Recap Lecture 5

- **Gibbs-Duhem equation:** \[ dG = -SdT + VdP \]
- **Clapeyron equation:** \[ \frac{dP}{dT} = \frac{\Delta S_R}{\Delta V_R} \]
- **Gibbs phase rule:** \[ f = c + 2 - \Phi \]
Recap Lecture 5

\[ f = c + 2 - \Phi \]
Composition as a variable

• Constant X: one component diagram
• Constant T: isothermal diagram
• Constant P: isobaric diagram

\[ f = c + 1 - \Phi: \text{“reduced” phase rule} \]
Binary systems: \( f = 2 + 1 - \Phi \)

- \( \Phi_{\text{max}} = 3 \)
- 2 different cases:
  - System with eutectic
  - System with solid solution
Binary systems: $f = 2 + 1 - \Phi$

- $\Phi_{\text{max}} = 3$

- 2 different cases:
  - System with eutectic
    - System with a simple eutectic
    - System with an intermediate stable phase
    - System with an intermediate unstable phase
  - System with solid solution
    - Simple system
    - System with solubility gap
Construction of a binary phase diagram

One atmosphere furnace

http://nai.nasa.gov/annual-reports/2011/rpi/project-6-the-environment-of-the-early-earth/
Construction of a binary phase diagram

**CaAl$_2$Si$_2$O$_8$ - SiO$_2$**

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>% SiO$_2$</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>1360</td>
<td>0</td>
<td>An</td>
</tr>
<tr>
<td>1540</td>
<td>0</td>
<td>An</td>
</tr>
<tr>
<td>1560</td>
<td>0</td>
<td>Gl.</td>
</tr>
<tr>
<td>1350</td>
<td>20</td>
<td>An + Qz</td>
</tr>
<tr>
<td>1400</td>
<td>20</td>
<td>An+Gl</td>
</tr>
<tr>
<td>1520</td>
<td>20</td>
<td>Gl</td>
</tr>
<tr>
<td>1350</td>
<td>60</td>
<td>An+Qz</td>
</tr>
<tr>
<td>1400</td>
<td>60</td>
<td>Qz+Gl</td>
</tr>
<tr>
<td>1700</td>
<td>100</td>
<td>Qz</td>
</tr>
<tr>
<td>1720</td>
<td>100</td>
<td>Gl</td>
</tr>
<tr>
<td>...</td>
<td>...</td>
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</tr>
</tbody>
</table>

[Graph showing the phase diagram with labels for Liquidus and Solidus, and markers for different phases such as An, Gl, Qz.]

CaAl$_2$Si$_2$O$_8$ - SiO$_2$
Syst. With Eutectic

Syst. With Solid solution

Diagram 1: Syst. With Eutectic
- Liquid phase
- A + Liq
- B + Liq
- TE
- A + B

Diagram 2: Syst. With Solid solution
- Liquid phase
- AB ss + liq
- AB ss
Case of a simple eutectic

**Liquidus:** separate the field with only liquid from the other fields

**Solidus:** separate the field with only solid phase(s) form the other fields

**Eutectic point:**
- separate the field with only solid phase(s) form the other fields
- lowest $T$ at which liquid is stable
- $\Phi_{\text{max}}$

**Lever rule:** phase proportions
Case of a simple eutectic
Case of a simple eutectic

Equilibrium crystallization of composition X \((T \text{ decreases})\)

1. 100% Liquid with composition \(X = 20\%B\)
2. Liquidus: first crystal of A appears
3. \(T_1: \text{Mnl} A + \text{liquid}\)
   - Liquid composition: 56\%B
   - Liquid proportion: \(a/(a+b) = 20/56 = 35.7\%\)
   - Mnl A proportion: \(1-a/(a+b) = b/(a+b)\)
4. Eutectic point:
   - Phase proportion when it reaches \(T_S\):
     - % liq = 20/61 = 32.8\%
     - % A = 1 - 20/61 = 67.2\%
     - %B = 0\%
   - Crystallization of the liquid in the proportion of the eutectic:
     Liq \(\rightarrow\) 39\% A + 61\% B
   - Liquid proportion when it leaves \(T_S\): 0\%
5. Solid state: mix between crystals of A and B:
   - % A: \(f/(e+f) = (100-20)/100 = 80\%\)
Case of a simple eutectic

