

#### Sarah Lambart - 2016

## LECTURES 6-9: TWO-COMPONENT SYSTEMS

#### Recap Lecture 5

Gibbs-Duhem equation: dG = -SdT + VdP

• Clapeyron equation:  $dP/dT = \Delta S_R / \Delta V_R$ 

• Gibbs phase rule:  $f = c + 2 - \Phi$ 



## Composition as a variable

- Constant X: one component diagram
- Constant T: isothermal diagram
- Constant P: isobaric diagram  $f = c + 1 - \Phi$ : "reduced" phase rule

## Binary systems: $f = 2 + 1 - \Phi$

- **Φmax = 3**
- 2 different cases: System with eutectic

System with solid solution

## Binary systems: $f = 2 + 1 - \Phi$

- **Φmax = 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-ofthe-early-earth/

Construction of a binary phase diagram

#### CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub> - SiO<sub>2</sub>

T (°C)	% SiO2	Product
1360	0	An
1540	0	An
1560	0	GI.
1350	20	An + Qz
1400	20	An+Gl
1520	20	GI
1350	60	An+Qz
1400	60	Qz+Gl
1700	100	Qz
1720	100	GI

![](_page_7_Figure_3.jpeg)

#### Syst. With Eutectic

# Syst. With Solid solution

![](_page_8_Figure_2.jpeg)

![](_page_8_Figure_3.jpeg)

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

Lever rule: phase proportions

![](_page_10_Figure_1.jpeg)

В

А

![](_page_11_Figure_1.jpeg)

Equilibrium crystallization of composition X (*T decreases*)

- (1) 100% Liquid with composition X = 20%B
- (2) Liquidus: first crystal of A appears
- (3) T1: Mnl A + 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:

 $Liq \rightarrow 39\% \text{ A} + 61\% \text{ B}$ 

- 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%

![](_page_12_Figure_1.jpeg)

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

- (1) 100% solid: mix of A and B A%=f/(e+f) = (100-80)/100=20%
- (2) Eutectic point: first melt appears
- Melting of the solid in the eutectic proportions: 61% B + 39% A  $\rightarrow$  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) T1: 100% MnI B (4) Liquidus:  $B_{solid} \rightarrow B_{liquid}$ 

Note: unlike during the equilibrium melting, the last melt to be formed doesn't have the same composition than the initial solid.

![](_page_13_Figure_1.jpeg)

![](_page_14_Figure_1.jpeg)

(3) T1: Mnl AB + Liquid

- Liquid composition: 43.5% B
- Liquid proportion: b/(a+b) = (62-51)/(62-43.5) = 59.4%
- (4) Liquidus: the last crystal of AB melts
- (5) 100% liquid Liquid composition: Z = 51% B

Equilibrium melting of composition Z (T increases) (1) 100% solid: mix of A and AB A% = (62-51)/62 = 17.7%(2) Eutectic point: first melt appears - Melting of the solid in the eutectic proportions: ((62-37.5)/62=) 39.5% A + 60.5% AB  $\rightarrow$  Liq - Liquid composition: 37.5% B - Phase proportions when it leaves  $T_S$ :

- % A = 0%

- % B = 55%

![](_page_15_Figure_1.jpeg)

Equilibrium melting of composition W (*T* increases) (1) 100% mnl AB (2)  $T_1$ : 100% mnl AB (3)  $T_{AB}$ : Congruent melting: AB<sub>solid</sub>  $\rightarrow$  AB<sub>liquid</sub> (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

![](_page_16_Figure_1.jpeg)

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

(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<sub>S2</sub>: 0%AB (all crystal separated),
  100% Liq, 0%B
- Liquid crystallizes to form AB and B in eutectic proportions:
- Liq → ((100-76)/(100-62)=) 63% AB + 37% B
- Last solid to be formed: mix of 63% AB 37%B
- (5) 100% solid: 63% AB + 37% B solid composition: 76%

![](_page_17_Figure_1.jpeg)

## Equilibrium crystallization of composition U (T decreases)

![](_page_18_Figure_2.jpeg)

- (1) 100% Liquid with composition X = 21%B
- (2) Liquidus: first crystal of A appears
- (3) T1: Mnl A + liquid
- Liquid composition: 43%B
- Liquid proportion: a/(a+b)=21/43=48.8%
- MnI A proportion: 51.2%

#### (4) Peritectic point:

- Phase proportion when it <u>reaches</u>  $T_P$ :
  - % 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  $\rightarrow$  AB - Liquid proportion when it leaves T<sub>P</sub>: 0% (5) Solid state: mix between crystals of A and AB: % A: d/(c+d)=(31-21)/31=32%

Fractional crystallization of composition U (T decreases and minerals

![](_page_19_Figure_2.jpeg)

(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 <u>reaches</u> T<sub>P</sub>: 100% Liq (compo 45% B): no crystals A to react with.

- Phases when it leaves T<sub>P</sub>: 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:

Liq → ((100-62)/(100-31)=) 55% AB + 45% B

- Last solid to be formed: mix of 55% AB – 45% B

(7) 100% solid: 55% AB + 45% B – solid composition: 62% B

## Equilibrium crystallization of composition S (*T decreases*)

![](_page_20_Figure_2.jpeg)

- (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 <u>reaches</u> T<sub>P</sub>: 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  $\rightarrow$  AB

- Phases when it leaves  $T_{P}$ : Lig + AB

% Liq: c'/(c'+d) = (41-31)/(45-31) = 71.4%

- (5) AB + liquid
- % Liq: e/(f+e) = (41-31)/(59-31) = 35.7%
- Liq comp: 59%B
- (6) Eutectic point:
- Phases when it <u>reaches</u> T<sub>E</sub>: 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:

 $Liq \rightarrow ((100-62)/(100-31)=)55\% AB + 45\% B$ 

- (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

![](_page_21_Figure_1.jpeg)

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*)

![](_page_22_Figure_2.jpeg)

(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: d/(c+d) = (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<sub>2</sub>: ABss +Liq - Compo AB: 5%B - Compo lig: 61%B -% liq: a/(a+b) = (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

![](_page_23_Figure_1.jpeg)

(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)  $B_{liquid} \rightarrow B_{solid}$ (5) 100%  $B_{solid}$ 

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 mnls composition along the solidus will be formed and separated from the liquid

![](_page_24_Picture_0.jpeg)

#### **TO READ:** Chapters 3 Ehlers (smartsite)

### **FIGURE PRESENTATION**