# Acid-base reactions

**Concepts:** chemical equilibrium, energetics of acid-base reactions, carbonate equilibria, alkalinity, mineral precipitation, the influence of pH and environmental redox state on the formation of minerals, precipitation and dissolution of carbonates in surface and deep ocean and sediments, weathering of carbonates and silicates, T/$CO_2$/weathering feedback

**Readings:** Morel and Hering, Aquatic chemistry, Ridgwell and Zeebe, 2005

**Homework:** problem set will be posted on-line

# Soils are products of weathering

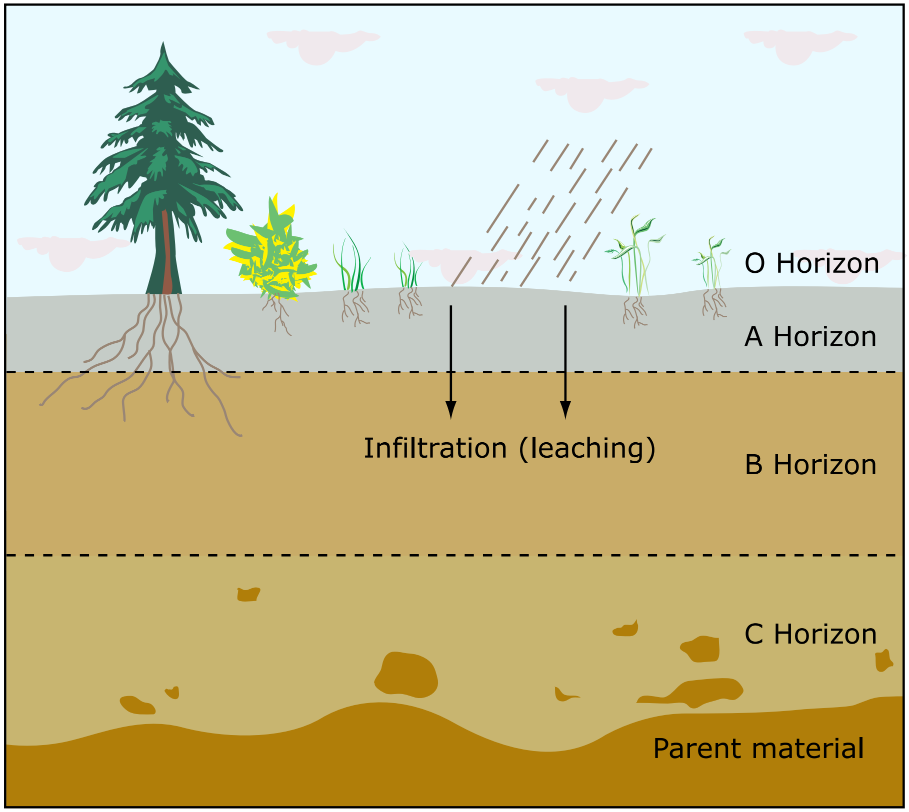



Image by MIT OpenCourseWare.

http://en.wikipedia.org/wiki/File:Stagnogley.JPG.

# Caliche- calcium carbonate deposits in soils

Image courtesy of USGS.

http://en.wikipedia.org/wiki/File:San-miguel-island-caliche.jpg

Gibbs free energy: work obtainable from an isothermal system at p=constant

G is minimized in equilibrium

$\Delta G=0$ in equilibrium for either direction so

$\Delta G^0$ (the energy to assemble the system from a reference point – enthalpy or standard free energy of change)

is equal to -RTlnK (change in entropy)

$\Delta G^0/RT= - \ln K$ where K is the equilibrium constant

In general: $\Delta G = \Delta G^0 + RT\ln Q$ (removed from equilibrium)