Fractional melting of composition $Y$ ($T$ increases and melt is extracted at each step)

1. 100% solid: mix of A and B
   
   $A\% = \frac{f}{(e+f)} = \frac{100-80}{100} = 20\%$

2. Eutectic point: first melt appears
   - Melting of the solid in the eutectic proportions: 61% B + 39% A → Liq
   - Liquid composition: 61% B
   - Phase proportions when it leaves $T_S$:
     - % A = 0%
     - % Liq = 0% (all the liquid is instantaneously extracted)
     - % B = 100%

3. $T_1$: 100% Mnl B

4. Liquidus: $B_{\text{solid}} \rightarrow B_{\text{liquid}}$

Note: unlike during the equilibrium melting, the last melt to be formed doesn’t have the same composition than the initial solid.
System with an intermediate stable phase
System with an intermediate stable phase

Equilibrium melting of composition $Z$ \((T \text{ increases})\)

1. $100\%$ solid: mix of $A$ and $AB$
   
   \[
   A\% = \frac{(62-51)}{62} = 17.7\%
   \]

2. Eutectic point: first melt appears
   - Melting of the solid in the eutectic proportions: \((\frac{(62-37.5)}{62}=) 39.5\%
   
   \[A + 60.5\% \text{AB} \rightarrow \text{Liq}\]
   - Liquid composition: $37.5\%$ $B$
   - Phase proportions when it leaves $T_{S}$:
     - $% A = 0\%$
     - $% \text{Liq} = \frac{(62-51)}{(62-37.5)} = 45\%$
     - $% B = 55\%$

3. $T_{1}$: Mnl $\text{AB} + \text{Liquid}$
   - Liquid composition: $43.5\%$ $B$
   - Liquid proportion: \(\frac{b}{(a+b)} = \frac{(62-51)}{(62-43.5)} = 59.4\%\)

4. Liquidus: the last crystal of $\text{AB}$ melts

5. $100\%$ liquid – Liquid composition: $Z = 51\%$ $B$
System with an intermediate stable phase

Equilibrium melting of composition W \((T\text{ increases})\)

1. 100% ml AB
2. \(T_1\): 100% ml AB
3. \(T_{AB}\): Congruent melting:
   \[\text{AB}_{\text{solid}} \rightarrow \text{AB}_{\text{liquid}}\]
4. 100% liquid AB – Liquid composition: 62%B

Note: Composition W behaves as a one component system (such as composition 100% A and composition 100% B)
System with an intermediate stable phase

1. **100% liquid**
   - Liquid composition: V = 69% B

2. **Liquidus**: first crystal of AB appears and is instantaneously separated.

3. **$T_1$**: New bulk composition = 71% B
   - Crystals of AB continue to be formed and separated

4. **Eutectic point**: first crystal of B appears
   - Phase proportion when it reaches $T_{S2}$: 0% AB (all crystal separated), 100% Liq, 0%B
   - Liquid crystallizes to form AB and B in eutectic proportions:
     
     \[
     \text{Liq} \rightarrow \left(\frac{(100-76)}{(100-62)}\right) = 63\% \text{ AB} + 37\% \text{ B}
     \]
   - Last solid to be formed: mix of 63% AB – 37%B

5. **100% solid**: 63% AB + 37% B – solid composition: 76%

Fractional crystallization of composition V ($T$ decreases and crystals are separated at each step)

Note: at each step you form a new melt composition ⇒ Formation of magmatic series
System with an intermediate unstable phase
System with an intermediate unstable phase

Equilibrium crystallization of composition U ($T$ decreases)

1. 100% Liquid with composition $X = 21\%B$
2. Liquidus: first crystal of A appears
   - Liquid composition: 43\%B
   - Liquid proportion: $a/(a+b) = 21/43 = 48.8\%$
   - Mnl A proportion: 51.2\%
3. Peritectic point:
   - Phase proportion when it reaches $T_P$:
     - \% liq = $21/45 = 46.7\%$
     - \% A = $1 - 21/45 = 53.3\%$
     - \%AB = 0\%
   - Incongruent crystallization of AB in the proportion of the peritectic:
     (31/45=) 68.9\%Liq + 31.1\% A → AB
4. Solid state: mix between crystals of A and AB:
   - Liquid proportion when it leaves $T_P$: 0\%
   - % A: $d/(c+d) = (31-21)/31 = 32\%$
System with an intermediate unstable phase

