DISSOLVED INORGANIC CARBON SPECIES

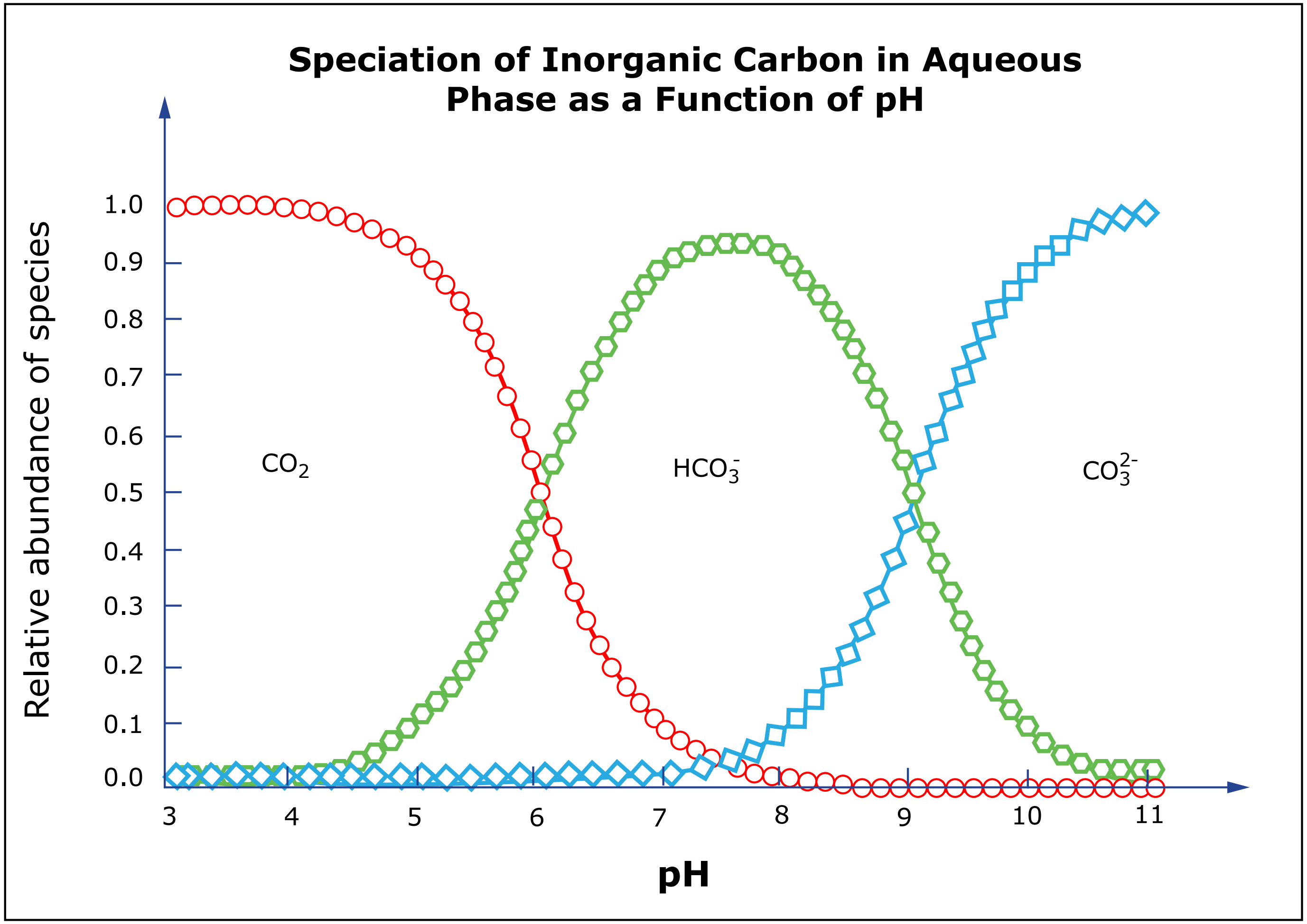
