

From thermodynamics to geodynamics: An overview of the geophysical thermodynamics of phase relations – Melting

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Derivatives of the Gibbs Free Energy: $G(P, T, \{N_i\})$

entropy

$$(\partial G / \partial T)_{P, \{N_j\}} = -S$$

volume

$$(\partial G / \partial P)_{T, \{N_j\}} = V$$

enthalpy

$$\Delta G = \Delta H - T \Delta S$$

chemical potential

$$(\partial G / \partial N_i)_{P, T, (N_{j \neq i})} = \mu_i$$

Gibbs Potential: $G \equiv U - TS + PV = H - TS = G(T, P, \{N_i\})$

$$dG \equiv \left(\frac{\partial G}{\partial T} \right)_{P, \{N_i\}} dT + \left(\frac{\partial G}{\partial P} \right)_{T, \{N_i\}} dP + \sum_i \left(\frac{\partial G}{\partial N_i} \right)_{T, P, \{N_{j \neq i}\}} dN_i = -SdT + VdP + \sum_i \mu_i dN_i$$

$$G = \sum_i \mu_i N_i, \quad 0 = SdT - VdP + \sum_i N_i d\mu_i$$

$$S = S(T, P, \{N_i\}), \quad V = V(T, P, \{N_i\}), \quad \mu_i = \mu_i(T, P, \{N_i\})$$

Equilibrium minimizes G at constant P and T .

For each potential: line 1 gives name, definition (if applicable), and fundamental equation; line 2 gives total differential; line 3 gives Euler equation and Gibbs-Duhem relation; line 4 gives three equations of state associated with fundamental equation; line 5 gives equilibrium extremum principle.

$2 + R(N - 1)$ Unknowns:

$$\left\{ \begin{array}{c} P, T \\ X_1^{\phi_1}, X_2^{\phi_1}, \dots, X_{N-1}^{\phi_1} \\ X_1^{\phi_2}, X_2^{\phi_2}, \dots, X_{N-1}^{\phi_2} \\ \dots \\ X_1^{\phi_R}, X_2^{\phi_R}, \dots, X_{N-1}^{\phi_R} . \end{array} \right.$$

*derivation of the
phase rule*

$(R - 1)N$ Equations:

$$\left\{ \begin{array}{c} \mu_1^{\phi_1} = \mu_1^{\phi_2} = \dots = \mu_1^{\phi_R} \\ \mu_2^{\phi_1} = \mu_2^{\phi_2} = \dots = \mu_2^{\phi_R} \\ \dots \\ \mu_N^{\phi_1} = \mu_N^{\phi_2} = \dots = \mu_N^{\phi_R} . \end{array} \right.$$

Degrees of Freedom:

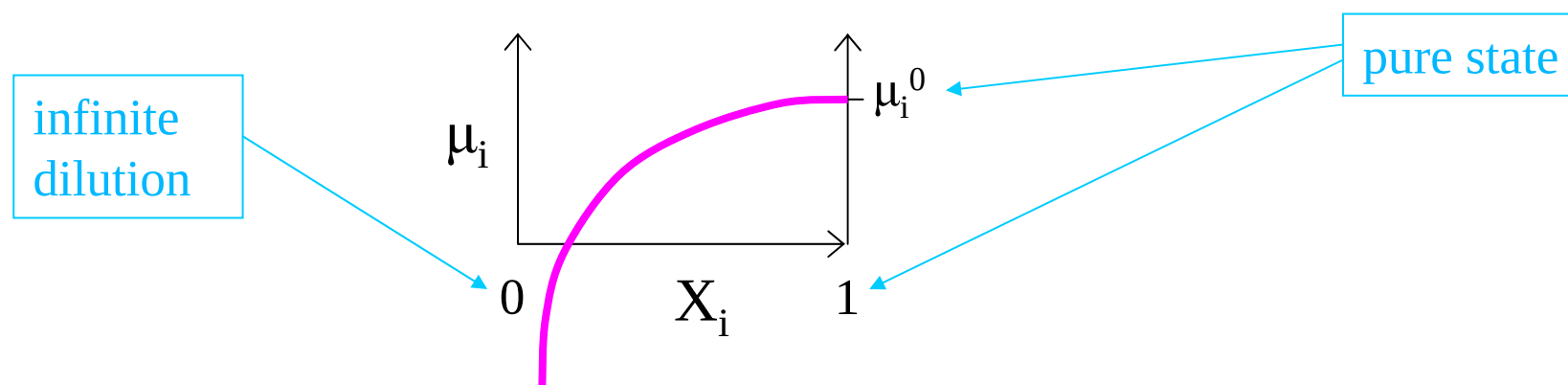
$$F = [2 + R(N - 1)] - [(R - 1)N] = N + 2 - R .$$

$$F = N + 2 - R$$

Compositional (Concentration) Dependence of $\mu_i(P,T,X)$

$$\mu_i = \mu_i^0 + nRT \ln a_i$$

$$a_i \leq 1 \rightarrow RT \ln a_i \leq 0$$



Dilute solutions have lower chemical potentials (lower free energies) than pure end-members.

Complex solutions have expanded stability fields.

$$(\partial\mu_i^0/\partial T)_P \sim -S_i^0$$

$$(\partial\mu_i/\partial T)_P \sim -S_i^0 + nR \ln a_i$$

entropy of mixing

SOLVING FOR PHASE COEXISTENCE

Two Components ($Fo = \text{Mg}_2\text{SiO}_4$ and $Fa = \text{Fe}_2\text{SiO}_4$):

Two Phases (α and γ): $R = 2 \rightarrow F = 2$ (divariant):

$$\begin{aligned} 0 &= \Delta\mu_{Fo}^{\alpha \rightarrow \gamma}(P, T, X_{Fo}^{\alpha}, X_{Fo}^{\gamma}) \\ &= \mu_{Fo}^{\gamma}(P, T, X_{Fo}^{\gamma}) - \mu_{Fo}^{\alpha}(P, T, X_{Fo}^{\alpha}) \\ 0 &= \Delta\mu_{Fa}^{\alpha \rightarrow \gamma}(P, T, X_{Fa}^{\alpha}, X_{Fa}^{\gamma}) \\ &= \mu_{Fa}^{\gamma}(P, T, X_{Fa}^{\gamma}) - \mu_{Fa}^{\alpha}(P, T, X_{Fa}^{\alpha}) \end{aligned}$$

For the simplest case, of single-site ideal solution:

$$\begin{aligned} \Delta\mu_{Fo}^{\alpha \rightarrow \gamma}(P, T, X_{Fo}^{\alpha}, X_{Fo}^{\gamma}) &=^{\circ} \Delta\mu_{Fo}^{\alpha \rightarrow \gamma}(P, T) + RT \ln \frac{X_{Fo}^{\gamma}}{X_{Fo}^{\alpha}} \\ ^{\circ} \Delta\mu_{Fo}^{\alpha \rightarrow \gamma}(P, T) &\equiv \Delta h_{Fo}^{\alpha \rightarrow \gamma}(P_0, T) - T \Delta s_{Fo}^{\alpha \rightarrow \gamma}(P_0, T) \\ &\quad + \int_{P_0}^P \Delta v_{Fo}^{\alpha \rightarrow \gamma}(\hat{P}, T) d\hat{P} \end{aligned}$$

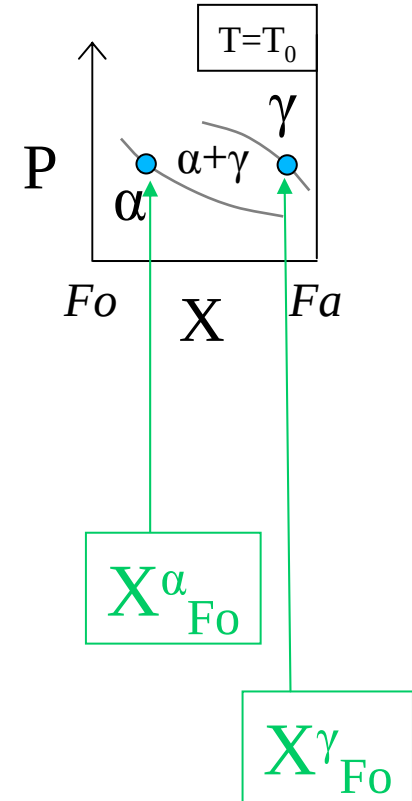
We can find the compositions of the coexisting phases:

$$\begin{aligned} X_{Fo}^{\alpha}(P, T) &= \frac{1 - e^{\frac{-^{\circ} \Delta\mu_{Fa}^{\alpha \rightarrow \gamma}(P, T)}{RT}}}{e^{\frac{-^{\circ} \Delta\mu_{Fo}^{\alpha \rightarrow \gamma}(P, T)}{RT}} - e^{\frac{-^{\circ} \Delta\mu_{Fa}^{\alpha \rightarrow \gamma}(P, T)}{RT}}} \\ X_{Fo}^{\gamma}(P, T) &= e^{\frac{-^{\circ} \Delta\mu_{Fo}^{\alpha \rightarrow \gamma}(P, T)}{RT}} \left(\frac{1 - e^{\frac{-^{\circ} \Delta\mu_{Fa}^{\alpha \rightarrow \gamma}(P, T)}{RT}}}{e^{\frac{-^{\circ} \Delta\mu_{Fo}^{\alpha \rightarrow \gamma}(P, T)}{RT}} - e^{\frac{-^{\circ} \Delta\mu_{Fa}^{\alpha \rightarrow \gamma}(P, T)}{RT}}} \right) \end{aligned}$$

[Note that $X_{Fo}^{\alpha}(z)$ and $X_{Fo}^{\gamma}(z)$ are non-linear].



$N=2, R=2: F=2$
 $(N=2, R=2: F'=1)$



Compositions of Coexisting Phases

Consider, for example, a simple binary (*i.e.*, two-component) system A - B in which two phases α and β may coexist. At equilibrium with respect to mass transfer between the phases, the chemical potential of component A must be the same in both phases, and the chemical potential of component B must be the same in both phases, as stipulated in equations (3.8). Hence, we have:

$$\begin{aligned}\mu_A^\alpha(P, T, X_B^\alpha) &= \mu_A^\beta(P, T, X_B^\beta) \\ \mu_B^\alpha(P, T, X_B^\alpha) &= \mu_B^\beta(P, T, X_B^\beta),\end{aligned}\quad \boxed{N=2, R=2: F=2} \quad (4.4)$$

where we have indicated the functional dependence of the chemical potentials upon pressure, temperature, and phase composition. The Gibbs phase rule (4.3) indicates that this system possesses two degrees of freedom. Thus, we may freely vary any two of the unknowns (*e.g.*, P and T), and the remaining variables (*e.g.*, X_B^α and X_B^β) will be fully determined by the constraining equations. Hence, at any fixed pressure and temperature we have two equations (4.4) in two unknowns, X_B^α and X_B^β , so that we may solve for the equilibrium compositions of the two phases.

Relative Proportions of Coexisting Phases

The relative proportions of the α and β phases in the equilibrium phase assemblage can be determined by applying the mass-balance conditions known as the “lever rule” [*cf.* Callen, 1960, pp. 154-156]:

$$X_\alpha^{equil} = \frac{X_B^{bulk} - X_B^\beta}{X_B^\alpha - X_B^\beta}, \quad \boxed{\text{lever rule}} \quad (4.5)$$

where X_B^{bulk} is the mole fraction of component B in the bulk composition of the system, and X_α^{equil} is the mole fraction of phase α in the system at equilibrium.

THE LEVER RULE

Two Components ($Fo = \text{Mg}_2\text{SiO}_4$ and $Fa = \text{Fe}_2\text{SiO}_4$):

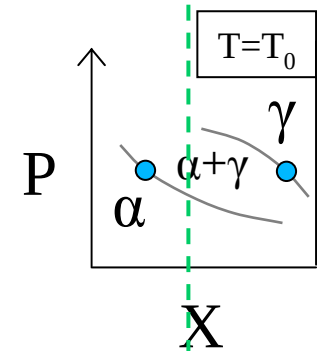
Two Phases (α and γ):

$$\mu_{Fo}^{\alpha}(P, T, X_{Fo}^{\alpha}) = \mu_{Fo}^{\gamma}(P, T, X_{Fo}^{\gamma})$$

$$\mu_{Fa}^{\alpha}(P, T, X_{Fa}^{\alpha}) = \mu_{Fa}^{\gamma}(P, T, X_{Fa}^{\gamma})$$

$R = 2 \rightarrow F = 2$ (divariant)

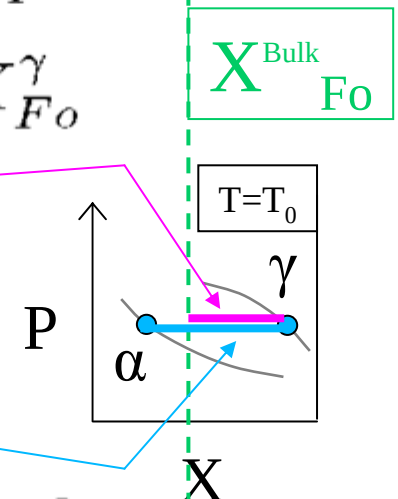
$N=2, R=2: F=2$
 $(N=2, R=2: F'=1)$



We can find the total fraction of Fo in the bulk composition:

$$X_{Fo}^{BULK} = X_{\alpha} X_{Fo}^{\alpha} + X_{\gamma} X_{Fo}^{\gamma} = X_{\alpha} X_{Fo}^{\alpha} + (1 - X_{\alpha}) X_{Fo}^{\gamma}$$

$$\rightarrow X_{\alpha} = \frac{X_{Fo}^{BULK} - X_{Fo}^{\gamma}}{X_{Fo}^{\alpha} - X_{Fo}^{\gamma}}$$



➔ [Note that both $X_{Fo}^{\alpha}(z)$ and $X_{\alpha}(z)$ are non-linear].

