Chemistry in Sediments: Aerobic to Anaerobic Diagenesis

OCN 623 – Chemical Oceanography

Reading: Libes, Chapter 12
Why Study Sediments?

- Very large surface area of sediments with respect to the volume of seawater:
  - Vertical distance = 4 - 6 km
  - Horizontal distance = 1000’s km
- Large area of contact between seawater and sediment
- Strong potential for the two reservoirs to interact
Types of sediments

- **Hydrogenous**: formed by reactions in the water
  - manganese nodules, iron hydroxides, sulfates, …

- **Biogenic**: produced by living organisms
  - calcite, silica, …

- **Lithogenic**: produced from the weathering
  - Al silicates, quartz, …

- **Cosmogenic**: produced from extraterrestrial sources
  - Ferric meteorites from space
What is Diagenesis?

- Greek etymology: *dia* -- “passing through”
  
  *genesis* -- “origin, birth”

- Diagenesis is the “sum of all processes that change a sediment or sedimentary rock subsequent to its deposition from water, but excluding metamorphism and weathering” (Berner, 1980)

- Simply: “Reactions in Modern sediments…”

Other geochemical transformations of sediments:

- **Metamorphism**: burial reactions that take place at high pressure and temperatures >150°C

- **Weathering**: reactions resulting from the effect of atmospheric contact on sediments (after uplift)
Why is Diagenesis Important?

• Important part of global biogeochemical cycles because of size of sedimentary reservoir

• Geochemical balances of many elements depend on balance between burial and remobilization

• Surface sediments are habitat for a wide range of organisms

• Production of petroleum via diagenesis and further processing of organic rich sediments
Today’s topic

Reactions that occur at sediment depths shallower than a few 100 m

Reactions that occur at low temperature

Uplift above sea-level does not occur, hence all interstitial space is filled with water

Includes:

- Chemical reactions
- Dissolution of solids
- Diffusion of dissolved species
- Precipitation of dissolved species
- Microbial activity
- Compaction
- Dewatering
- Bioturbation of solids
- Irrigation
**Overall Result of Diagenesis**

Terrestrial debris (inorganic, organic) + Reactive marine organic matter / biogenic debris

<table>
<thead>
<tr>
<th>Product</th>
<th>Fate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Remineralized (inorganic) C, N, P</td>
<td>Released, buried</td>
</tr>
<tr>
<td>Authigenic minerals (C, P, S, Si, Mn-Fe)</td>
<td>Buried</td>
</tr>
<tr>
<td>(grow in place, not transported)</td>
<td></td>
</tr>
<tr>
<td>Residual OM</td>
<td>Buried</td>
</tr>
</tbody>
</table>
Composition of Marine Sediments

Relative Proportion of Inner (< 60 m) Continental Shelf Deposits:

What regions might have shelf dominated by muddy sediments?

How about gravel?
Physical Changes that Impact Sedimentary Diagenesis

- Alteration in particle size
- Changes in sediment porosity
- Compaction (which results in porewater advection)
- Burrowing/feeding of biota ("Bioturbation")
  - Depth of bioturbation: <10 cm to more than 1 m
  - Prevents formation of chemical gradients
  - Introduces $O_2$-rich bottom water into sediments
Compaction & Porosity

\[ \phi = \text{porosity of sediment} \]
\[ (\text{cm}_{\text{water}}^3 / \text{cm}_{\text{sed}}^3) \]

Mechanical compaction
- rearrangement
- bending & ductile deformation
- breakage of grains

**Figure 3-6.** Initial porosity \( \phi_0 \) as a function of grain size for terrigenous surficial sediments. The increase of porosity with decreasing median size reflects increasing proportions of clay minerals. (After Meade, 1966.)