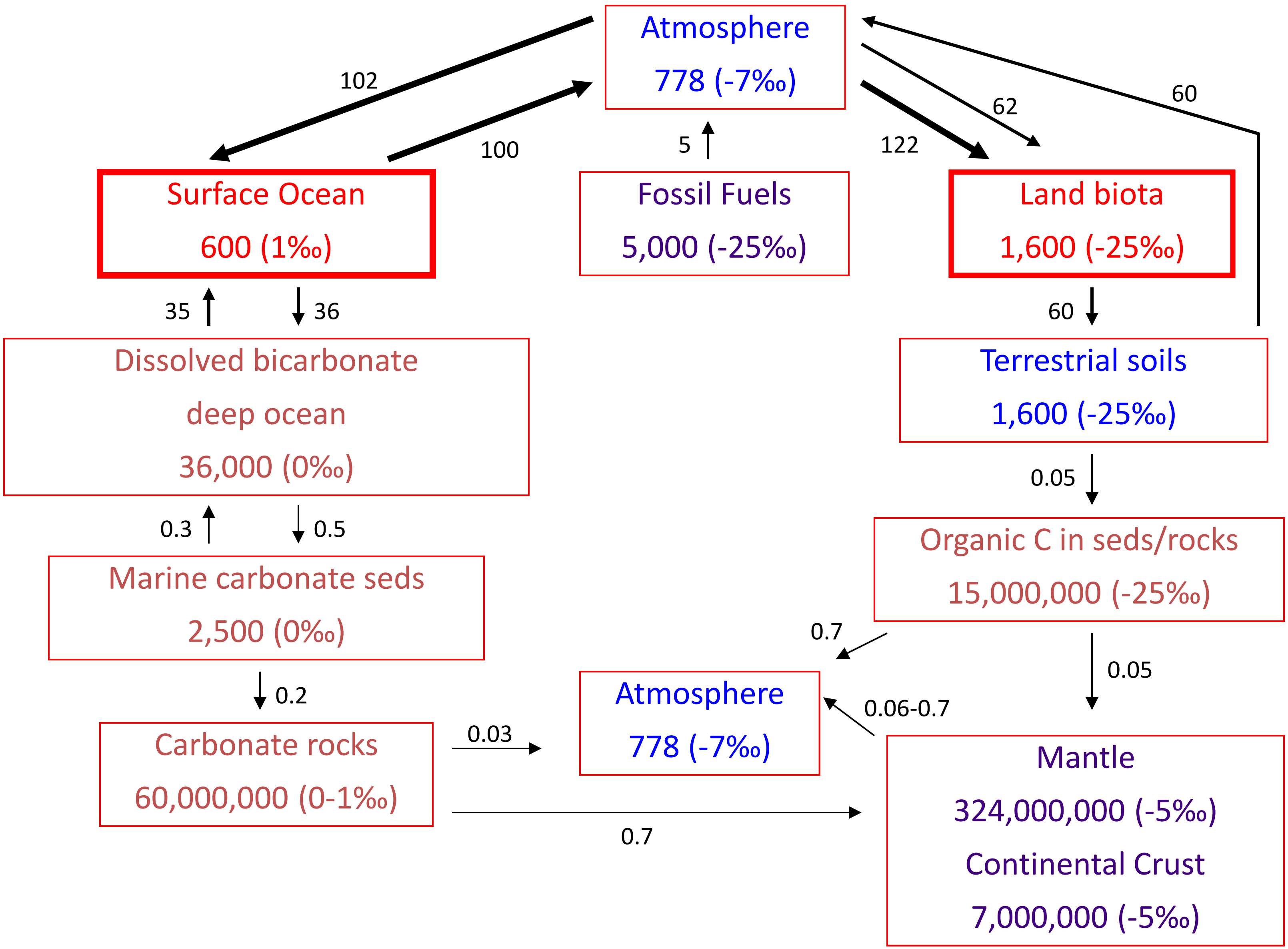