THE CLAPEYRON SLOPE

$$dG^\phi = -S^\phi dT + V^\phi dP + \sum_i \mu_i^\phi dN_i^\phi$$

Free energy, entropy, and volume vary with composition:

$$\begin{aligned} \left(\frac{\partial G^\phi}{\partial N_i^\phi} \right)_{P,T,N_{j \neq i}} &= \mu_i^\phi \\ \left(\frac{\partial S^\phi}{\partial N_i^\phi} \right)_{P,T,N_{j \neq i}} &= s_i^\phi = - \left(\frac{\partial \mu_i^\phi}{\partial T} \right)_{P,N_j} \\ \left(\frac{\partial V^\phi}{\partial N_i^\phi} \right)_{P,T,N_{j \neq i}} &= v_i^\phi = \left(\frac{\partial \mu_i^\phi}{\partial P} \right)_{T,N_j} \end{aligned}$$

One Component ($For = Mg_2SiO_4$): $N = 1$

Two Phases (α and β): $R = 2$

$$\mu_{For}^\alpha(P, T) = \mu_{For}^\beta(P, T)$$

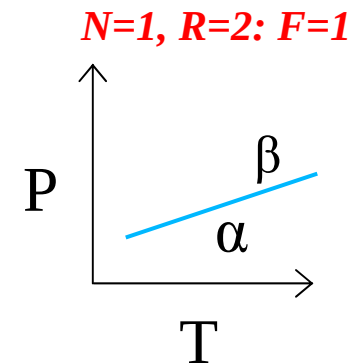
$$\rightarrow \Delta \mu_{For}^{\alpha \rightarrow \beta}(P, T) = \mu_{For}^\beta(P, T) - \mu_{For}^\alpha(P, T) = 0$$

$$d\Delta \mu_{For}^{\alpha \rightarrow \beta} = \left(\frac{\partial \Delta \mu_{For}^{\alpha \rightarrow \beta}}{\partial T} \right)_P dT + \left(\frac{\partial \Delta \mu_{For}^{\alpha \rightarrow \beta}}{\partial P} \right)_T dP$$

$$= -\Delta s_{For}^{\alpha \rightarrow \beta} dT + \Delta v_{For}^{\alpha \rightarrow \beta} dP = 0$$

$$\rightarrow \frac{dP}{dT} = \frac{\Delta s_{For}^{\alpha \rightarrow \beta}(P, T)}{\Delta v_{For}^{\alpha \rightarrow \beta}(P, T)}$$

[Note that $\frac{dP}{dT}$ may vary with P and T .]



$$dP / dT = \Delta S / \Delta V$$

Clapeyron slopes are only defined for $N = 1$ and can be reasonably extended to $N > 1$ only for univariant ($F = 1$) cases.

MELTING

- One-component melting
 - Melting curve **inflections** at phase boundaries
- Two-component (**binary**) melting
 - **Eutectic** systems (no solid solution, **congruently** melting end-members)
 - **Peritectic** systems (no solid solution, congruently melting end-members, **incongruently** melting intermediate compound)
 - Liquid **immiscibility**
 - Complete **solid solution**
 - Phase **exsolution**
 - Relationships to **non-ideality** of mixing
- Three-component (**ternary**) melting
 - Three binary **eutectics**
 - A binary with a **congruently** melting intermediate compound
 - A binary with an **incongruently** melting intermediate compound
 - A binary with complete **solid solution**

One-Component Systems: C, SiO₂

$$\mu_{\text{SiO}_2}^{\text{stish}} = \mu_{\text{SiO}_2}^{\text{coes}} = \mu_{\text{SiO}_2}^{\text{liq}}$$

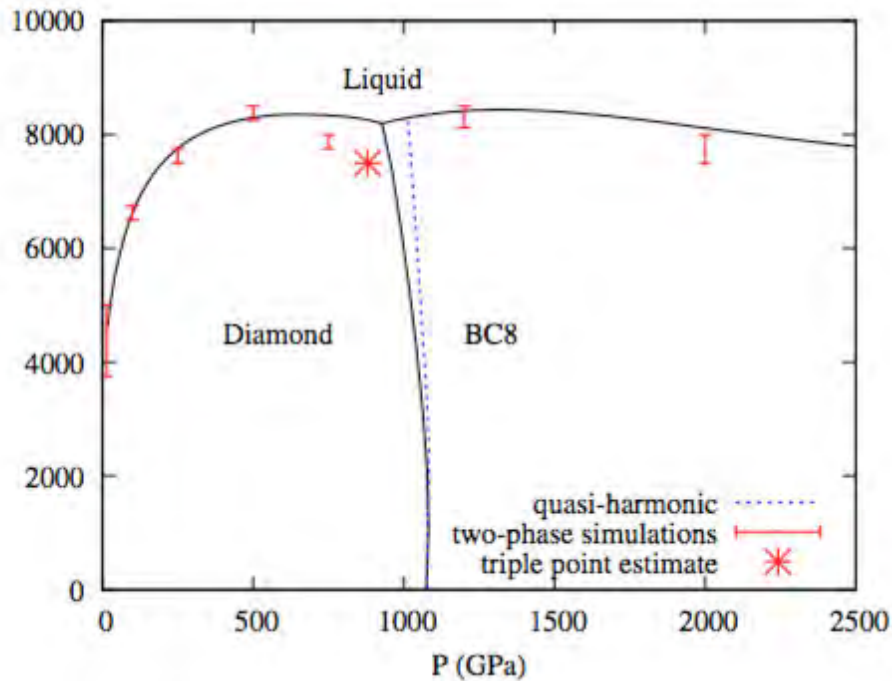
$$F = C+2-P = 1+2-3 = 0$$

$$\mu_{\text{SiO}_2}^{\text{stish}} = \mu_{\text{SiO}_2}^{\text{coes}}$$

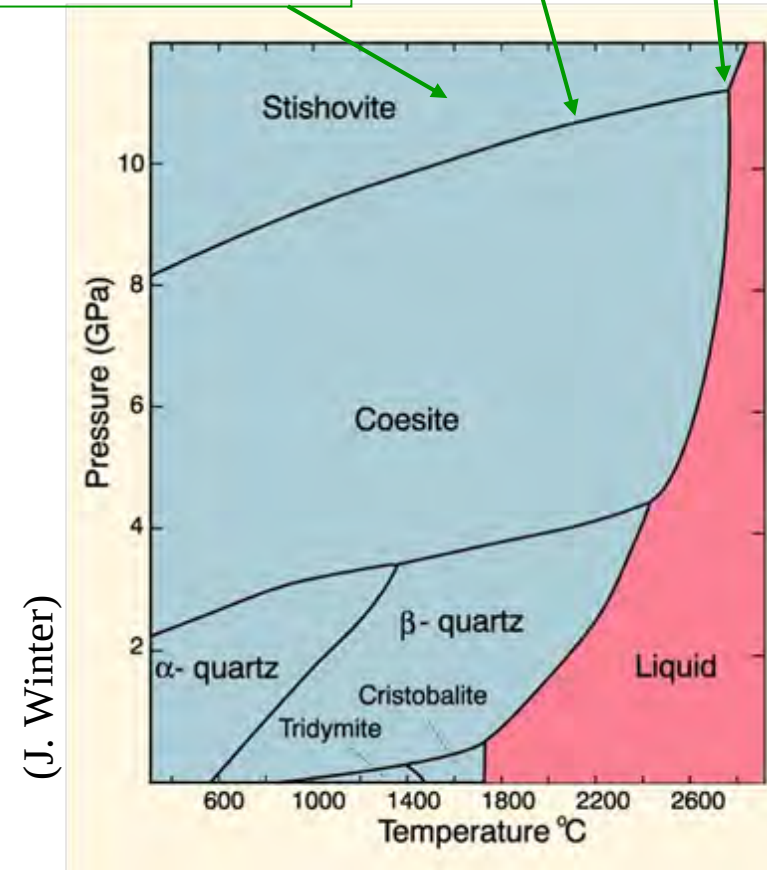
$$F = C+2-P = 1+2-2 = 1$$

$$\mu_{\text{SiO}_2}^{\text{stish}}(P,T)$$

$$F = C+2-P = 1+2-1 = 2$$



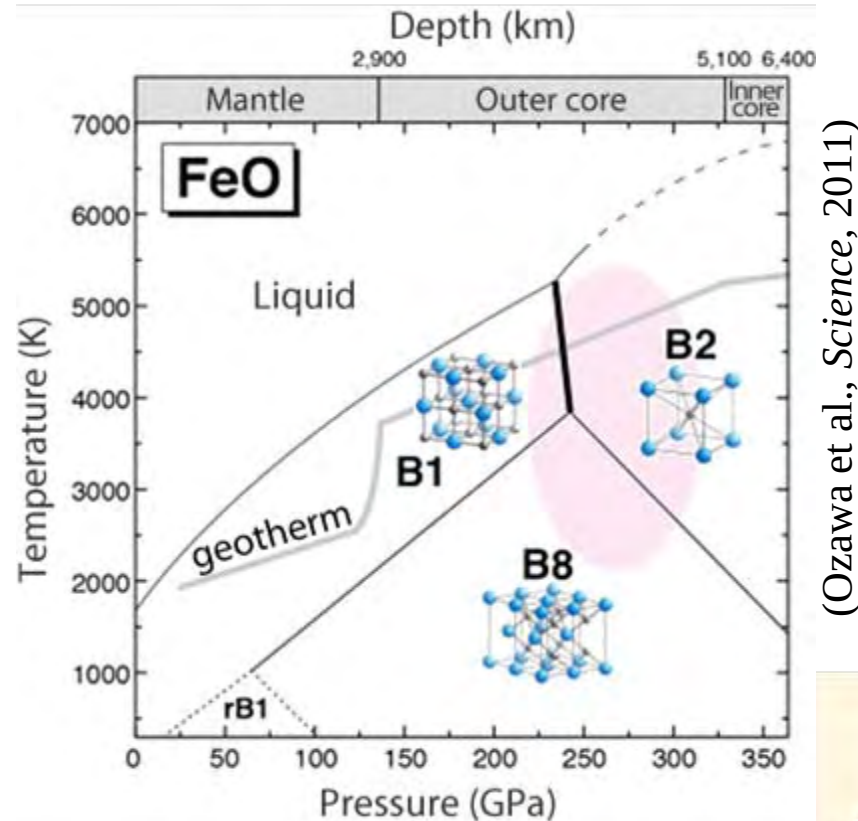
(Correa et al., Phys. Rev. B, 2008)



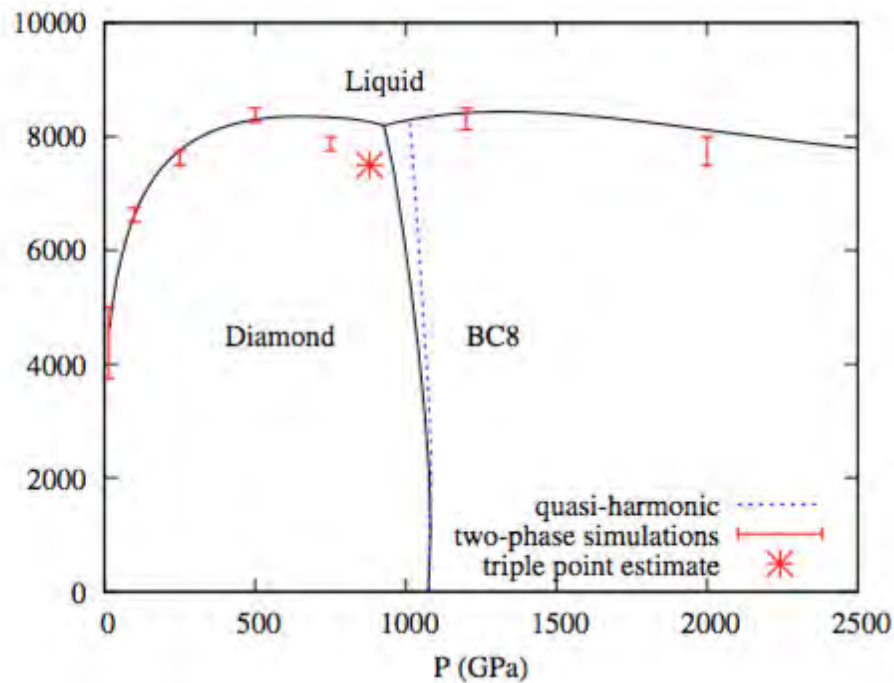
(J. Winter)

(C.Bina, 5/2012)