- Grain rotation
- Bending and ductile ductile deformation
- Grain crushing
Compaction & Porosity

\[ \phi = \frac{\text{porosity of sediment}}{\text{(cm}_{\text{water}}^3 / \text{cm}_{\text{sed}}^3)} \]

Idealized porosity estimation as an exponential function of an initial porosity at the surface

\[ \phi = \phi_0 e^{-cz} \]

c is average compressibility
z is depth

**Figure 3-9.** Porosity of clay sediments. Composite based on data for Recent, Tertiary, and Lias sediments. (After Engelhardt, 1977.)
Compaction & Porosity

Real porosity differs from the exponential function.

Each sediment layer has its own composition & compressibility.

Degree of compaction also depends on effective stress (geothermal gradients).
Bioturbation

$L = \text{depth range of bioturbation}$
Bioturbation

aRPD = apparent redox potential discontinuity
NO Sedimentary Diagenesis

Figure 2-1. Diagrammatic illustration of situation of no diagenesis. Upon burial, the value of property $p$ changes for a fixed depth, $x_1$ (or $x = 0$), but does not change for a given layer $A$. 
FIGURE 2-2. Diagrammatic illustration of situation of steady state diagenesis. Upon burial, the value of property $p$ does not change for a fixed depth, $x_1$ (or $x = 0$), but does change for a given layer $A$. (Modified after Berner, 1971.)
Sedimentary Diagenesis

(a) Linear, diffusion

(b) Convex, removal

(c) Concave, production

(d) Production/consumption
Redox Control of Diagenesis

- Diagenesis driven by decomposition of organic matter (OM)
  - OM in sediments is thermodynamically unstable
- Decomposition occurs by various processes, each of which leads to formation of specific species in solution and precipitation of authigenic minerals
  - Involves series of reactions using electron acceptors that are consumed sequentially
  - Each successive reaction is energetically less favorable, and does not occur until the electron acceptor from the (previous) more favorable reaction has been mostly consumed
Why is organic matter an electron donor?

• Example: net reaction for aerobic oxidation of organic matter:

\[ \text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} \]

• In this case, oxygen is the \textit{electron acceptor} – the half-reaction is:

\[ \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O} \]

• Different organisms use different electron acceptors, depending on availability due to local \textit{redox potential}

• The more oxidizing the environment, the higher the energy yield of the OM oxidation (the more negative is \(\Delta G\), the Gibbs free energy)
Z-scheme for photosynthetic electron transport

Falkowski and Raven (1997)

Energy from sun converted to C-C, energy rich, chemical bonds
Redox Reaction Succession
Sequence of dominant OM oxidizers

Diagenetic reactions occur (with increasing depth in the sedimentary column) according to the free energy released.
**Oxic respiration**

\[ \Delta G^o_R = -3190 \text{ kJ/mol CH}_2\text{O} \]

\[ \text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} \]

(see Table 12.1 in Libes for full reactions)

- Common in oxygenated waters
- Common in surface sediments
- Typically there is much more OM in sediments than \( \text{O}_2 \) available, so \( \text{O}_2 \) is generally depleted rapidly in interstitial waters of sediments
Manganese Reduction

\[ \Delta G^o_R = -3090 \text{ kJ/mol CH}_2\text{O} \]

\[ \text{CH}_2\text{O} + \text{MnO}_2 + 2 \text{H}^+ \rightarrow \text{Mn}^{2+} + \text{CO}_2 + \text{H}_2\text{O} \]

- Solid-phase MnO\textsubscript{2} is reduced and released to solution
- Dissolved Mn\textsuperscript{2+} thendiffuses upwards to the oxygenated zone of the sediments, is reoxidized and precipitated as manganese oxides
- Leads to build-up of Mn in shallow sediments (see text)
Nitrate Reduction

\[ \Delta G^o_R = -3030 \text{ kJ/mol CH}_2\text{O} \]

\[ \text{CH}_2\text{O} + \text{HNO}_3 \rightarrow \text{N}_2 + \text{CO}_2 + \text{H}_2\text{O} \]