Image by MIT OpenCourseWare.

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

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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)

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http://www.awi.de/fileadmin/user_upload/News/Press_Releases/2008/3._Quartal/Sedimentkerne_p.jg.

http://soundwaves.usgs.gov/2012/10/images/Methane3SulfidicMudDES-lg.jpg

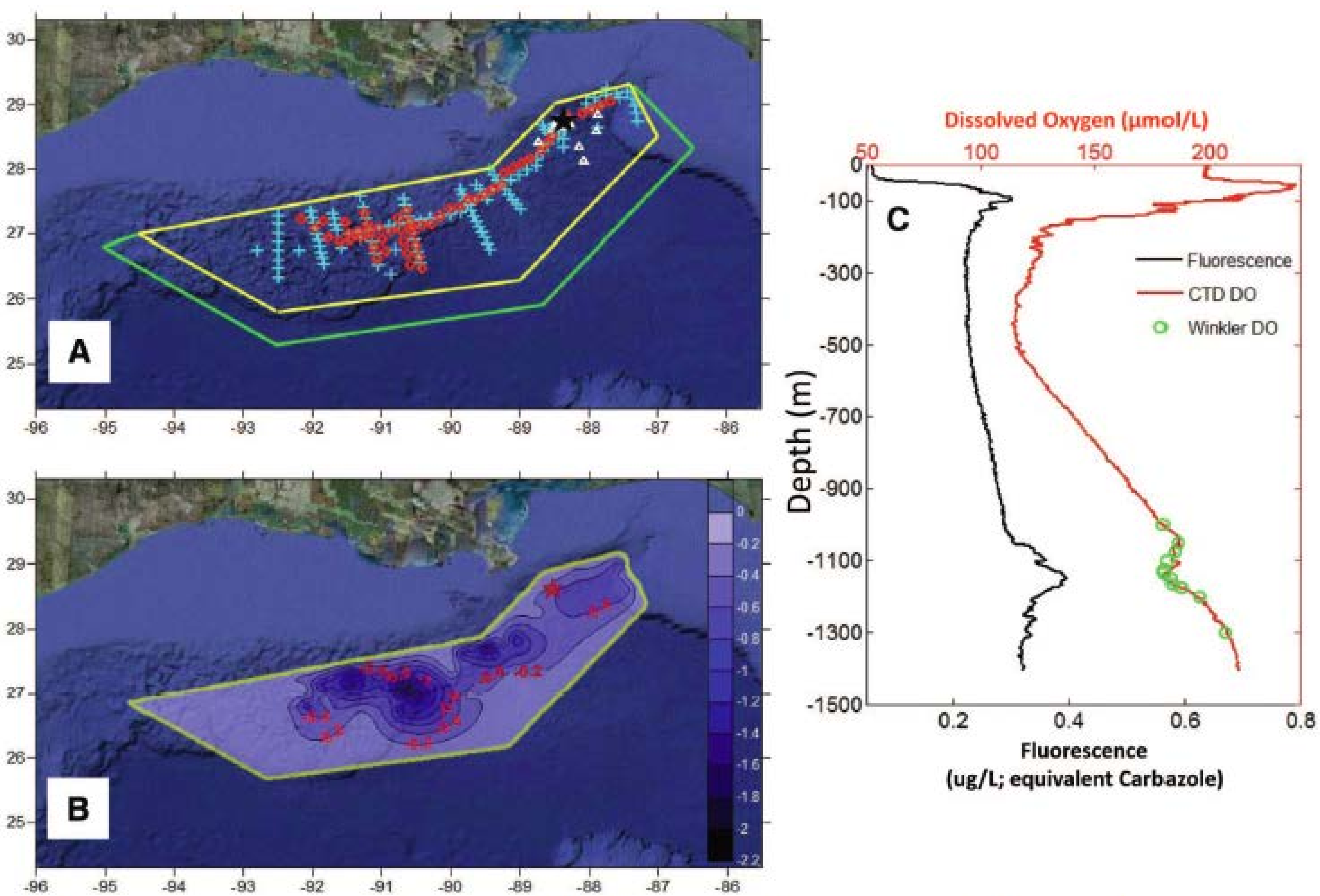


Fig. 1. (**A**) Sampling stations overlaid on a Google Earth image highlighting the area of the intrusion. Blue plus, red diamond, and white triangle symbols indicate sampling stations for the 18 August–2 September, 7–17 September, and 22 September–4 October 2010 expeditions, respectively. The yellow 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 Augu 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 s ples. CTD indicates conductivity, temperature, and depth.

Image courtesy of DOE.

(Kessler et al., 2011)

Acid-mine drainage

Image courtesy of NASA.