One-Component Systems: C, SiO₂, FeO

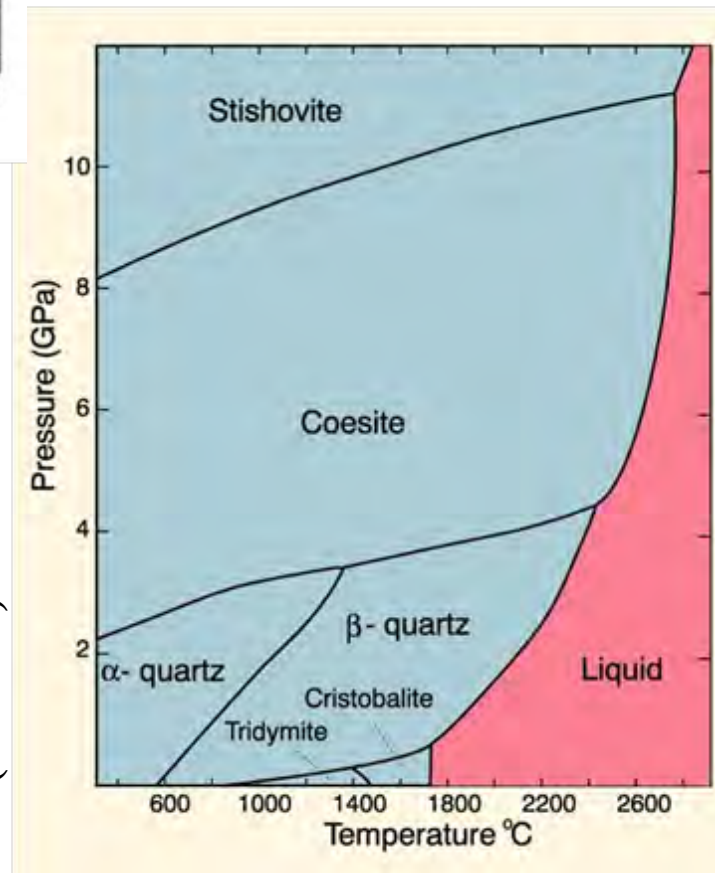


(Ozawa et al., Science, 2011)



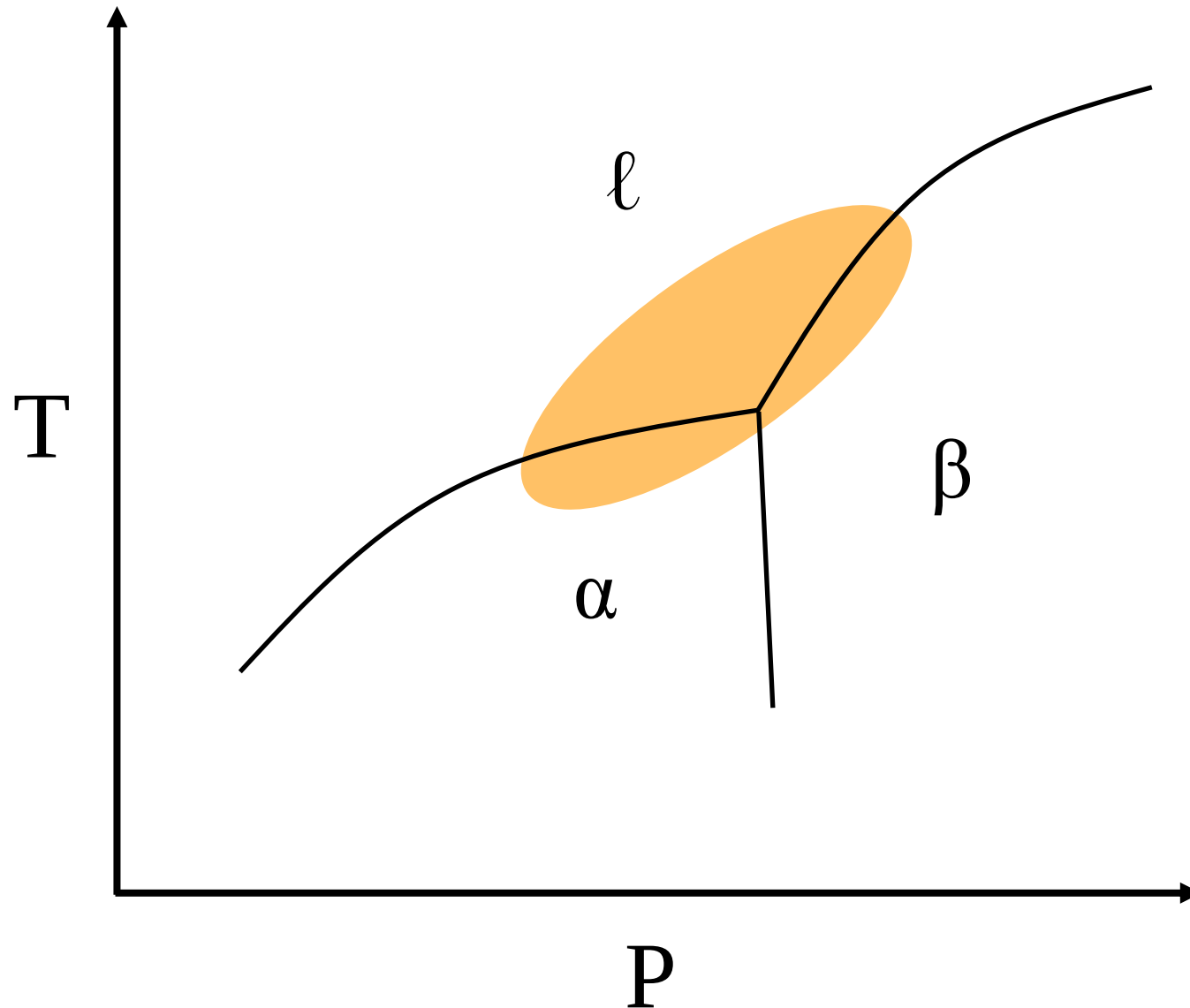
(Correa et al., Phys. Rev. B, 2008)

(J. Winter)



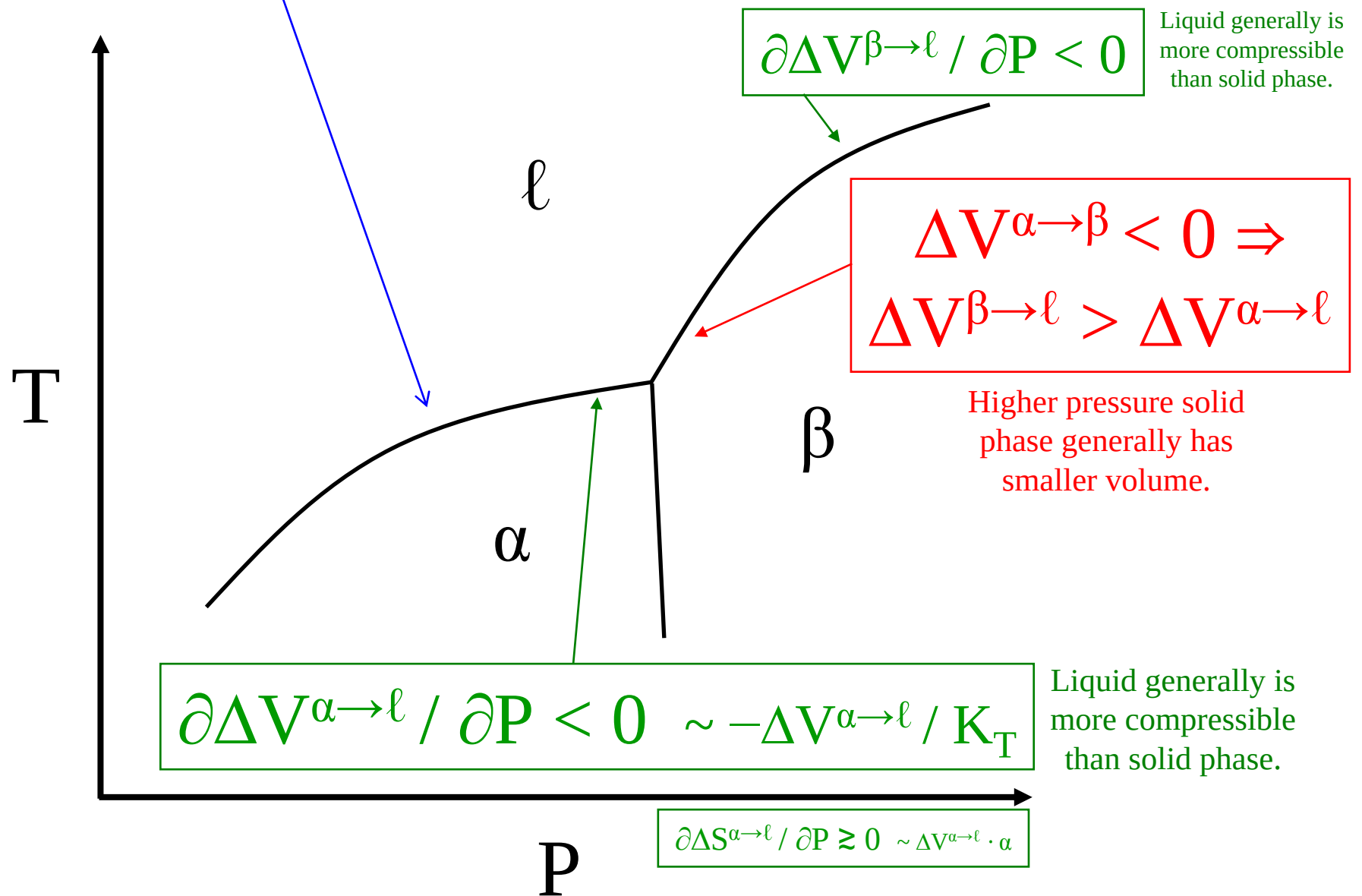
(C.Bina, 5/2012)

What accounts for this distinctive shape of the melting curve where it intersects a phase boundary?



Liquid generally has larger volume and larger entropy than solid phase.

$$dT / dP = \Delta V^{\alpha \rightarrow \ell}(P, T) / \Delta S^{\alpha \rightarrow \ell}(P, T) \sim +/+ > 0$$



Two-Component Systems:

Eutectic Melting

pure end-member:

$$F = 1 + 1 - 1 = 1$$

$$F = 1 + 1 - 2 = 0$$
$$\mu_A^{\text{solid}} = \mu_A^{\text{liquid}}$$

$$F = 1 + 1 - 1 = 1$$

Gibbs Phase Rule:

$$F = C + 2 - P$$

at fixed pressure:

$$F = C + 1 - P$$

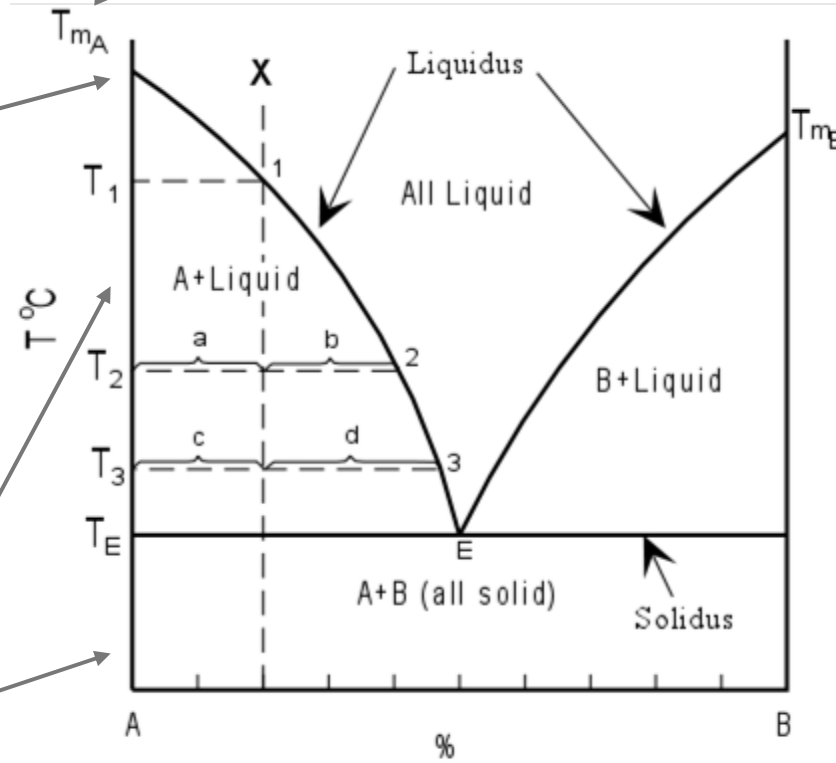


Figure 1

(S. A. Nelson, 2011)

Two-Component Systems:

