Lecture 10

Hard Tissues, Biomineralization, and Our Health (3)
Interfacial energy is due to the breakage of bonds at the interface

Energy increase at site $b$?

- $\phi$: Bond energy
- $r_o$: length of bond

The interfacial energy is the energy INCREASE by creating a unit area of the interface between surfaces of different materials.
The interfacial energy is the energy INCREASE by creating a unit area of the interface between surfaces of different substances.
Outline

- Water-acidic and basic conditions, pH
- Biomaterials – nucleation and growth
- Heterogeneous nucleation and templating packing of biomineral crystallites.
Some more examples
# Crystal vs Crystal Structure

\[ L = ma + nb + pc, \quad m,n,p: \text{any integer} \]

<table>
<thead>
<tr>
<th>7 crystal systems</th>
<th>Crystal axes</th>
<th>Angles between axes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triclinic</td>
<td>(a, b, c\text{ any value})</td>
<td>(\alpha, \beta, \gamma\text{ any value})</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>(a, b, c\text{ any value})</td>
<td>(\alpha=\beta=90^\circ, \gamma\text{ any value})</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>(a, b, c\text{ any value})</td>
<td>(\alpha = \beta = \gamma = 90^\circ)</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>(a = b; c\text{ any value})</td>
<td>(\alpha = \beta = \gamma = 90^\circ)</td>
</tr>
<tr>
<td>Trigonal</td>
<td>(a = b = c,)</td>
<td>(\alpha = \beta = \gamma \neq 90^\circ)</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>(a = b; c\text{ any value})</td>
<td>(\alpha = \beta = 90^\circ, \gamma = 120^\circ)</td>
</tr>
<tr>
<td>Cubic</td>
<td>(a = b = c)</td>
<td>(\alpha = \beta = \gamma = 90^\circ)</td>
</tr>
</tbody>
</table>
CaCO₃ may crystallize in different crystal systems.

CaCO₃ may crystallize in different crystal systems:
- Mineral: Calcite (Trigonal)
- Mineral: Aragonite (Orthorhombic)
- Mineral: Vaterite (Hexagonal)

CaCO₃ may also exist in non-crystalline states:
- Biominerals: Amorphous (Non-crystalline state)
Some more examples

Calcium carbonate: $\text{CaCO}_3$

<table>
<thead>
<tr>
<th>Polymorphs</th>
<th>Symmetry</th>
<th>Hardness</th>
<th>Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite</td>
<td>Trigonal</td>
<td>3</td>
<td>2.71</td>
</tr>
<tr>
<td>Aragonite</td>
<td>Orthorhombic</td>
<td>3.5-4</td>
<td>2.54</td>
</tr>
<tr>
<td>Vaterite</td>
<td>Hexagonal</td>
<td>3</td>
<td>2.95</td>
</tr>
<tr>
<td>Amorphous</td>
<td>--</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The dissolution and formation...
pH of Water:
Acids

- Acids
  - Dissociate in water and release hydrogen ions \( (H_2O \leftrightarrow H^+ + OH^-) \)
  - Hydrochloric acid (stomach acid) is a gas with symbol HCl
    - In water, it dissociates into \( H^+ \) and \( Cl^- \)
    - Dissociation of HCl is almost total, therefore it is a strong acid
pH of Water: Bases

- Bases:
  - Either take up hydrogen ions (H\(^+\)) or release hydroxide ions (OH\(^-\))
  - Sodium hydroxide (drain cleaner) is a solid with symbol NaOH
    - In water, it dissociates into Na\(^+\) and OH\(^-\)
    - Dissociation of NaOH is almost total, therefore it is a strong base
pH Scale

- pH (\(= -\log C_{H^+}\)) scale used to indicate acidity and alkalinity of a solution.
  - Values range from 0-14
    - 0 to <7 = Acidic
    - 7 = Neutral
    - >7 to 14 = Basic (or alkaline)
  - Logarithmic Scale
    - Each unit change in pH represents a change of 10X
    - pH of 4 is 10X as acidic as pH of 5
    - pH of 10 is 100X more basic than pH of 8
The pH Scale

Acidic

0 hydrochloric acid
1 stomach acid
2 lemon juice
3 soda, vinegar
4 beer, wine
5 tomatoes
6 bread, black coffee
7 normal rainwater
8 root beer, urine
9 milk
10 pure water, tears
11 human blood
12 egg whites, seawater
13 baking soda, stomach antacids
14 Great Salt Lake
15 household ammonia
16 bicarbonate of soda
17 oven cleaner
18 sodium hydroxide (NaOH)

Neutral pH

7 neutral pH

Basic

10 baking soda, stomach antacids
11 egg whites, seawater
12 human blood
13 pure water, tears
14 milk
15 normal rainwater
16 root beer, urine
17 bread, black coffee
18 tomatoes
19 soda, vinegar
20 beer, wine
21 lemon juice
22 stomach acid
23 hydrochloric acid
Biomineralization-thermodynamics

Crystallization: first order phase transition

\[ C_i < C_{eq} \]

Demineralization: Dissolution of biominerals

\[ C_i > C_{eq} \]

Biomineralization/remineralization: Crystallization of biominerals

3D long range ordering

Crystal phase

5 \mu m
Biomineralization: *how does it occur?*

\[
\text{Ca}^{2+} + \text{CO}_3^{2-} \xleftrightarrow{\text{H}^+} \text{CaCO}_3 \downarrow
\]

\[
C_{\text{CO}_3^{2-}} \quad C_{\text{Ca}^{2+}}
\]

Crystal stable

\[
\text{CaCO}_3 \downarrow
\]

Solution stable

\[
\text{Ca}^{2+}, \text{CO}_3^{2-}
\]

\[
[H^+]
\]

pH
Question:

- The precipitation of $\text{CaCO}_3, \text{Ca}_5(\text{PO}_4)_3\text{OH}$ is ...
- But we need...