$H_2S + 2\ O_2 \rightarrow H_2SO_4$

$2\ H_2S + O_2 \rightarrow 2\ S^{\circ} + 2\ H_2O$

$2\ S^{\circ} + 3\ O_2 + 2\ H_2O \rightarrow 2\ H_2SO_4$

$Na_2S_2O_3 + 2\ O_2 + H_2O \rightarrow Na_2SO_4 + H_2SO_4$

$4\ Na_2S_2O_3 + O_2 + 2\ H_2O \rightarrow 2\ Na_2S_4O_6 + 4\ NaOH$

$2\ Na_2S_4O_6 + 7\ O_2 + 6\ H_2O \rightarrow 2\ Na_2SO_4 + 6\ H_2SO_4$

$2\ KSCN + 4\ O_2 + 4\ H_2O \rightarrow (NH_4)_2SO_4 + K_2SO_4 + 2\ CO_2$

$5\ H_2S + 8\ KNO_3 \rightarrow 4\ K_2SO_4 + H_2SO_4 + 4\ N_2 + 4\ H_2O$

$5\ S^{\circ} + 6\ KNO_3 + 2\ H_2O \rightarrow 3\ K_2SO_4 + 2\ H_2SO_4 + 3\ N_2$

$2\ FeS_2 + 2\ H_2O + 7\ O_2 \rightarrow 2\ FeSO_4 + 2\ H_2SO_4$

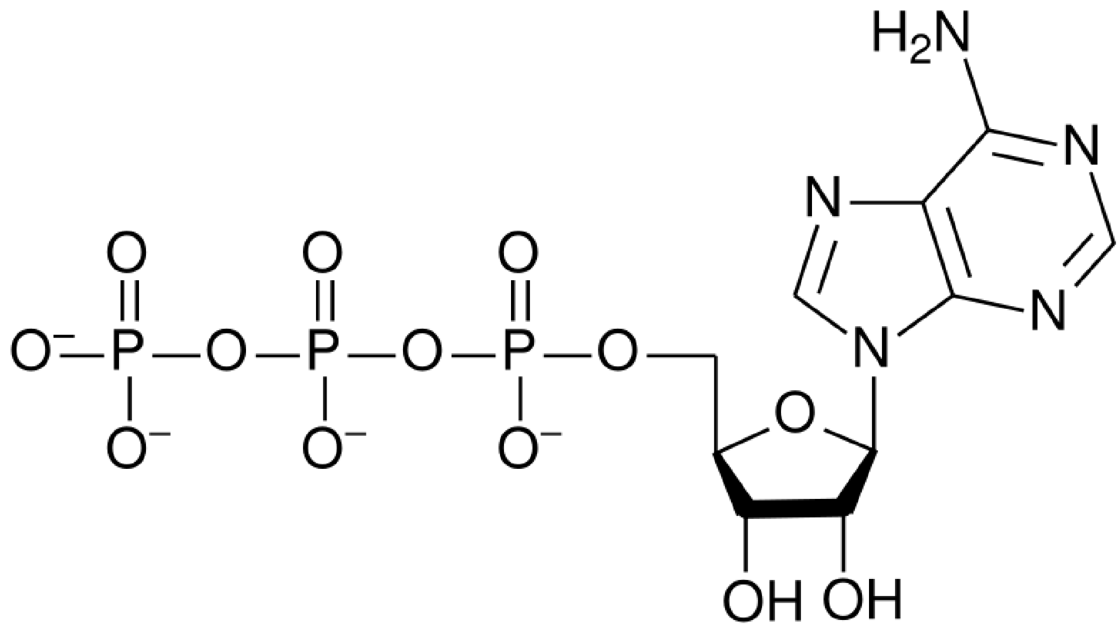
$4\ FeSO_4 + O_2 + 2\ H_2SO_4 \rightarrow 2Fe_2(SO_4)_3 + 2\ H_2O$

Thiobacillus ferooxidans

Energy	Electrons	Carbon
Photo-	**Organo-**	**Hetero-**
	Litho-	**Auto-**
Chemo-	**Organo-**	**Hetero-**
	Litho-	**Auto-**