Eutectic Melting

Gibbs Phase Rule:

$$F = C + 2 - P$$

at fixed pressure:

$$F = C + 1 - P$$

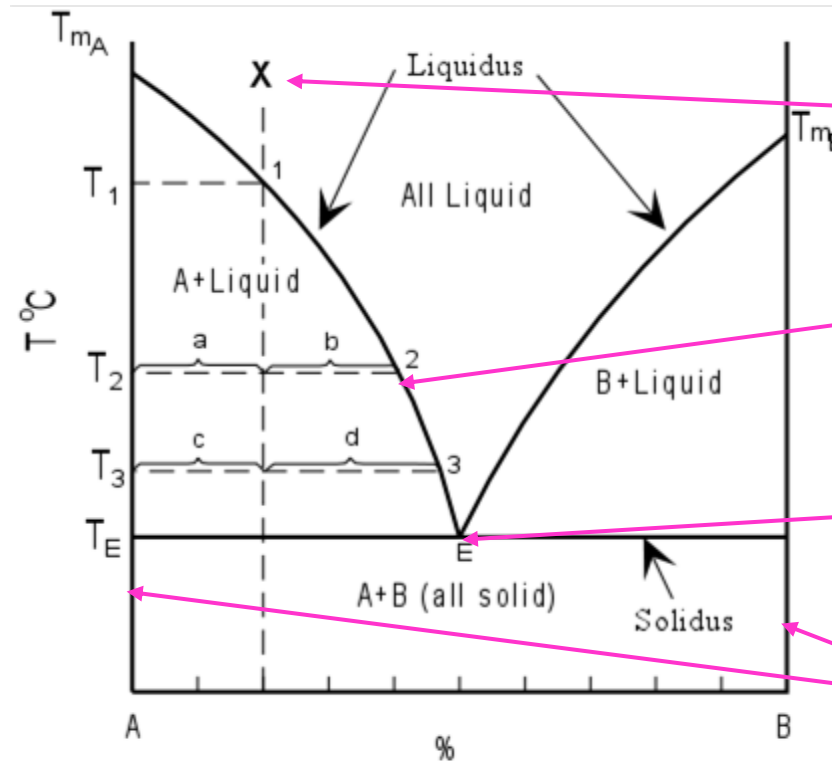


Figure 1

$$F = 2 + 1 - 1 = 2$$

$$F = 2 + 1 - 2 = 1$$
$$\mu_A^{\text{solid}} = \mu_A^{\text{liquid}}$$

$$F = 2 + 1 - 3 = 0$$
$$\mu_A^{\text{solid}} = \mu_A^{\text{liquid}}$$
$$\mu_B^{\text{solid}} = \mu_B^{\text{liquid}}$$

$$F = 1 + 1 - 1 = 1$$

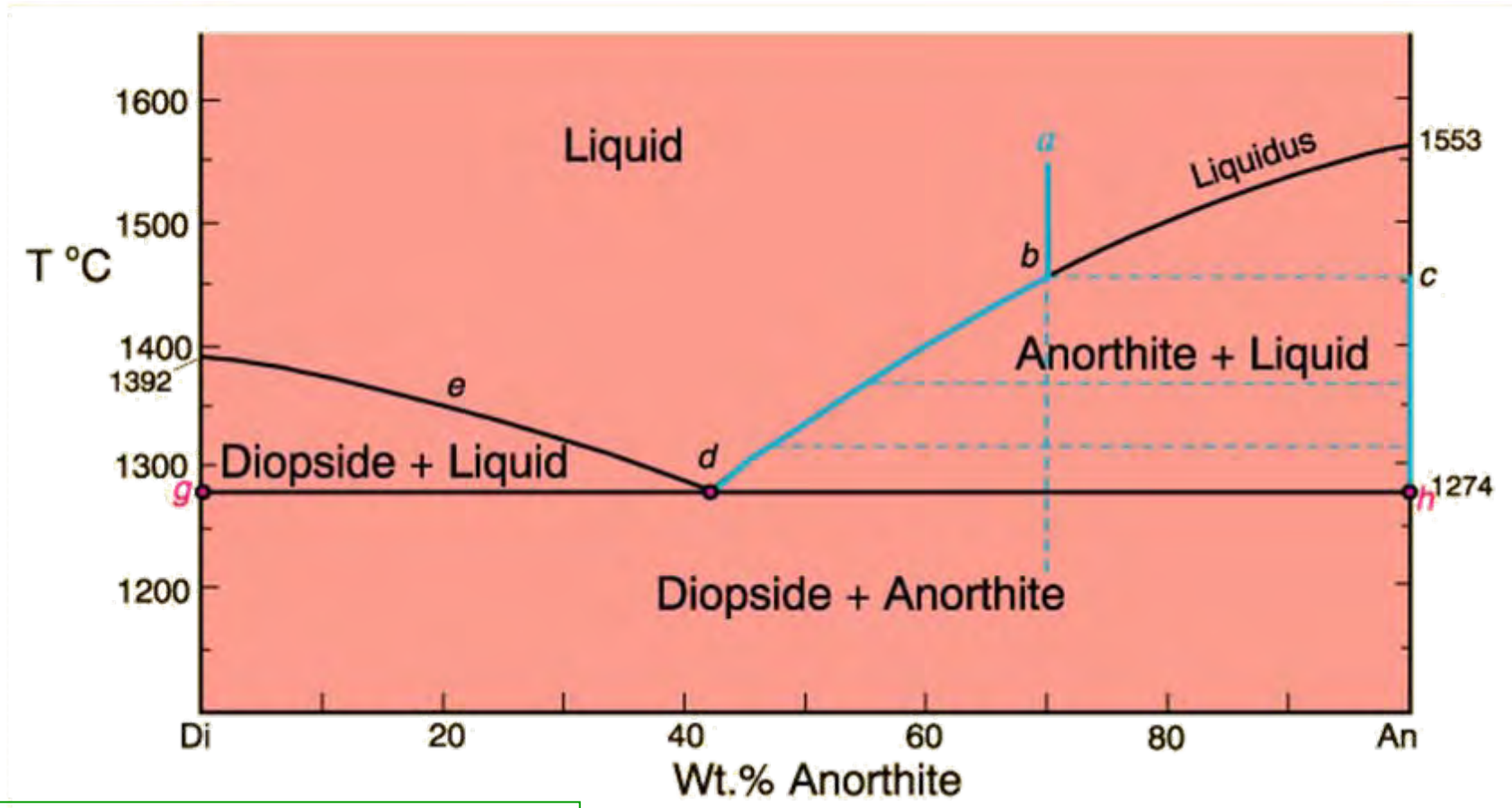
(S. A. Nelson, 2011)

Two-Component Systems:

Eutectic Melting

Diopside ($\text{CaMgSi}_2\text{O}_6$) – Anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$)

No Solid Solution – Congruently Melting End-Members



Note that temperature and composition of first melt **do not** depend upon the initial bulk composition.

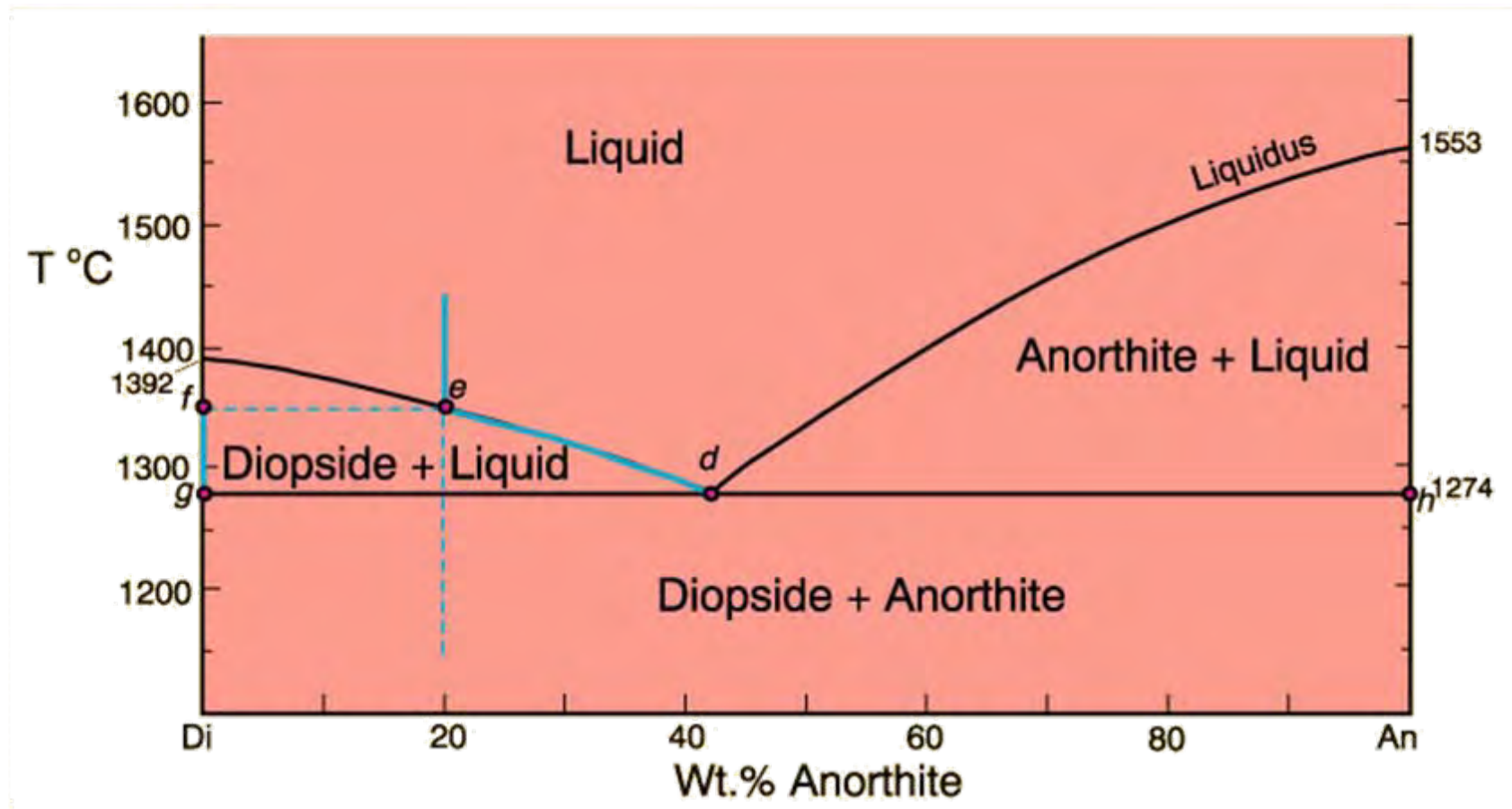
(J. Winter)

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(J. Winter)

Two-Component Systems:

Eutectic Melting

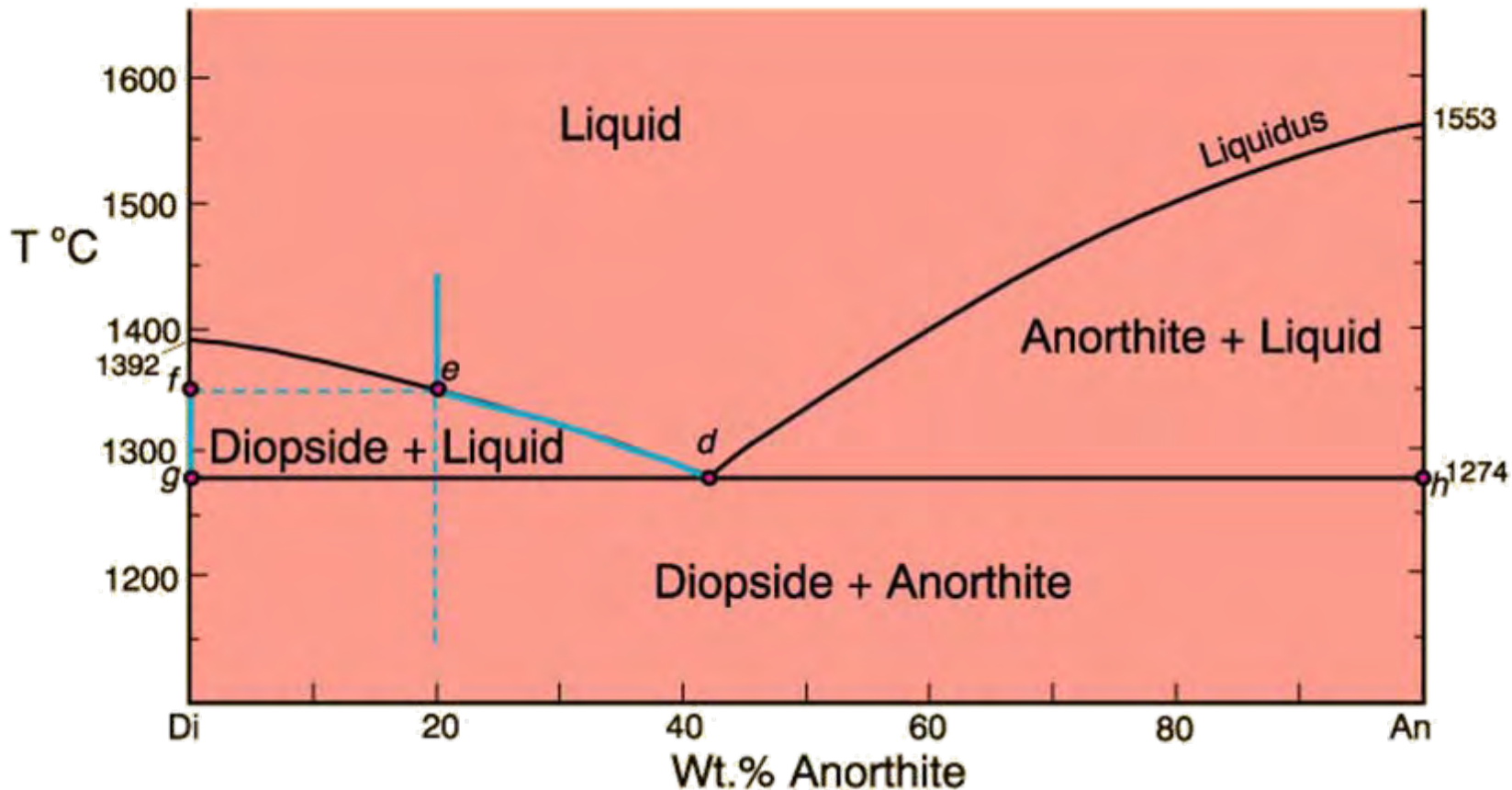
Diopside ($\text{CaMgSi}_2\text{O}_6$) – Anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$)

No Solid Solution – Congruently Melting End-Members

*Note that we are discussing **equilibrium** (“batch”) melting, where liquids remain in contact with solids.*

What happens if the liquid is drained away (“fractional” melting) at point e?