- The question is how?
Biomineralization: construction of ordered assembly

• If we have $C > C_{eq}$, does it mean biomineralization will certainly occur?

• No. Biominerals are crystalline. The formation of crystalline materials will experience a nucleation and growth process!

• How does the ordered structure of HAP crystallite assembly occur?
Crystallization: 3D Nucleation: nucleation barrier

Potential difference

-\phi: Bond energy

\[ E \]
Dam: to prevent the flooding from the reservoir

Crystallization: 3D Nucleation: nucleation barrier

Dam

Kinetic barrier (nucleation barrier)

Chem. Potential difference
**Bulk Energy** $E_b$ vs **Surface Energy** $E_s$

Total Bulk Energy without considering the surfaces

$$E_b = 4 \times (-1/2 \phi) \times 4 = -8\phi$$

Total Bulk Energy considering the surfaces

$$E_b' = -4\phi$$

Total Surface Energy

$$E_s = E_b' - E_b = 4\phi$$

$$\gamma = \frac{1}{2} \phi / A$$

As the size of the crystal increases, the total Bulk Energy decreases. However, the surface energy increases.
Crystallization: 3D Nucleation: nucleation barrier (cont’d)

- Under the crystallization condition, the total bulk free energy will decrease with increasing the size of ice clusters.
- On the other hand, the surface energy will increase.
- In conclusion, the total free energy will increase with the size of ice clusters at the beginning, and reach the maximum at $r = r_c$.
- $\Delta G^*$ nucleation barrier.
**Crystallization: 3D Nucleation:**

**nucleation barrier (cont’d)**

- Nucleation is the process for crystal clusters to overcome the nucleation barrier in order to grow spontaneously.
- The occurrence of nucleation barrier is due to the existence of the interfacial (free) energy.

\[ \Delta G = \Delta G^* + \Delta G^s + \Delta G^b \]

\( r_c \)

\( r \)

\( \Delta G^b = \Delta G^s + \Delta G^b \)

\( \Delta G^s \)

\( \Delta G^b \)

\( \Delta G^* \)

\( \Delta G^s \)

\( \Delta G^b \)

\( r_c \)

\( \Delta G^* \)

\( r \)

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\( \Delta G^* \)

\( \Delta G^s \)
Biomineralization: 3D Nucleation: nucleation barrier (cont’d)

- Those “clusters” with high (kinetic) energy will be able to surpass the barrier.
- The higher the nucleation barrier, the more difficult the nucleation will be (the longer the time it will take.)

The Magnum XL-200 roller coaster
Q: Would the nucleation barrier still exist if the surface (free) energy is equal to zero?
Homogeneous nucleation vs heterogeneous nucleation

\[ \gamma' \ll \gamma \]

The substrate will reduce the surface/interfacial energy between the crystal and the ambient phase.

\[ -\phi' \]
Homogeneous nucleation vs heterogeneous nucleation

Substrate will lower the nucleation barrier to promote nucleation.

Nucleation promoted by foreign bodies is heterogeneous nucleation.

Nucleation without any assistance of foreign bodies is homogeneous nucleation.

Substrate lowers interfacial energy between biomineral and template.
Heterogeneous nucleation & templating

How to lower the interfacial energy between biomineral and template…

Partial structural match - moderate interaction between the crystal and the substrate.

Excellent structural match - very strong interaction between the crystal and the substrate.
Template effect

- A better structural match (template) between bio-mineral crystals and the substrates will give rise to a stronger interaction between them.

- The Template effect will effectively reduce the surface/interfacial energy, therefore lower the nucleation barrier.

- Consequently, bio-mineralization will be promoted.
Implication of (2)

- The structure of the promoted biominerals should be very similar to the template-template effect
The template effect in biomineralization

The sequential mineralization stages of an eggshell. Upon the rough collagen membrane, charged sites of nucleating protein are deposited first, then exposed to calcium and carbonate to nucleate crystals. Subsequent chemical species in the fluid control the crystal growth and orientation. B) Scanning electron micrograph of an eggshell membrane at the early stage, showing the fibers of collagen and the first nucleated crystals.
Remodeling of Bones: reconstruction of ordered structure of bone

- Why will bio minerals grow along bio substrates (Osteoid)?
- Good template!
Biomineralization by templating

Templating: ordered

Random
Review

- Water-acidic and basic conditions, pH
- Biomaterials – nucleation and growth
- Template effect and the ordered packing of biomineral crystallites.
Main reference

- Oral Histology: Development, Structure, and Function