Mixotrophs: mixed sources of energy/carbon

ATP – energy currency of the cell



ATP SYNTHASE

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

   H_2, O_2, S^0

2. The oxidation state is equal to an ion's charge

   $Fe^{3+} = 3$, $H^+ = 1$

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

4. A neutral molecule has zero net redox state

   H_2O

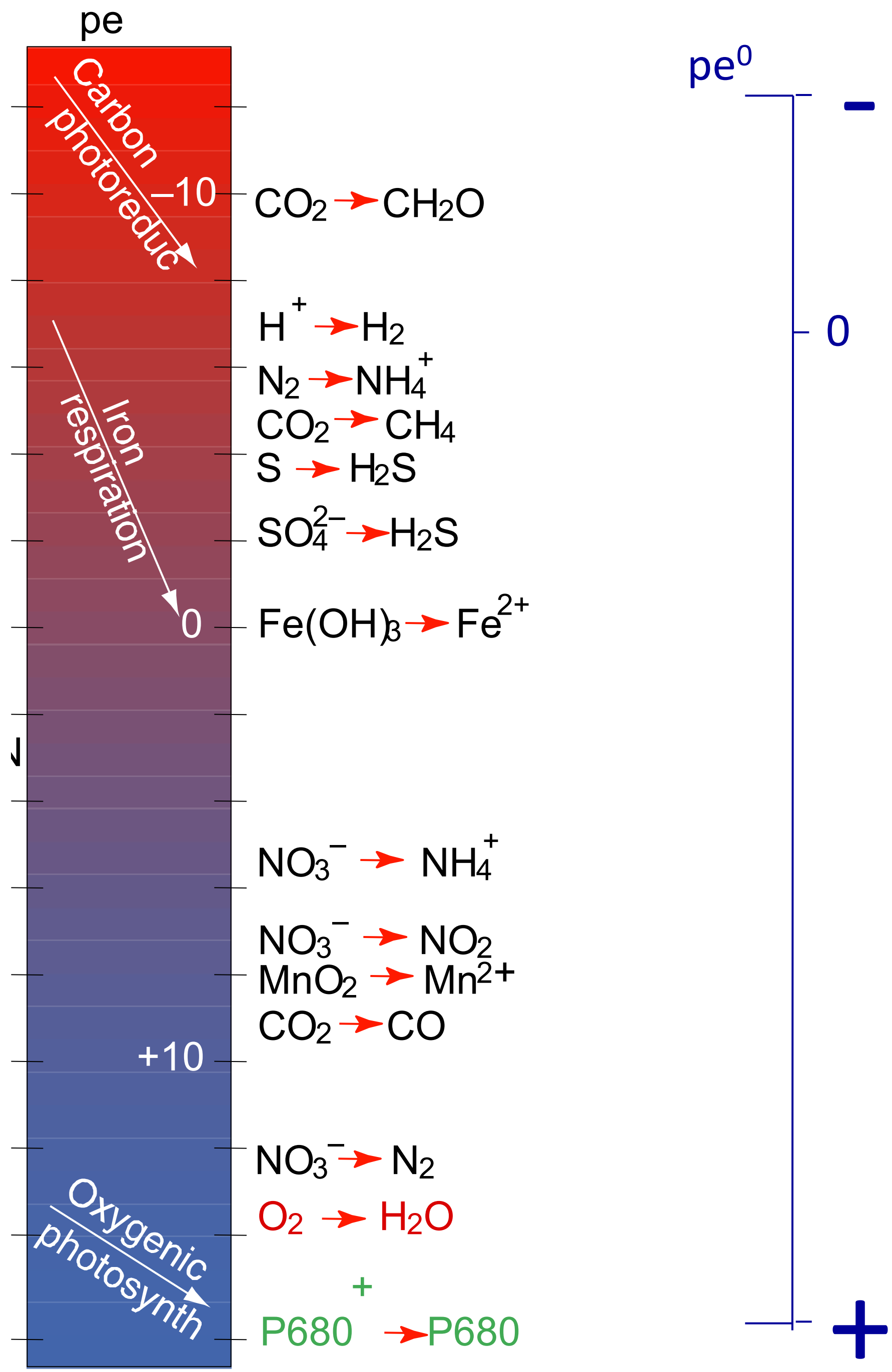
5. A charged species has net redox state equal to its charge

   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 H_2O 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