- Nitrate that is released during oxic respiration is consumed in this process

- Several different species of reduced N can be produced
Iron Reduction

$\Delta G^o_R = -1410 \text{ kJ/mol CH}_2\text{O}$

$\text{CH}_2\text{O} + \text{Fe}_2\text{O}_3 + 2 \text{H}^+ \rightarrow \text{Fe}^{2+} + \text{CO}_2 + \text{H}_2\text{O}$

- Reduces solid-phase iron oxy-hydroxides to soluble Fe$^{2+}$
- Reduced Fe$^{2+}$ typically combines at depth in the sediments with S$^{2-}$ to form iron-monosulfide (FeS), then pyrite (FeS$_2$)
- Slightly different $\Delta G^o_R$ depending on whether using Fe$_2$O$_3$ or FeOOH (-1410 vs –1330)
Sulfate Reduction

\[ \Delta G^o_R = -380 \text{ kJ/mol CH}_2\text{O} \]

\[ \text{CH}_2\text{O} + \text{SO}_4^{2-} \rightarrow \text{S}^{2-} + \text{CO}_2 + \text{H}_2\text{O} \]

- Sulfate reduction is very important in marine sediments because sulfate is a major constituent of seawater (28 mM)
Methanogenesis

\[ \Delta G^\circ_R = -350 \text{ kJ/mol CH}_2\text{O} \]

2 CH\text{O} → CH\text{4} + CO\text{2}

- Occurs below the zone of sulfate reduction -- \textit{i.e.}, after all the sulfate in the porewater has been depleted
Types of metabolism

- Light used directly by phototrophs
- Hydrothermal energy utilized via heat-catalyzed production of inorganics

Nealson and Rye 2004
Deep Sea Sediment

Concentration

Depth

Zone of bioturbation

Oxic

Suboxic

A few meters

\( \text{MnO}_2 \)

\( \text{Mn}^{2+} \)

\( \text{NO}_3^- \) (from OM oxid)

\( \text{O}_2 \)
Nearshore Sediment

Concentration

Depth

10s of cm

Oxic
Suboxic
Anoxic

microlayer

NO$_3^-$
Fe$^{2+}$
SO$_4^{2-}$
HS$^-$
CH$_4$
Estimating Benthic Fluxes From Concentration Profiles

- Measure the slope of profile at given depth (dC/dZ, moles/cm³/cm)
- Measure porosity of sediment (φ) (cm_{water}³/cm_{sed}³)
- Estimate bulk sediment diffusivity (D_s, cm²/sec)
- Assume no bioturbation or irrigation
- Apply modification of Fick’s 1st law of diffusion:

\[ \text{Vertical flux} = F_z = - D_s \phi (dC/dZ) \text{ (moles/cm}^2\text{/sec)} \]
Potential Problems:

1. Macrofaunal irrigation

2. $D_s$ is poorly known
   - $1 \times 10^{-5}$ cm$^2$/sec for seawater
   - $2-5 \times 10^{-6}$ cm$^2$/sec for muddy sediments

3. Effects of adsorption reactions

4. Reactions at sediment/water interface
Direct Measurement of Benthic Fluxes to Seawater

- Use of benthic “chambers” or “domes”
- Installed by divers or automated “benthic landers”
- Alternatively, can use cores in lab
- Measure concentration of parameter of interest over time in water
- Flux is proportional to slope of plot of conc. vs time (normalized to area under the dome)
A More Direct Measurement?

- Use of highly sensitive, high-resolution thermistors
- Based upon premise of diurnal temperature fluctuations in water column propagating (with a lag) into the upper sediment
- Couple *measured* porewater velocity and *measured* biogeochemical profiles for a *measured* flux

Fram et al. 2014
Often the calculated diffusion-supported surface flux is greater than the measured flux...  WHY?

Uptake at surface microlayer occurs, especially if:

- Dealing with flux of nutrients across an illuminated surface sediment
- Dealing with flux of reduced compounds into aerobic seawater

**Directions of common sediment fluxes:**

- $\text{NH}_4^+$ positive (*i.e.*, upwards)
- $\text{CH}_4$ positive
- $\text{HS}^-$ positive
- $\text{DOC}$ positive
- $\text{O}_2$ negative (*i.e.*, downwards)
- $\text{SO}_4^{2-}$ negative
Berner’s Sediment Classification

• Because of problems with Eh-pH measurements, and classification based on \( O_2 \) and \( HS^- + H_2S \) concentrations, each environment is characterized by a suite of authigenic minerals.