# DISSOLVED INORGANIC CARBON SPECIES

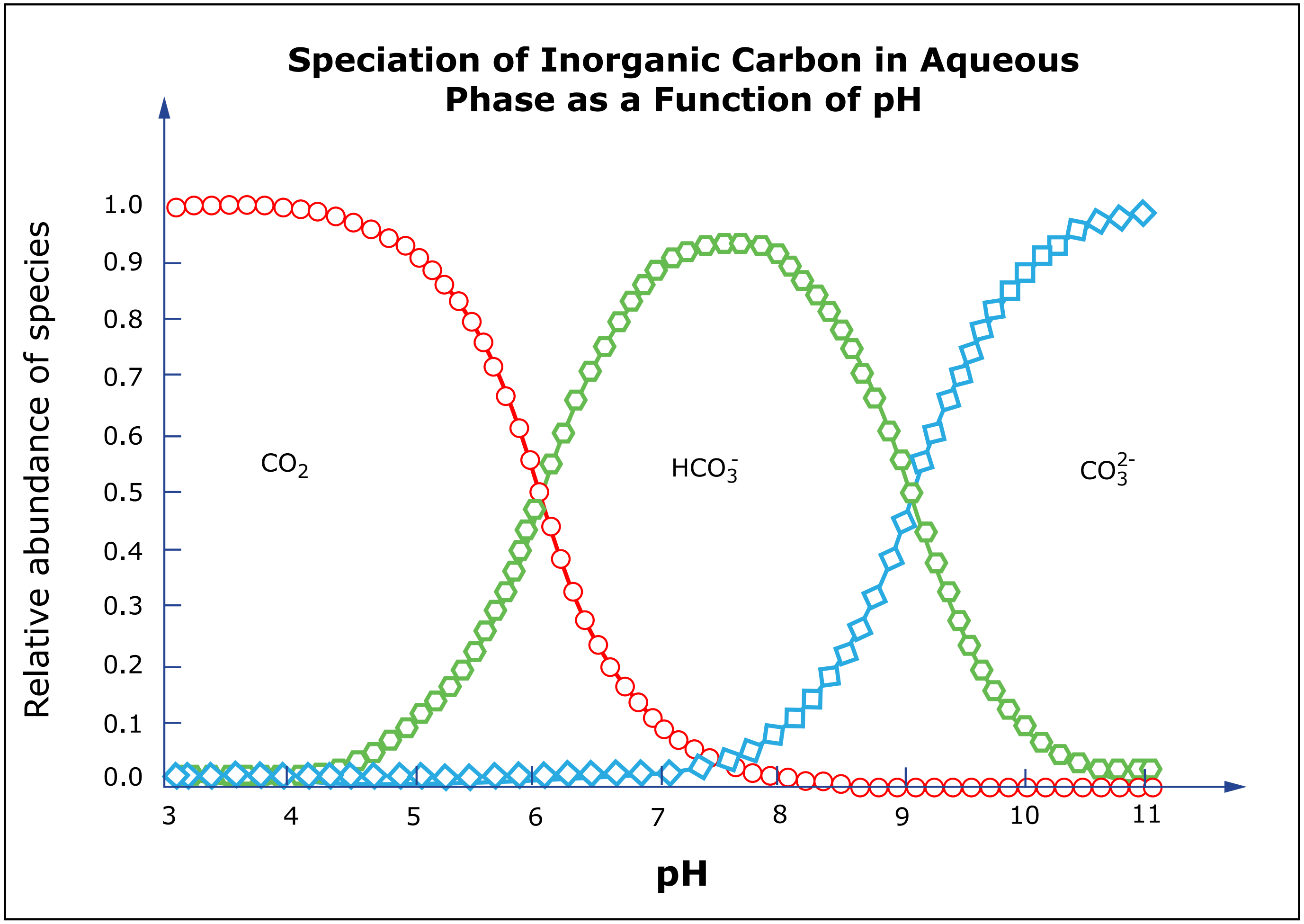



Image by MIT OpenCourseWare.