*Then the remaining solid is pure Di at point f:
temperature must rise to 1392 before melting can resume,
and the first melt will be pure Di in composition.*



(J. Winter)

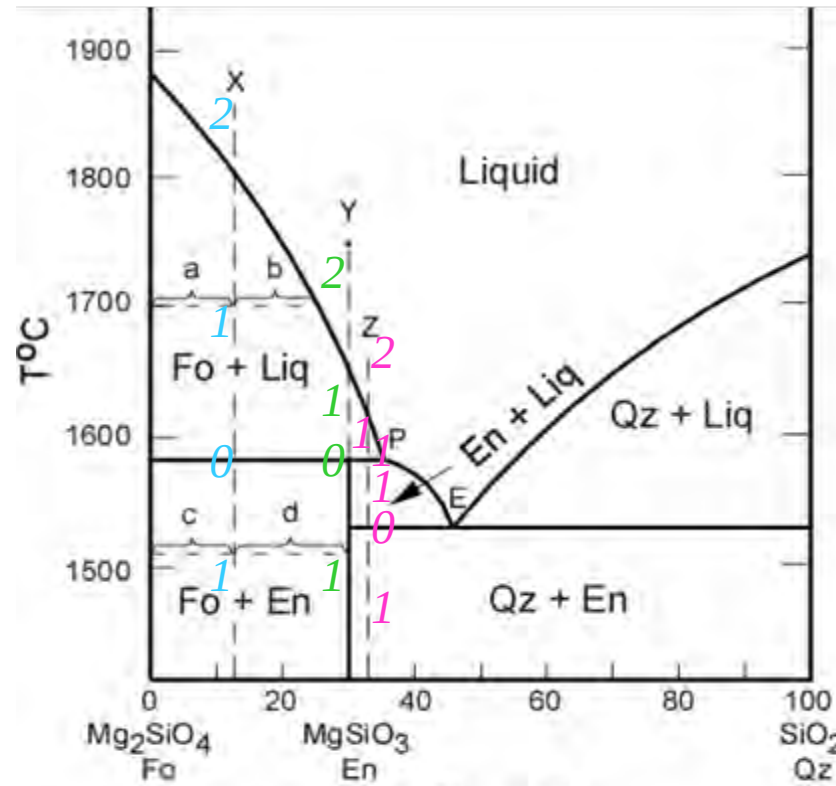
(C.Bina, 5/2012)

Two-Component Systems:

Peritectic Melting

Forsterite (Mg_2SiO_4) – Enstatite (MgSiO_3) – Quartz (SiO_2)

No Solid Solution – Congruently Melting End-Members –
Incongruently Melting Intermediate Compound



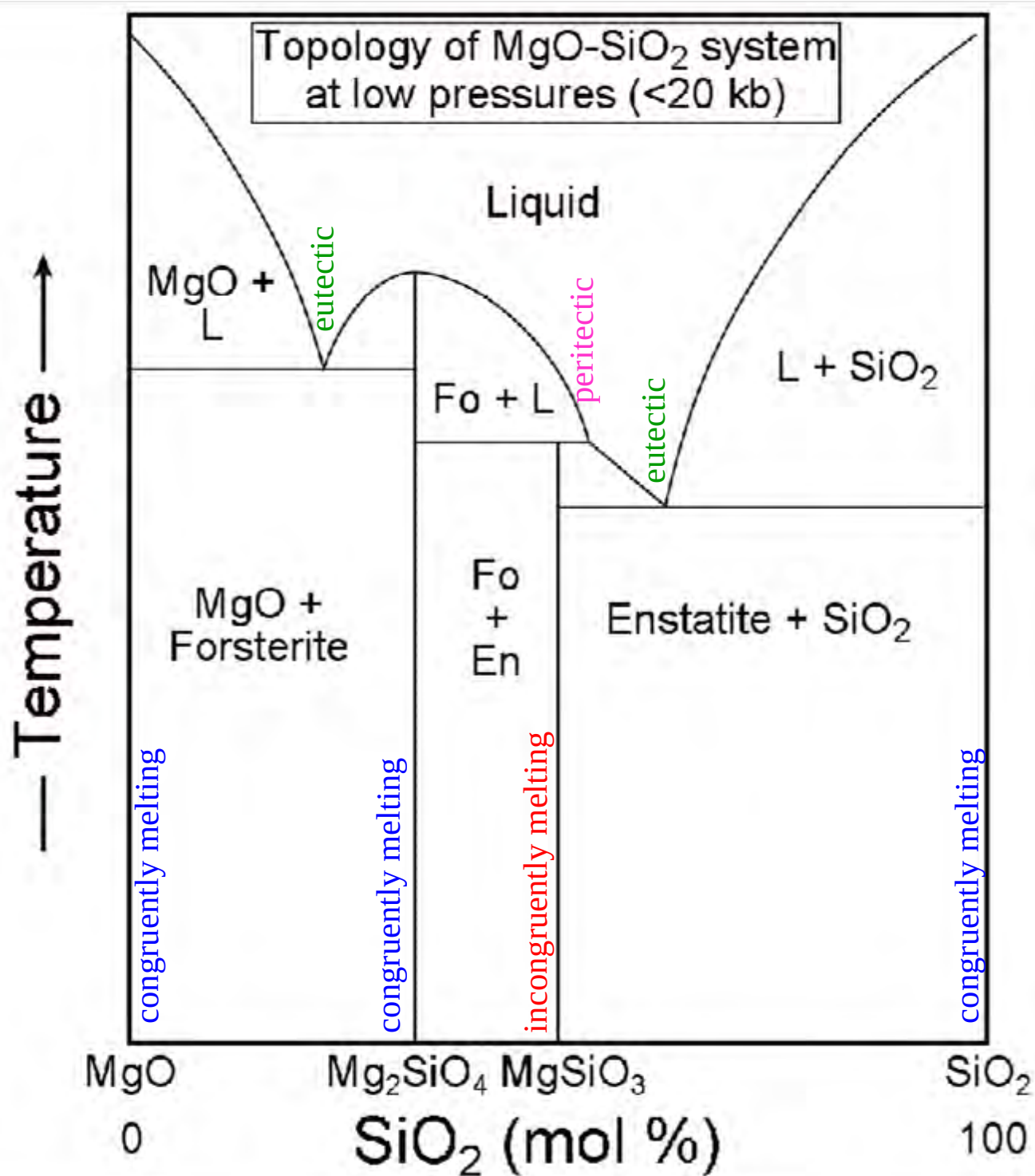
Gibbs Phase Rule:

$$F = C + 2 - P$$

at fixed pressure:

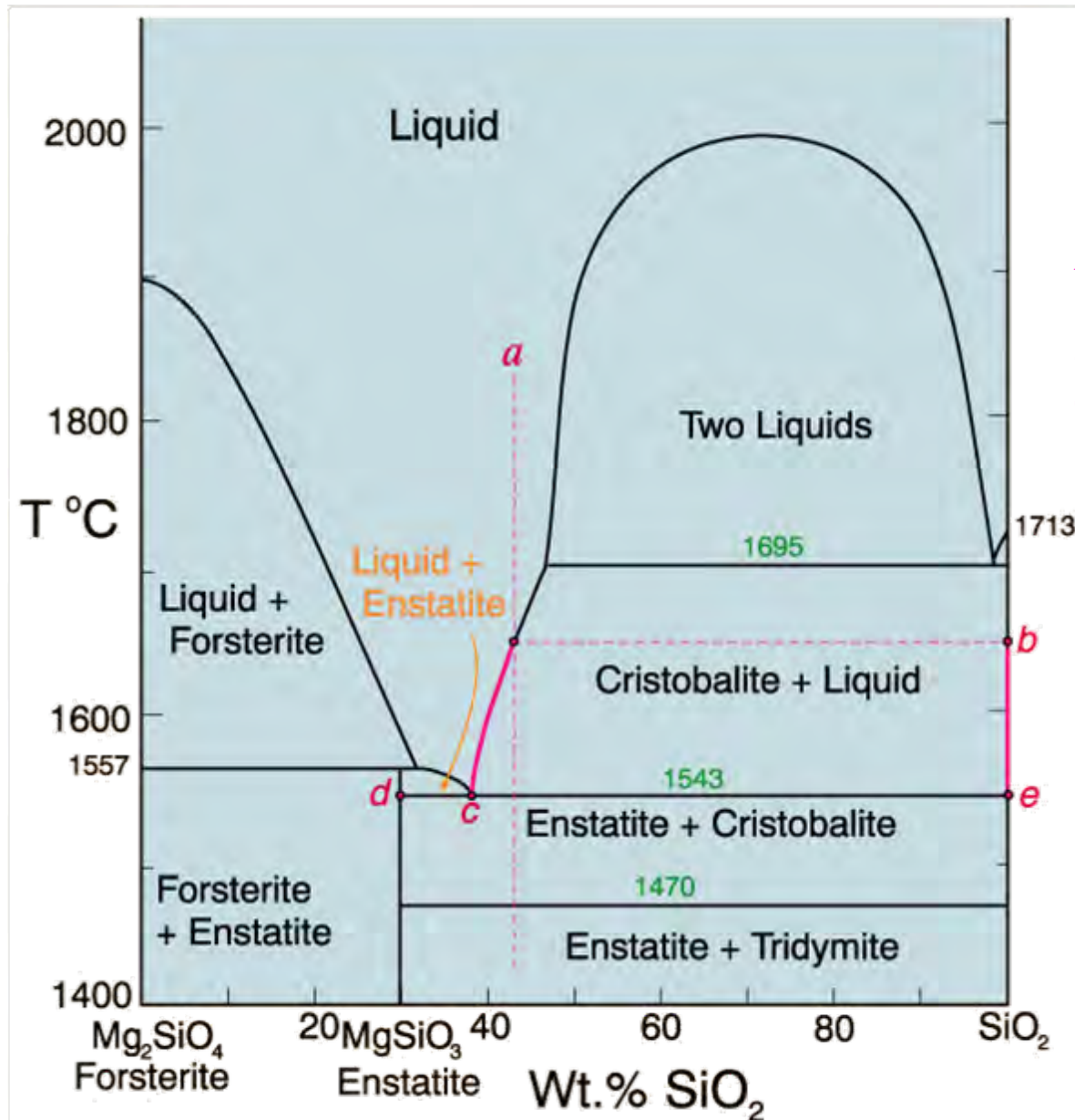
$$F = C + 1 - P$$

(S. A. Nelson, 2011)



(M. D. Barton)

Peritectic

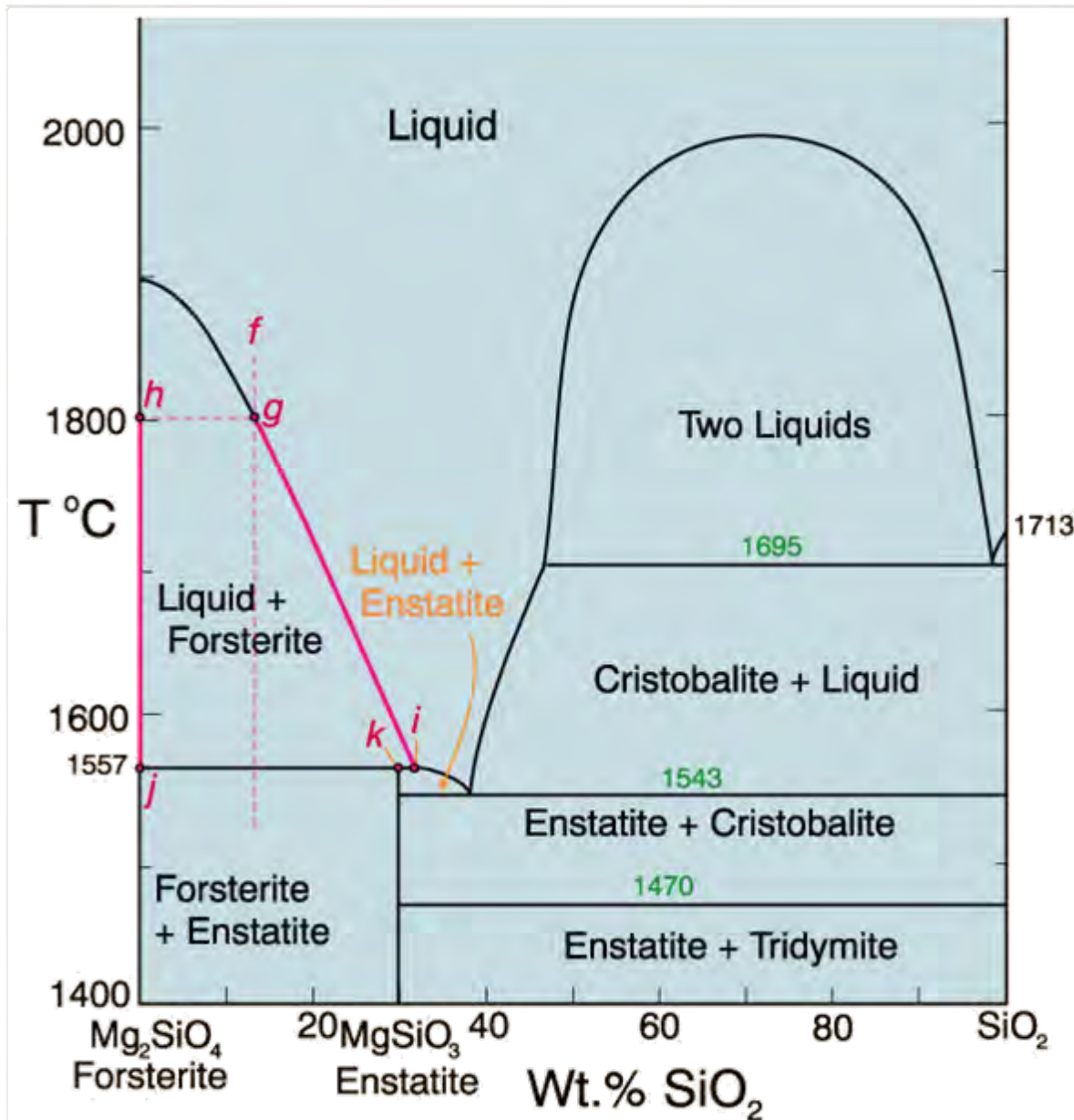


First melt appears at point c.