• The succession of sedimentary environments corresponds to the succession of reactions for the decomposition of OM:

\[
\text{Oxic} \rightarrow \text{Sub-oxic} \rightarrow \text{Sulfidic} \rightarrow \text{Methanogenic} \rightarrow \text{Anoxic}
\]
Oxic: $[O_2] > 100 \mu M$

- Oxidation of OM by molecular oxygen
- Relatively low OM (especially continental fluvial sediments) because the OM is partially oxidized prior to sediment burial
- Fe-oxy-hydroxide phases are not reduced -- they are transformed to hematite ($Fe_2O_3$) during diagenesis (e.g., Red beds)
- Presence of oxidized Mn phases
- Usually light brown sediment
**Suboxic: 100 µM > [O₂] > 1 µM**

Non-sulfidic environment -- [H₂S] < 1 µM

- Although the oxidation of OM consumes O₂, there is insufficient OM to generate much H₂S

- NO₃⁻, MnO₂, and FeOX reduction

- Fe²⁺ and Mn²⁺ increase and become supersaturated with respect to siderite (FeCO₃), rhodochrosite (MnCO₃), glauconite ((K,Na)(Fe³⁺,Al,Mg)₂(Si,Al)₄O₁₀(OH)₂), and vivianite (Fe₃(PO₄)₂·8(H₂O))

- Usually grey sediment
Anoxic: \([\text{O}_2] < 1 \mu\text{M}\)

1) Sulfidic environments -- \([\text{H}_2\text{S}] > 1 \mu\text{M}\)

Oxidation of OM is by sulfate reduction

- **Greigite** (Fe\(_3\)S\(_4\)) and **mackinawite** (Fe\(_{\text{HX}}\)S) are first formed metastably, then react with H\(_2\text{S}\) to produce iron monosulfide (FeS) and pyrite (FeS\(_2\)).

- **Alabandite** (MnS) is only stable under very high concentrations of H\(_2\text{S}\) -- thus rhodochrosite (MnCO\(_3\)) is more common

- Requires large OM deposition rate

- Usually black sediment
Towards a consistent classification scheme for geochemical environments, or, why we wish the term ‘suboxic’ would go away

Canfield & Thamdrup
2) Methanogenic environments

- Strongly reducing environments

- OM decomposition by fermentation, CH$_4$ forms

- All sulfate is reduced and H$_2$S is mostly removed by precipitation of sulfide minerals (requires Fe$^{2+}$) -- either iron monosulfide, pyrite, or marcasite (FeS$_2$).

- Continued Fe reduction and buildup of Fe$^{2+}$ in solution (also Mn$^{2+}$) and saturation wrt siderite, rhodochrosite and vivianite

- Common in non-marine sediments because little sulfate present (easy to deplete sulfate)

- Usually black sediment, buy may grade to grey
Layered microbial systems

Des Marais et al. 2003
Sippewissett Marsh
Shark Bay, Australia
Wisconsin & Australia
Banded iron formation
from last time…

- Iron (oxy)hydroxide binding phosphate
  - *Phosphate* (*$\text{HPO}_4^{2-}$*) *dissolved in seawater*
  - *Granular ferric oxide surface*
  - *Two ionic bonds at surface, displacing hydroxide*
  - *What about other ions?*
from last time...

- Fe-S-O-P recap
  - Phosphate release during respiration
  - Mineralization or sorption onto labile ferric oxyhydroxides
  - Reductive dissolution releases phosphate
  - Can lead to elevated bioavailable P levels in overlying water

Figure 1: Proposed diel (day-night) trapping or release of porewater phosphate, DOP, and iron as a consequence of diurnal shifts between benthic photosynthesis and respiration.