$CO_2$ is dissolved in water in the presence of a strong base

Alkalinity: net concentration of strong base in excess of strong acid

Alk= excess negative charge from weak acids

$$Alk = -[H^+] + [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] = [STRONG\ BASE]_T$$

# pH OF SEAWATER

Total Molar Composition of Seawater (Salinity = 35) Component Concentration (mol/kg)

| | |
|---|---|
| $H_2O$ | 53.6 |
| $Cl^-$ | 0.546 |
| $Na^+$ | 0.469 |
| $Mg^{2+}$ | 0.0528 |
| $SO^{2-}{}_4$ | 0.0282 |
| $Ca^{2+}$ | 0.0103 |
| $K^+$ | 0.0102 |
| $C_T$ | 0.00206 |
| $Br^-$ | 0.000844 |
| $B_T$ | 0.000416 |
| $Sr^{2+}$ | 0.000091 |
| $F^-$ | 0.000068 |

# $Ca^{+2}$ and $Mg^{+2}$

## Inputs and Outputs of Ca, Mg and $SO_4$ to/from the Ocean

***Calcium sulfate weathering input***

$CaSO_4 \rightarrow Ca^{++} + SO_4^{-}$

***Pyrite weathering input***

$4FeS_2 + 15O_2 + 8H_2O \rightarrow 2Fe_2O_3 + 8H_2SO_4$

***Silicate and Carbonate weathering input***

$2H_2CO_3 + H_2O + CaSiO_3 \rightarrow Ca^{++} + 2HCO_3^{-} + H_4SiO_4$

$H_2CO_3 + CaCO_3 \rightarrow Ca^{++} + 2HCO_3^{-}$

$2H_2CO_3 + H_2O + MgSiO_3 \rightarrow Mg^{++} + 2HCO_3^{-} + H_4SiO_4$

$2H_2CO_3 + CaMg(CO_3)_2 \rightarrow Ca^{++} + Mg^{++} + 4HCO_3^{-}$

$H_2SO_4 + 2CaCO_3 \rightarrow 2Ca^{++} + SO_4^{--} + 2HCO_3^{-}$

$H_2SO_4 + CaSiO_3 + H_2O \rightarrow Ca^{++} + SO_4^{--} + H_4SiO_4$

$2H_2SO_4 + 2CaMg(CO_3)_2 \rightarrow 2Ca^{++} + 2Mg^{++} + 2SO_4^{--} + 4HCO_3^{-}$

$H_2SO_4 + MgSiO_3 + H_2O \rightarrow Mg^{++} + SO_4^{--} + H_4SiO_4$

***Basalt-seawater reaction and dolomitization (output of Mg and input of Ca)***

$Mg^{++}$ + Ca-basalt $\rightarrow$ $Ca^{++}$ + Mg-basalt

$Mg^{++} + 2CaCO_3 \rightarrow Ca^{++} + CaMg(CO_3)_2$

***Outputs of Ca, Mg and $SO_4$ from the ocean***

$Ca^{++} + 2HCO_3^{-} \rightarrow CO_2 + H_2O + CaCO_3$

$Ca^{++} + SO_4^{--} \rightarrow CaSO_4$

$2Fe_2O_3 + 8Ca^{++} + 8SO_4^{--} + 8CO_2 \rightarrow 4FeS_2 + 15O_2 + 8CaCO_3$

$2Fe_2O_3 + 4Ca^{++} + 4Mg^{++} + 8SO_4^{--} + 8CO_2 \rightarrow 4FeS_2 + 15O_2 + 4CaMg(CO_3)_2$

# Common Ca-carbonate minerals

From public domain.

Image courtesy of USGS.

These two photos have been removed due to copyright restrictions.
Please see the photo on http://www.galleries.com/minerals/carbonat/dolomite/dolomite.jpg.

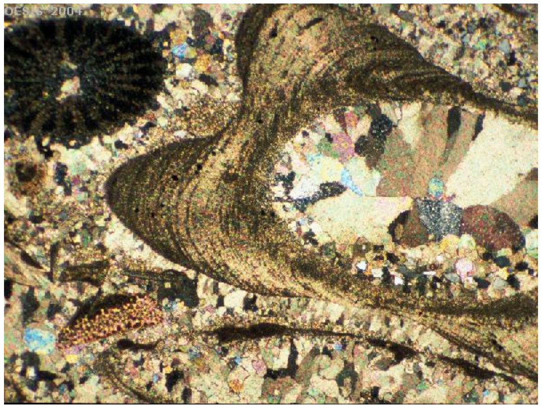
ARAGONITE

CALCITE

DOLOMITE

# Carbonate grains

OOIDS



http://en.wikipedia.org/wiki/File:PeloidsCarboniferousNV.jpg

PELOIDS

This image has been removed due to copyright restrictions. Please see the photo on http://en.wikipedia.org/wiki/File:Oncolites.jpg.