(Melt composition is between enstatite and silica.)

(J. Winter, after Bowen and Anderson (1914) and Grieg (1927))

Peritectic



First melt appears at point i.

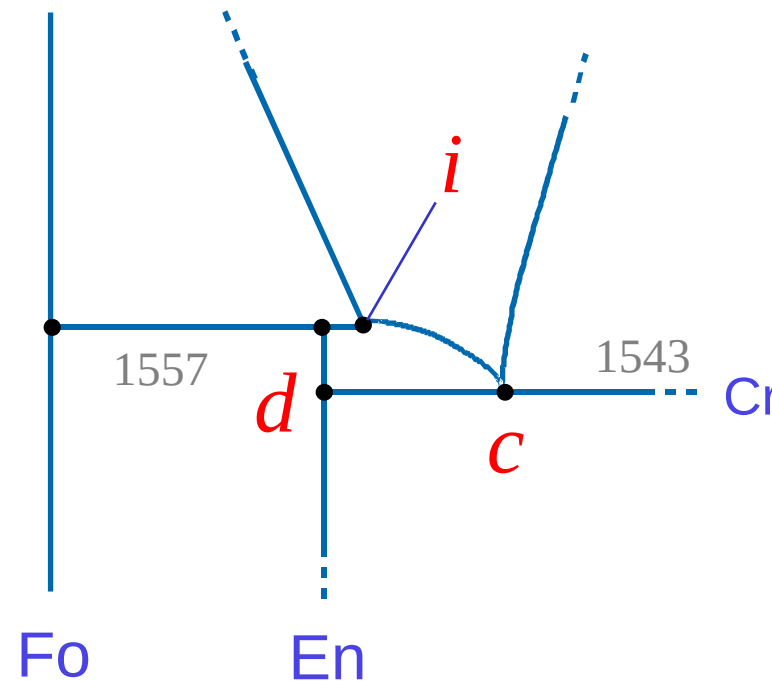
First melt composition is more silica-rich than either forsterite or enstatite!

This happens as enstatite breaks down (melts “incongruently”) to Si-poor forsterite and Si-rich liquid.

(J. Winter, after Bowen and Anderson (1914) and Grieg (1927))

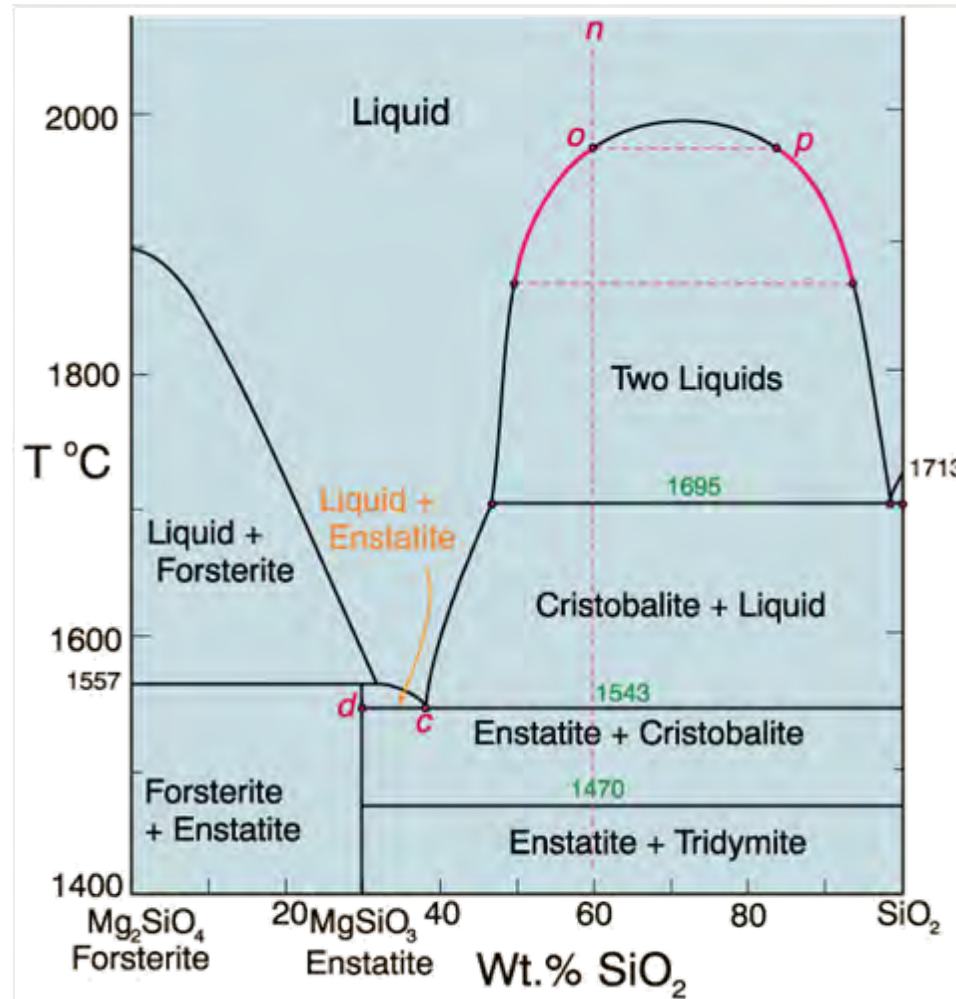
Incongruent Melting of Enstatite

- ➡ Melt of En does not $\rightarrow$ melt of same composition
- ➡ Rather **En $\rightarrow$ Fo + Liq *i*** at the peritectic



(J. Winter)

Immiscible Liquids



Two distinct liquids (one Si-poor and the other Si-rich) coexist. They mutually dissolve to form a single liquid only at higher temperatures.

(At 1695, the liquid will not accept more silica, so a second [Si-rich] liquid begins to form. This addition of another liquid phase removes a degree of freedom, so T remains fixed at 1695 until all silica has melted. As the solid phase is then gone, a degree of freedom is restored, and T can continue rising.)

(J. Winter, after Bowen and Anderson (1914) and Grieg (1927))

Pressure Effects

Different phases have different compressibilities

Thus P will change Gibbs Free Energy differentially

- Raises melting point
- Shift eutectic position (and thus X of first melt, etc.)

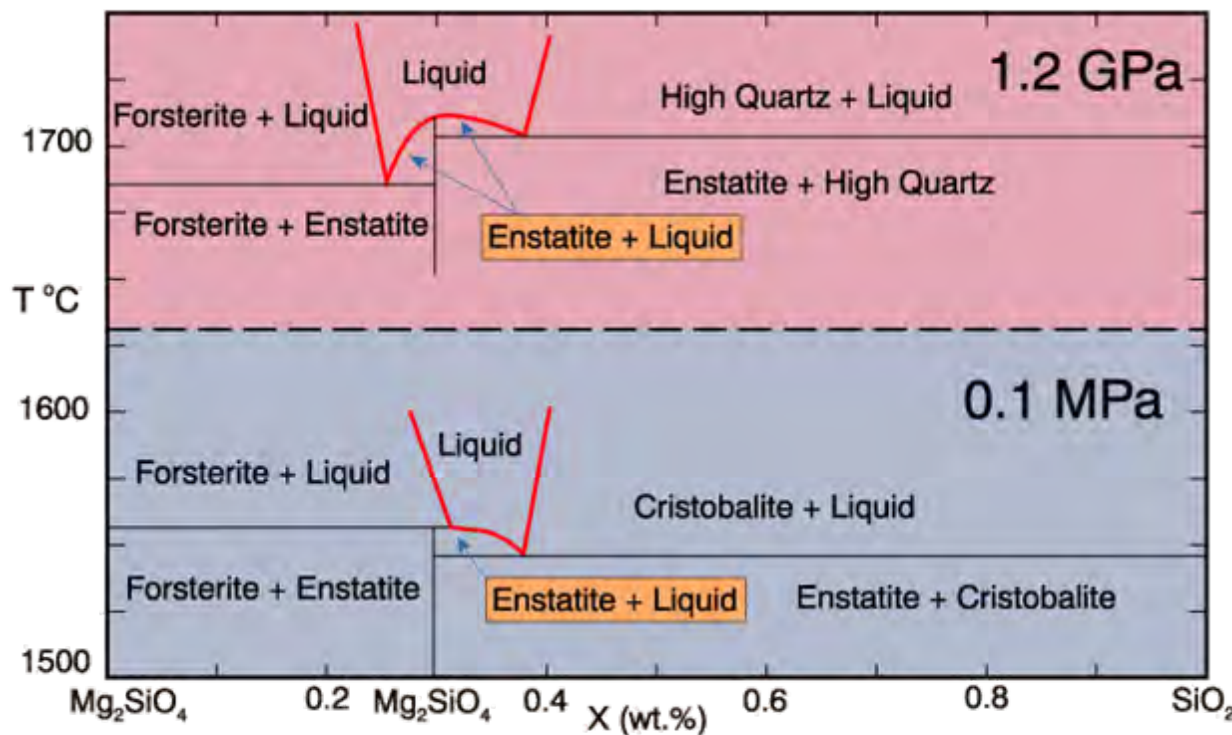
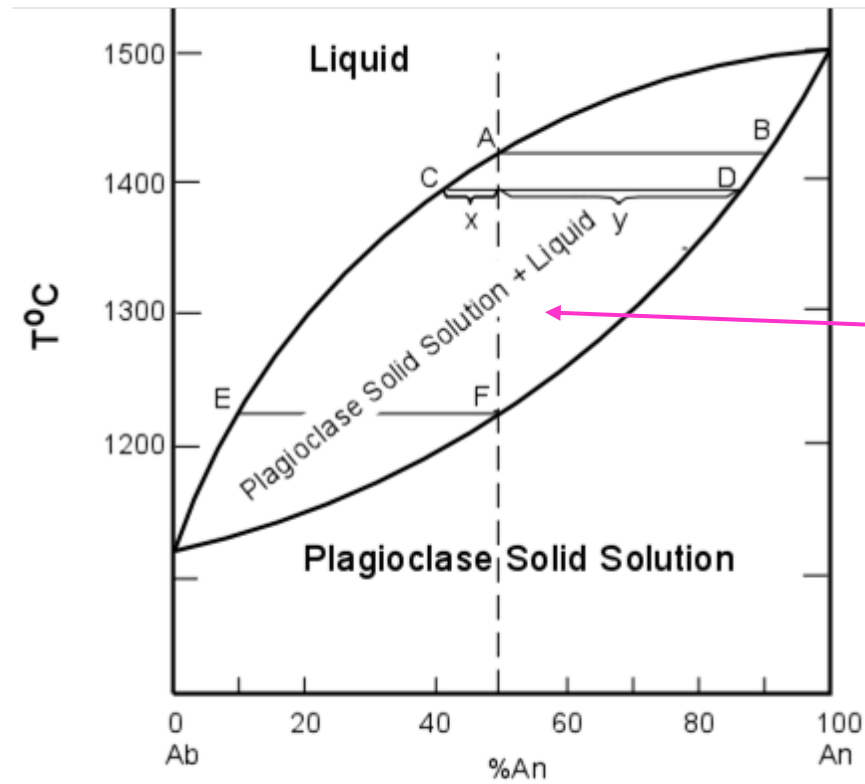


Figure 6.15. The system Fo- SiO_2 at atmospheric pressure and 1.2 GPa. After Bowen and Schairer (1935), Am. J. Sci., Chen and Presnall (1975) Am. Min.

Note evolution from incongruent to congruent melting of intermediate compound with increasing P.