Fractional crystallization of composition U \((T \text{ decreases and minerals separated})\)

(1) 100% Liquid with composition U = 21%B
(2) Liquidus: first crystal of A appears and is instantaneously separated from the melt
(3) \(T_1\): New bulk composition = 43% B – Crystals of A continue to be formed and separated
(4) Peritectic point:
- Phases when it reaches \(T_P\): 100% Liq (compo 45% B): no crystals A to react with.
- Phases when it leaves \(T_P\): 100% Liq
(5) AB + liquid (with AB separated instantaneously)
(6) Eutectic point
- first crystal of B appears
- Liquid crystallizes to form AB and B in eutectic proportions:
  \[ \text{Liq} \rightarrow \left(\frac{(100-62)}{(100-31)}\right) = 55\% \text{ AB} + 45\% \text{ B} \]
- Last solid to be formed: mix of 55% AB – 45% B
(7) 100% solid: 55% AB + 45% B – solid composition: 62% B
System with an intermediate unstable phase

Equilibrium crystallization of composition S \((T\) decreases\)

1. 100% Liquid with composition S = 41%B
2. Liquidus: first crystal of A appears
3. \(T_1\): Mnl A + liquid
   - Liquid compo.: 43%B
   - % Liq: \(a/(a+b)=41/43=95.3\%\)
4. Peritectic point:
   - Phases when it reaches \(T_P\): Liq + A
     - % Liq = 41/45 = 91.1%
     - % A = 1 – 41/45 = 8.9%
   - Incongruent crystallization of AB in the proportion of the peritectic:
     - (31/45=) 68.9%Liq + 31.1% A → AB
     - Phases when it leaves \(T_P\): Liq + AB
     - % Liq: \(c'/c'+d) = (41-31)/(45-31) = 71.4\%
     - % A = 1 – 41/45 = 8.9%
5. AB + liquid
   - % Liq: \(e/(f+e) = (41-31)/(59-31) = 35.7\%
   - Liq comp: 59%B
6. Eutectic point:
   - Phases when it reaches \(T_E\): Liq + AB
     - % liq = \(g/(g+h) = (41-31)/(62-31) = 32.2\%
     - liq compo: 62% B
   - Crystallization of the liquid in the proportion of the eutectic:
     Liq → ((100-62)/(100-31)=)55% AB + 45% B
7. Solid state: mix between crystals of AB and B:
   - % AB: \(i/(g+i)=(100-41)/(100-31)=85.6\%
   - Solid compo: S: 41%B
System with solid solution

Note: Mineral phases have intermediate compositions between pure end-members that evolve during the magmatic process.
System with solid solution

Equilibrium melting of composition R
(T increases)

(1) $T_1$: 2 immiscible liquids: A-rich ss and B-rich ss
   - A-rich ss compo: 21%B
   - B-rich ss compo: 81%B
   - %A-rich ss: \( \frac{d}{c+d} = \frac{81-25.5}{81-21} = 92.5\% \)

(2) $T_{ex}$: end of the immiscibility: only one solid solution of compo 25.5% B

(3) One solid phase with compo 25.5%B

(4) Solidus: first melt appears
   - Compo first melt: 88%B

(5) $T_2$: ABss +Liq
   - Compo AB: 5%B
   - Compo liq: 61%B
   - % liq: \( \frac{a}{a+b} = \frac{25.5-5}{61-5} = 36.6\% \)

(6) Liquidus: last crystal of ABss to melt
   Compo last crystal: 0.5%B

(7) 100% liquid – compo liq: 25.5% B
System with solid solution

Fractional crystallization of R

(1) 100% liquid of compo 25.5% B
(2) Liquidus: first crystal of Abss to crystallize.
   - compo first crystal: 0.5% B (almost pure A)
(3) New bulk composition: 61%B
   Compo crystal in equilibrium: 5%B
(4) $B_{\text{liquid}} \rightarrow B_{\text{solid}}$
(5) 100% $B_{\text{solid}}$

Note: As in systems with eutectic, during fractional crystallization, the final solid do not have the same composition than the initial liquid.

Between TL and TS, all the mnis composition along the solidus will be formed and separated from the liquid.
Ternary diagrams

NEXT TIME
Ternary diagrams

TO READ:
Chapters 3 Ehlers (smartsite)

FIGURE PRESENTATION