ONCOIDS

This image has been removed due to copyright restrictions. Please see the photo on http://www.earth.ox.ac.uk/%7Eoesis/micro/medium/limestone-xpl_pm14-09.jpg.

SKELETAL FRAGMENTS

This image has been removed due to copyright restrictions.

MUD

# Carbonate bank

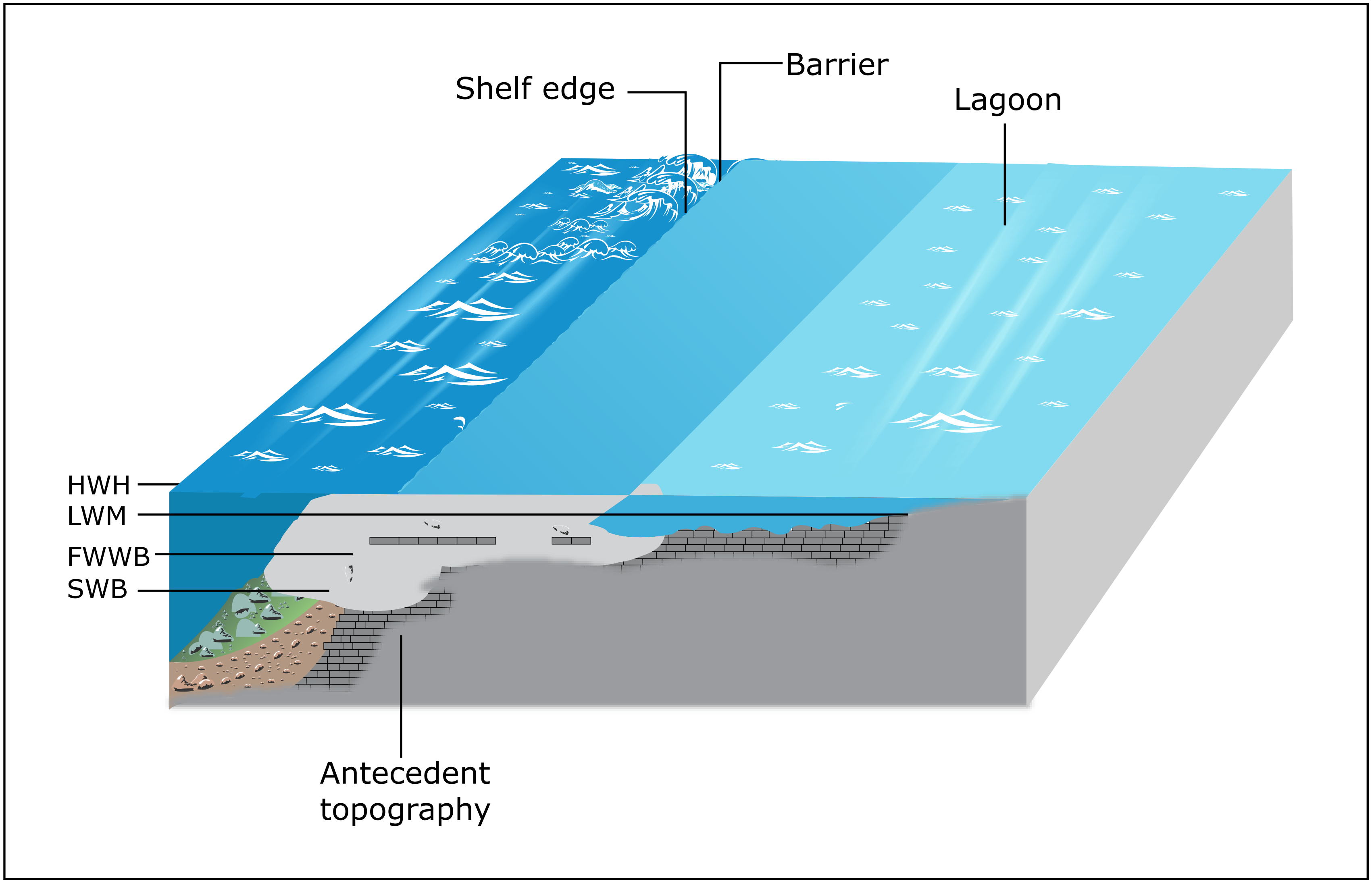



Image by MIT OpenCourseWare.

# Reefs

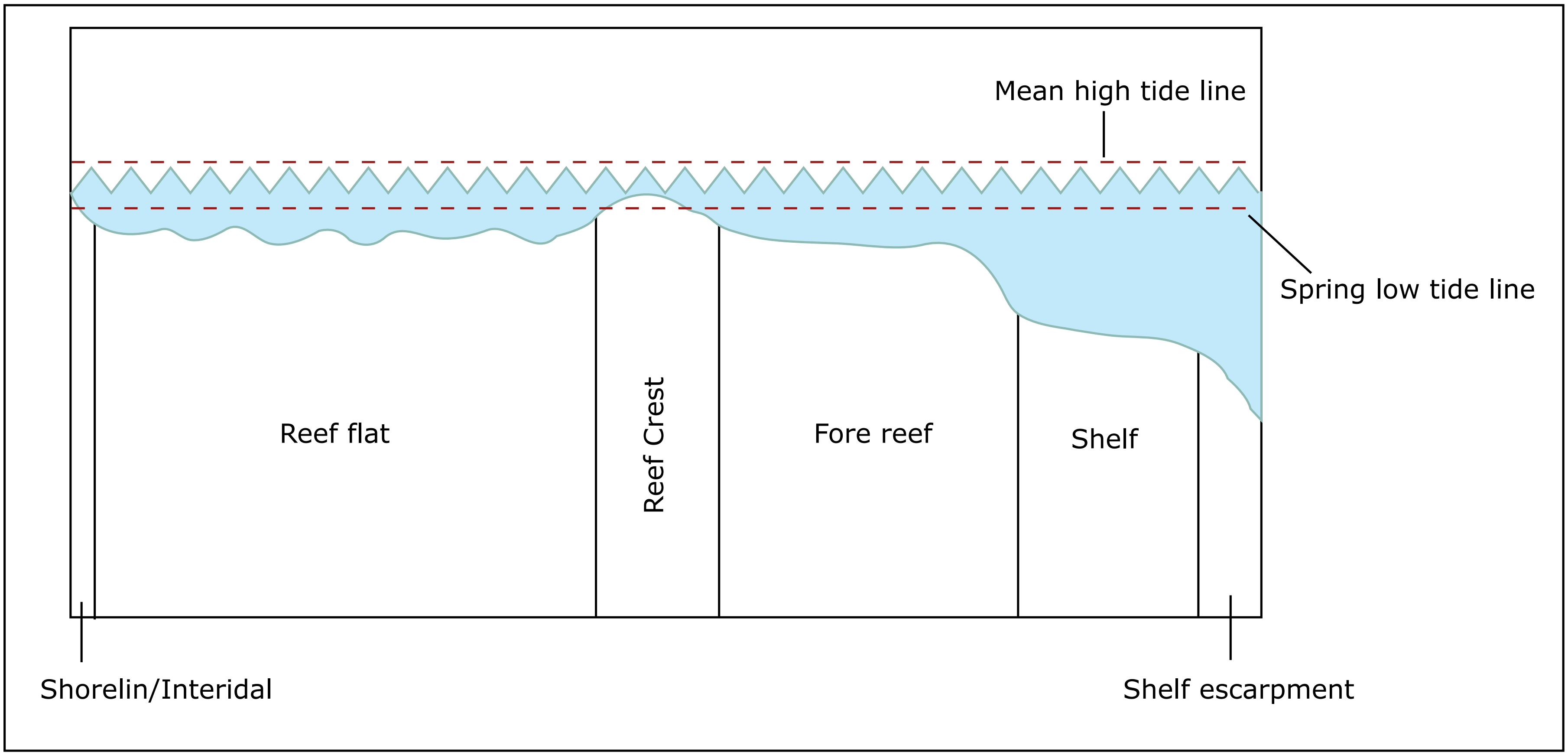



Image by MIT OpenCourseWare.