(J. Winter)

Solid-Solution Melting



$$F = 2 + 1 - 1 = 2$$

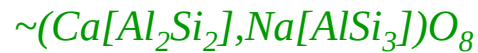
$$F = 2 + 1 - 2 = 1$$

$$\mu_{\text{Ab}}^{\text{solid}} = \mu_{\text{Ab}}^{\text{liquid}}$$

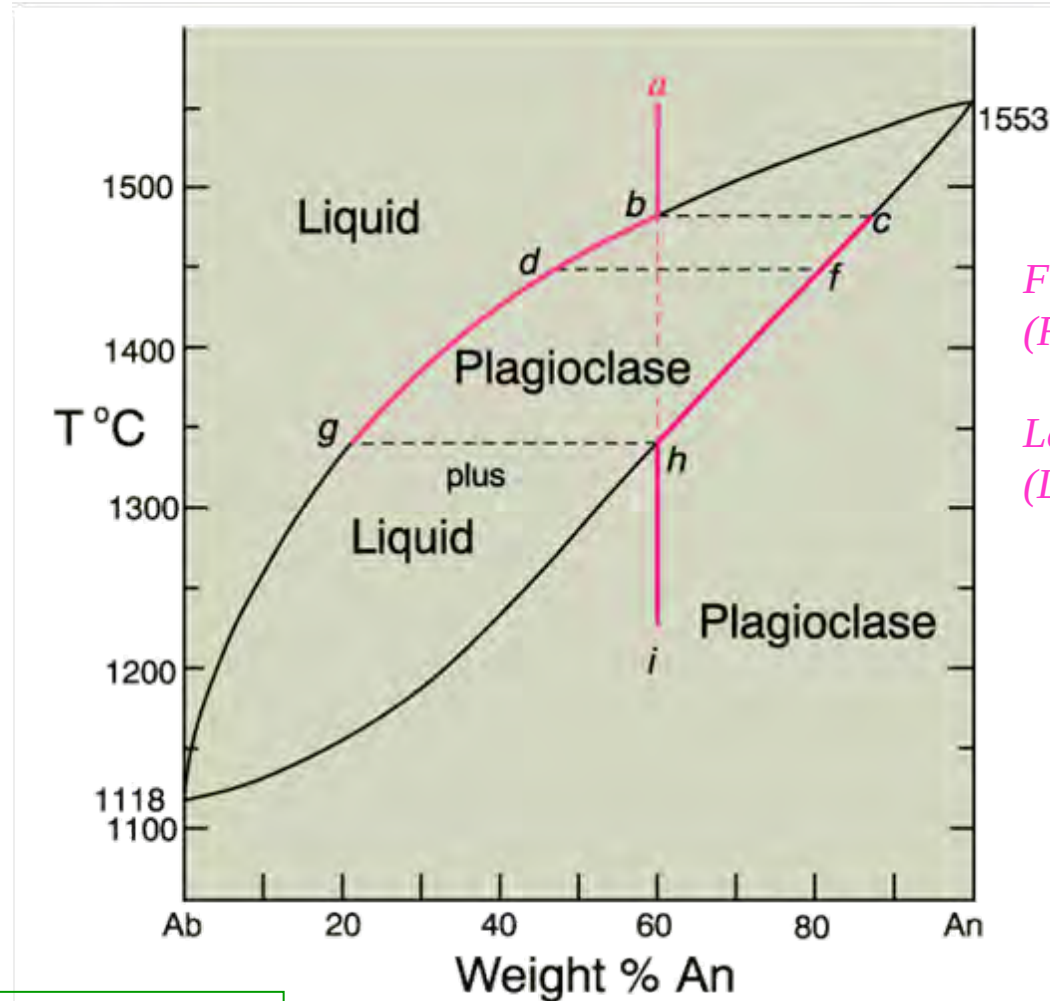
$$\mu_{\text{An}}^{\text{solid}} = \mu_{\text{An}}^{\text{liquid}}$$

$$F = 2 + 1 - 1 = 2$$

Figure 3



(S. A. Nelson, 2011)

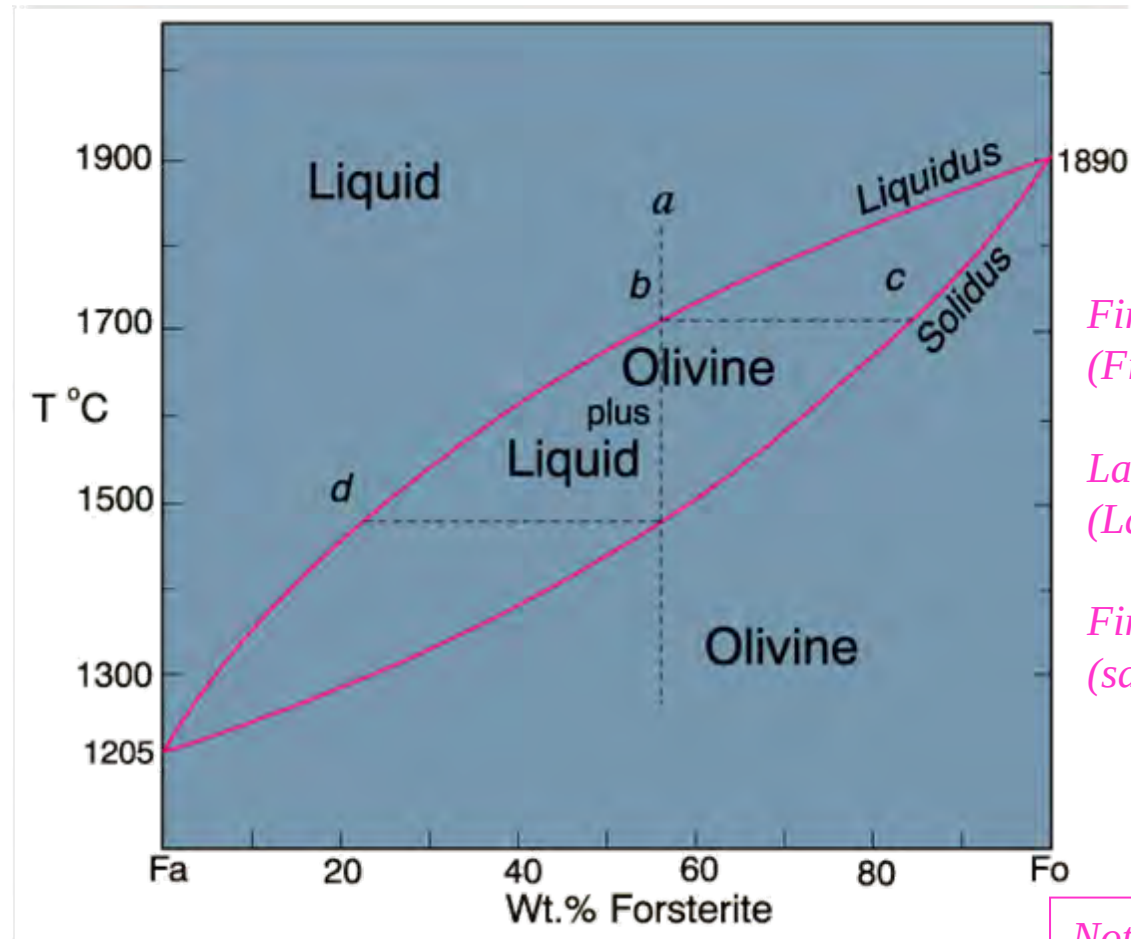
Plagioclase Solid Solution: Albite ($\text{NaAlSi}_3\text{O}_8$) – Anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$)

First melt appears at point *g*.
(First melt is Na-rich.)

Last solid disappears at point *c*.
(Last solid is Ca-rich.)

Note that temperature and composition of first melt **do** depend upon the initial bulk composition.

(J. Winter)

Olivine Solid Solution: Forsterite (Mg_2SiO_4) – Fayalite (Fe_2SiO_4)

$$F = 2 + 1 - 2 = 1$$

$$\mu_{\text{Fo}}^{\text{solid}} = \mu_{\text{Fo}}^{\text{liquid}}$$

$$\mu_{\text{Fa}}^{\text{solid}} = \mu_{\text{Fa}}^{\text{liquid}}$$

First melt appears at point d.
(First melt is Fe-rich.)

Last solid disappears at point c.
(Last solid is Mg-rich.)

Final melt composition is b
(same as initial solid).

Note that **partial** melting
extracts Fe-rich liquid, leaving
Mg-rich solid residue.

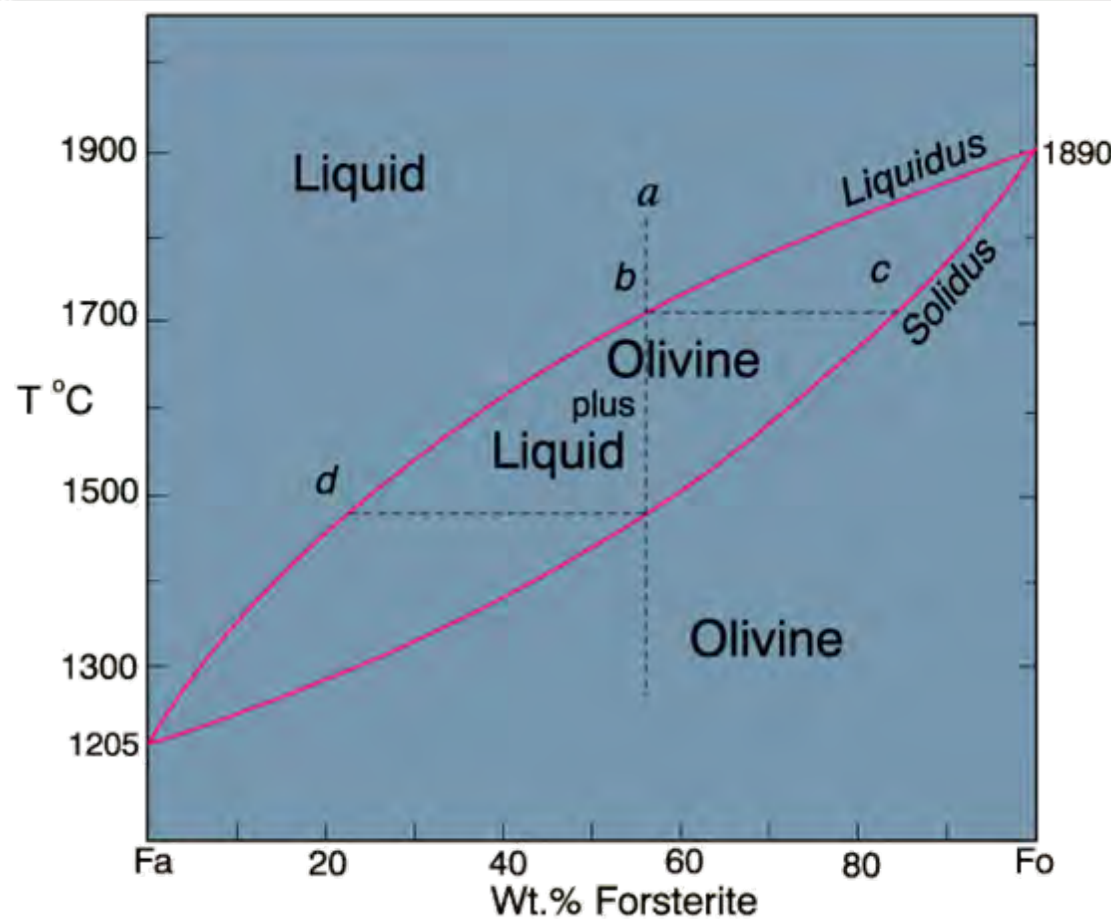
(J. Winter)

Olivine Solid Solution: Forsterite (Mg_2SiO_4) – Fayalite (Fe_2SiO_4)

*Note that we are discussing **equilibrium** (“batch”) melting, where liquids remain in contact with solids.*

What happens if the liquid is drained away (“fractional” melting) at point b?

Then the remaining solid is of composition c, and melting resumes immediately at point b, but now the final melt composition will be c (more Mg-rich) instead of b.



K-Feldspar Solid Solution: Albite ($\text{NaAlSi}_3\text{O}_8$) – Orthoclase (KAlSi_3O_8)

$$F = 2 + 1 - 2 = 1$$

$$\mu_{\text{Ab}}^{\text{Ab-rich_solid}} = \mu_{\text{Ab}}^{\text{liquid}}$$

$$\mu_{\text{Or}}^{\text{Ab-rich_solid}} = \mu_{\text{Or}}^{\text{liquid}}$$

This “mutual hostility” in the solid phase also affects the melting relationships.