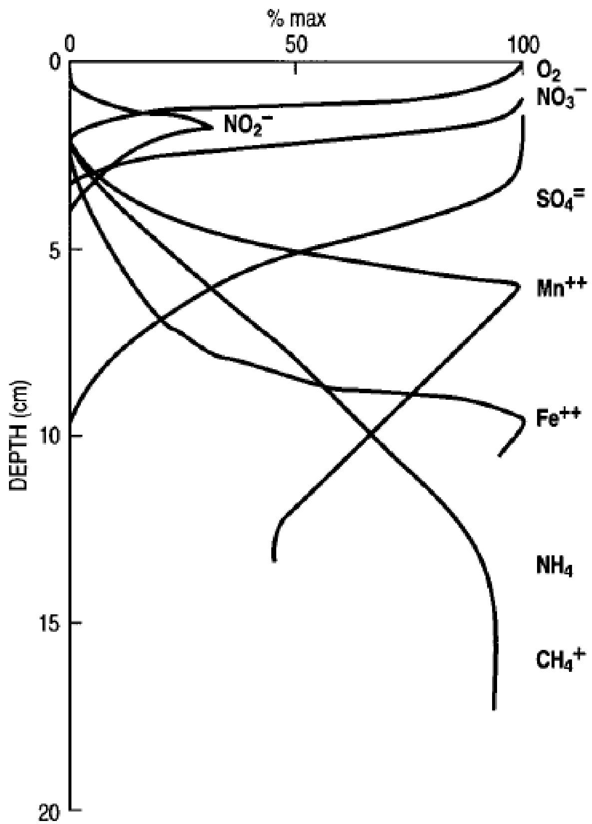
Adapted from The
Carl Sagan Lecture
By Joe Kirschvink



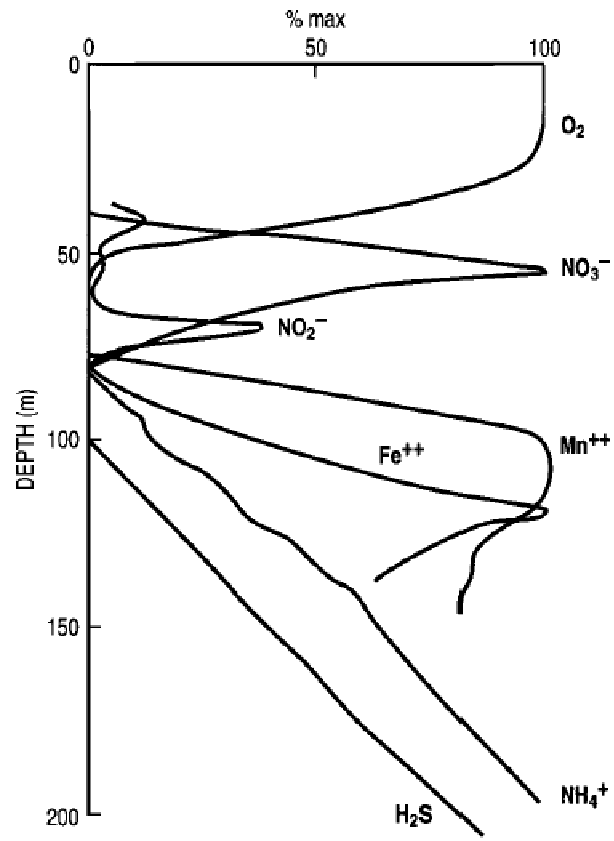
Energy	Electrons	Carbon
Photo-	**Organo-**	**Hetero-**
	Litho-	**Auto-**
Chemo-	**Organo-**	**Hetero-**
	Litho-	**Auto-**

Mixotrophs: mixed sources of energy/carbon

The electron tower generally explains porewater chemistry



Lake Michigan Sediment



Black Sea

Example of an anaerobic metabolism: Microbial growth in Mono Lake, CA

Image courtesy of USGS.

Image courtesy of State of California.

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This image has been removed due to copyright restrictions. Please see Figure 3 (a) on page http://onlinelibrary.wiley.com/doi/10.1016/j.femsec.2003.12.016/full.

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(Oremland et al., 2004)

$$Lactate^{-} + 2HAsO_4^{2-} + H^{+}$$

$$\longrightarrow Acetate^{-} + HCO_3^{-} + 2H_2AsO_3^{-}$$

$$(\Delta G'_0 = -156.8\ kJ\ mol^{-1}).$$

Image by MIT OpenCourseWare.

(Oremland et al., 2004)