# Evaporate sequence and mineral solubility in salterns

Halite (NaCl) : $Ks=10^{1.5}$

Calcite: $Ks=10^{-8.35}$

Gypsum: $Ks=10^{-4.6}$

Water flows in a cascade from the shallow ponds where calcite/dolomite precipitate, to ponds where gypsum precipitates, to ponds where NaCl precipitates (now devoid of other minerals).

# Evaporitic shallow lagoon

Tan layer: calcium carbonate precipitated out of the solution

# Kerogen preserved in $CaCO_3$

These images have been removed due to copyright restrictions.

(Cohen et al., submitted)

# Extracted kerogen

This image has been removed due to copyright restrictions.

(Cohen et al., submitted)

# Bacterial fossils preserved in chert ($SiO_2$)

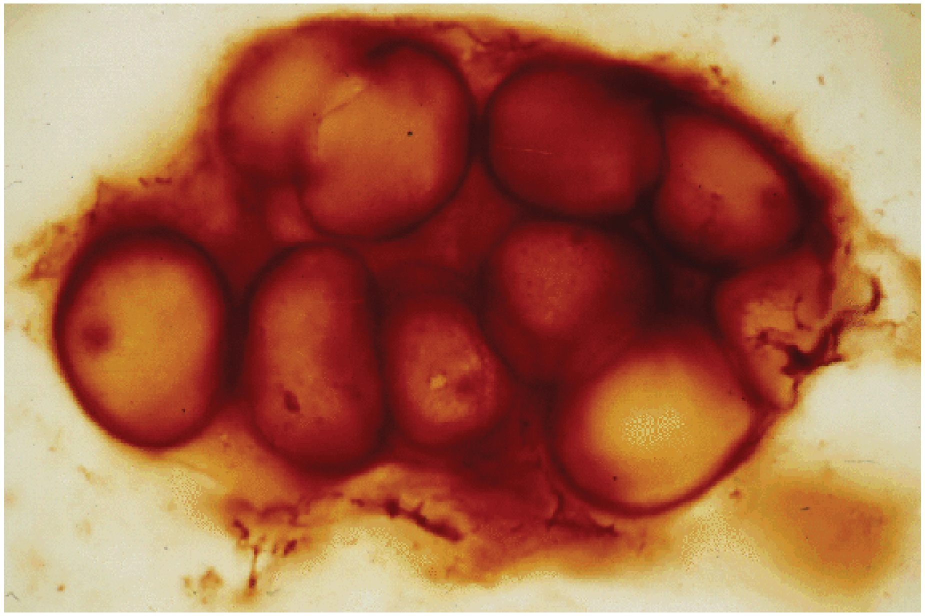


Image courtesy of ucmp.berkeley.edu. Used with permission.

