$5 \text{H}_2\text{S} + 8 \text{KNO}_3 \rightarrow 4 \text{K}_2\text{SO}_4 + \text{H}_2\text{SO}_4 + 4 \text{N}_2 + 4 \text{H}_2\text{O}$

$5 \text{S}^\circ + 6 \text{KNO}_3 + 2 \text{H}_2\text{O} \rightarrow 3 \text{K}_2\text{SO}_4 + 2 \text{H}_2\text{SO}_4 + 3 \text{N}_2$

$2 \text{FeS}_2 + 2 \text{H}_2\text{O} + 7 \text{O}_2 \rightarrow 2 \text{Fe}_2\text{SO}_4 + 2 \text{H}_2\text{SO}_4$

$4 \text{Fe}_2\text{SO}_4 + \text{O}_2 + 2 \text{H}_2\text{SO}_4 \rightarrow 2\text{Fe}_2(\text{SO}_4)_3 + 2 \text{H}_2\text{O}$

Thiobacillus ferooxidans

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http://www.torinoscienza.it/img/200x200/it/s00/00/0004/0000048c.png.
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Mixotrophs: mixed sources of energy/carbon
ATP – energy currency of the cell
ATP SYNTHASE

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Redox reactions - terminology

- **Redox couple**: any pair of species that have the same element in different oxidation states is a redox couple

- **Faraday constant**: charge of 1 mole of electrons (96500 C)

- **Standard free energy of a reaction**: 1 mole of reactants, std. conditions

- **Reductant**: e- donor

- **Oxidant**: e- acceptor

- **Oxidation**: loss of e-

- **Reduction**: gain of e-
5 rules for determining the formal charge of an atom

1. The elementary state has a redox state of 0
   \[ \text{H}_2, \text{O}_2, S^0 \]

2. The oxidation state is equal to an ion’s charge
   \[ \text{Fe}^{3+} = 3, \text{H}^+ = 1 \]

3. In most compounds... O = -2 and H = +1

4. A neutral molecule has zero net redox state
   \[ \text{H}_2\text{O} \]

5. A charged species has net redox state equal to its charge
   \[ \text{OH}^- = -1 \]
Steps for balancing redox reactions

1. Write the unbalanced half-reactions for the oxidation and reduction
2. Balance all elements other than H and O
3. Balance O with H₂O molecules
4. Balance H with H⁺ ions
5. Balance charge with e⁻
6. Balance number of e⁻ in two half-reactions
7. Add the two half-reactions
8. Adjust for pH if necessary
9. Check that charge and atoms balance
Adapted from The Carl Sagan Lecture
By Joe Kirschvink

 Courtesy of Joe Kirschvink. Used with permission.
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Mixotrophs: mixed sources of energy/carbon
The electron tower generally explains porewater chemistry
Example of an anaerobic metabolism: Microbial growth in Mono Lake, CA
Image courtesy of USGS.
This table has been removed due to copyright restrictions. Please see Table 3B-2 on page http://www.monobasinresearch.org/images/mbeir/dchapter3/table3b-2.pdf.
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These images have been removed due to copyright restrictions. Please see Figure 3 (b) and (c) on page http://onlinelibrary.wiley.com/doi/10.1016/j.femsec.2003.12.016/full.
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(Oremland et al., 2004)
Lactate$^-$ + 2HAsO$_4^{2-}$ + H$^+$
→ Acetate$^-$ + HCO$_3^-$ + 2H$_2$AsO$_3^-$
($\Delta G'_0 = -156.8$ kJ mol$^{-1}$).

(Oremland et al., 2004)
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