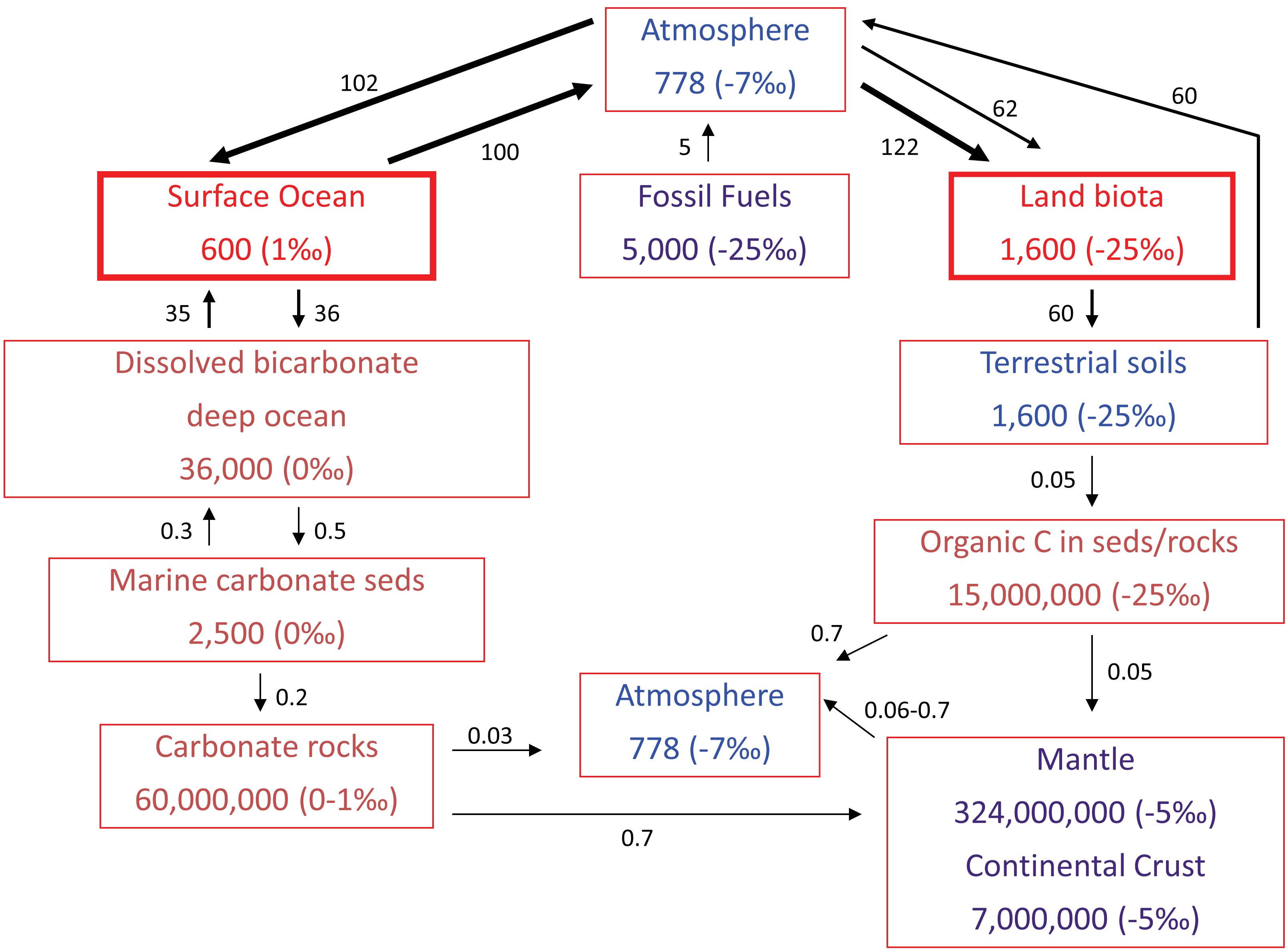
# WEATHERING OF SILICATE ROCKS

$K_2O{\cdot}Al_2O_3{\cdot}6SiO_2$ (s) + $2CO_2$ (aq) + 2.4 $H_2O$=
$2K^+$ + $2HCO_3^-$ + $Al_2O_3{\cdot}2SiO_2$ (s) + $2.6SiO_2$(s) + $1.4H_2SiO_3$ (aq)

Igneous rock + $CO_2$ + water = cations + clays + silicic acid + silica dioxide

Weathering of silicates removes $CO_2$ from the surface

# Carbon Cycle Fluxes and $\delta^{13}C$ Values




FLUXES IN GIGATONS OF CARBON/YEAR

These tables have been removed due to copyright restrictions. Please see Table 3.1 and 3.2 in the book: *Fundamentals of Geobiology*. ISBN: 9781405187527.

# Mycorrhizal fungi – promoters of weathering



Please see the images on http://mycorrhizas.info/vam.html.