Na and K do not “like” to be neighbors in the solid phase:

$$E_{\text{NaNa}} + E_{\text{KK}} < 2 \cdot E_{\text{NaK}}$$

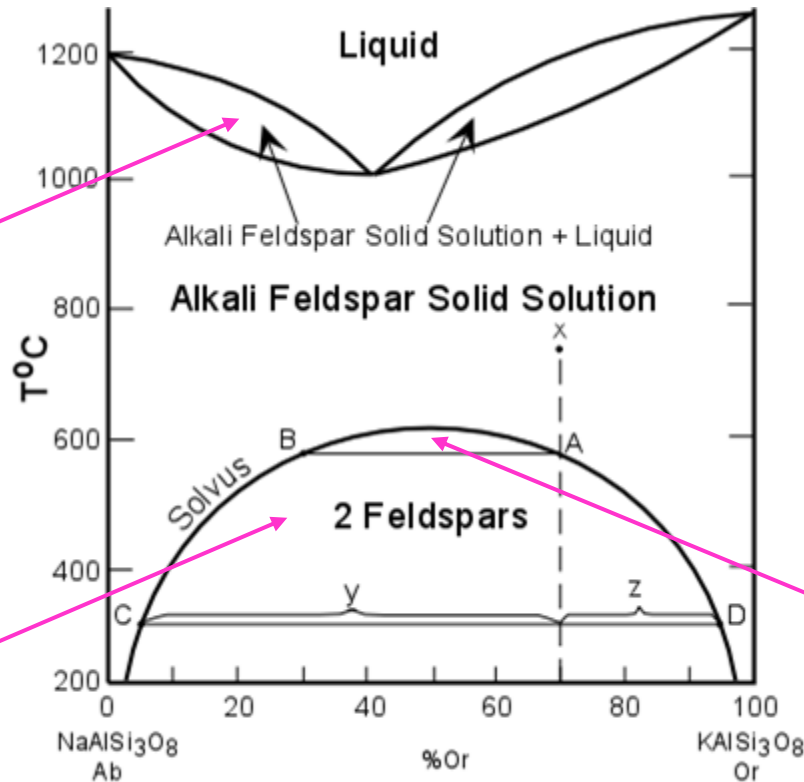


Figure 4

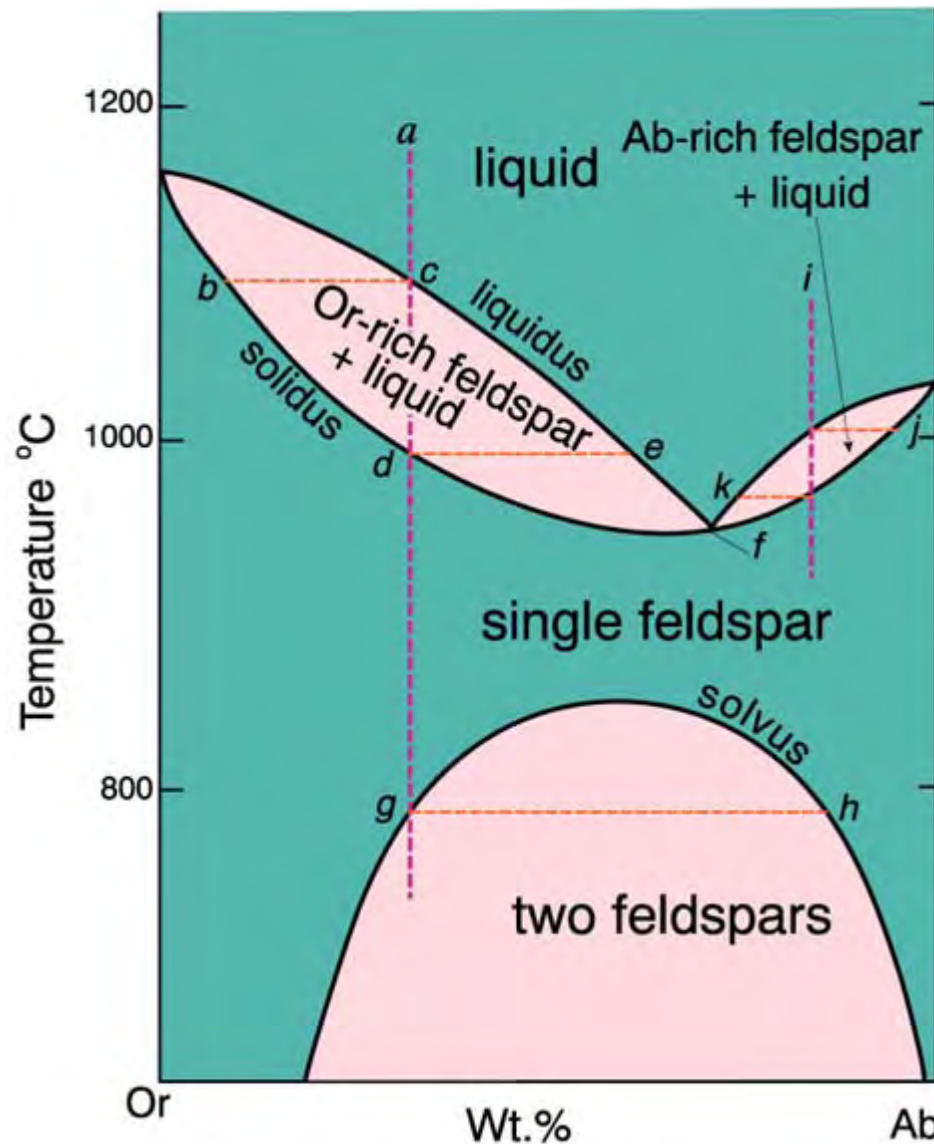
$$\mu_i = \mu_i^0 + nRT \ln a_i$$

The unfavorable energetics of mutual solid solution are gradually overcome by the amplification of the entropy of mixing at increasingly higher temperatures.

$$F = 2 + 1 - 1 = 2$$

(S. A. Nelson, 2011)

Solid Solution with a Minimum: Ab-Or (the alkali feldspars)



First melt appears at point e (for bulk composition g) or at point k (for composition h).

Coexisting solid is always closer to the end-member.

Note that a bulk composition of exactly f will melt completely at point f (the “minimum” of both solidus and liquidus), with no intervening two-phase field.

Effect of P_{H_2O} on Ab-Or

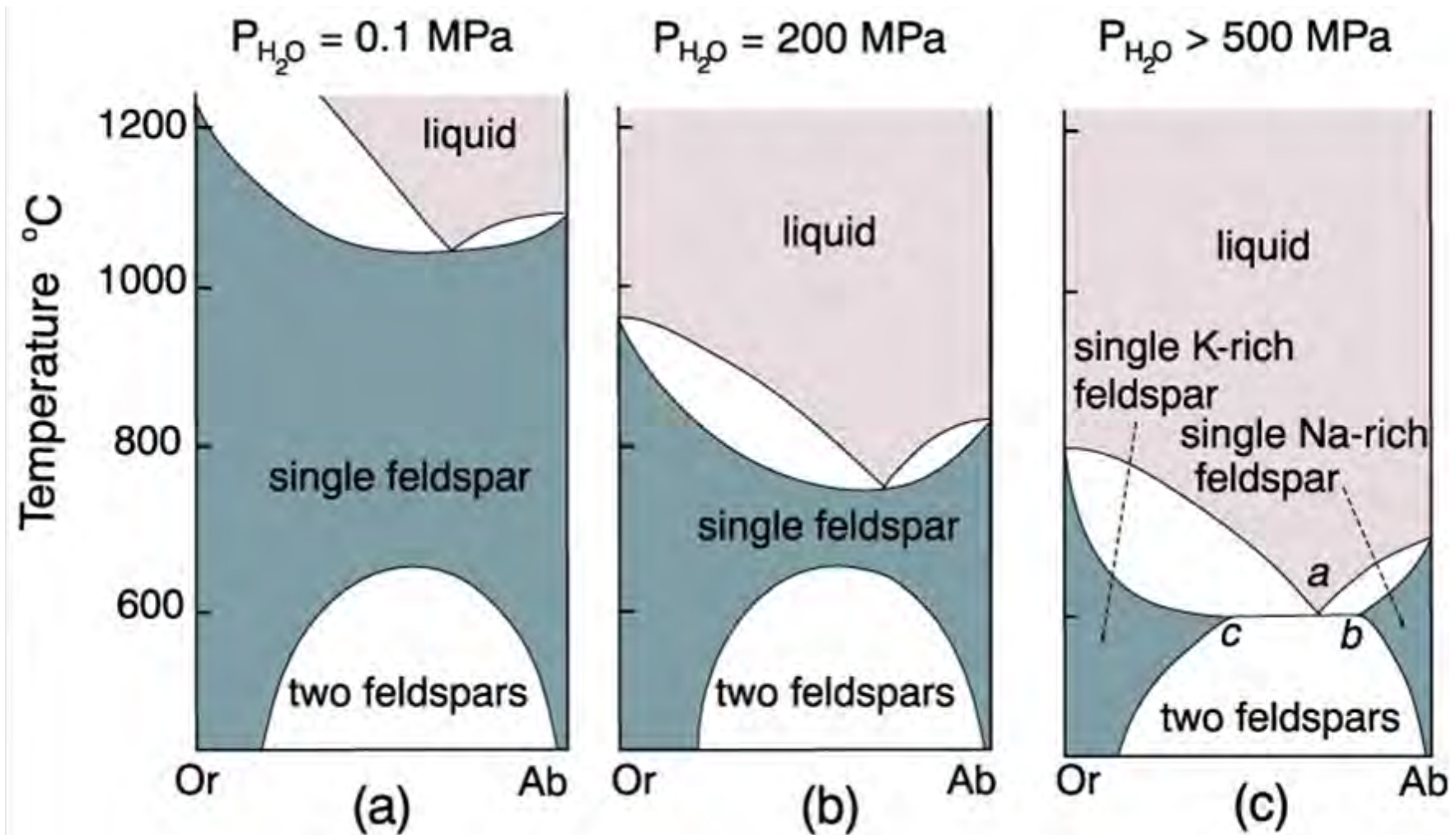


Figure 6.17. The Albite-K-feldspar system at various H_2O pressures. (a) and (b) after Bowen and Tuttle (1950), J. Geol, (c) after Morse (1970) J. Petrol.

(J. Winter)

Note evolution of minimum to eutectic with increasing partial pressure of water.

complete solid solution

$$(\partial\mu_i/\partial T)_P \sim -S_i^0 + nR \ln a_i$$

entropy of mixing

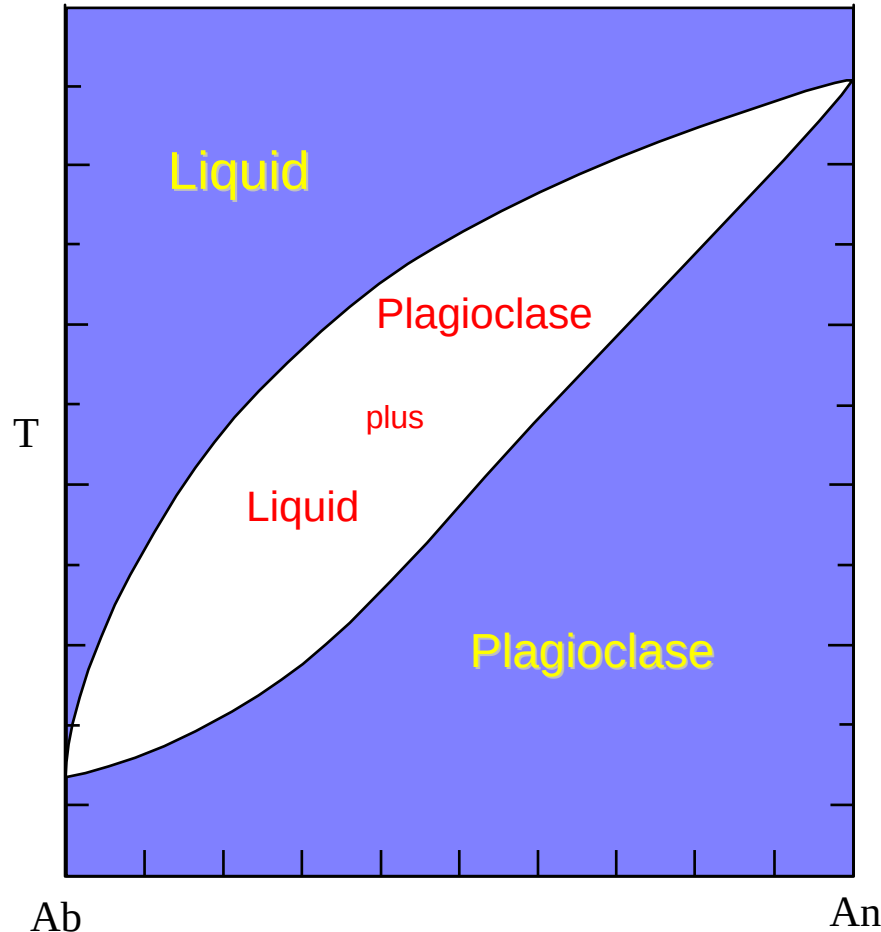
$$\begin{aligned}\mu_i &= \mu_i^0 + nRT \ln a_i \\ &= \mu_i^0 + nRT \ln \gamma_i X_i \\ &= \mu_i^0 + nRT (\ln X_i + \ln \gamma_i)\end{aligned}$$

$\gamma_i=1$: ideal solution

$$\mu_i = \mu_i^0 + nRT (\ln X_i + \delta \ni \delta=0)$$

$\Rightarrow$ complete solid solution

$$E_{AA} + E_{BB} = 2E_{AB}$$



(J. Winter)

solid solution $\rightarrow$ exsolution $\rightarrow$ eutectic

$$\gamma_i > 1 \rightarrow \gamma_i \gg 1$$

$$\begin{aligned}\mu_i &= \mu_i^0 + nRT \ln a_i \\ &= \mu_i^0 + nRT \ln \gamma_i X_i \\ &= \mu_i^0 + nRT (\ln X_i + \ln \gamma_i)\end{aligned}$$

$\gamma_i = 1$: ideal solution

$$\mu_i = \mu_i^0 + nRT (\ln X_i + \delta \ni \delta = 0)$$

$\Rightarrow$ complete solid solution

$$E_{AA} + E_{BB} = 2E_{AB}$$

$\gamma_i > 1$: positive deviation from ideality

$$\mu_i = \mu_i^0 + nRT (\ln X_i + \delta \ni \delta > 0)$$

$\Rightarrow$ miscibility gap (unmixing)

$$E_{AA} + E_{BB} < 2E_{AB}$$

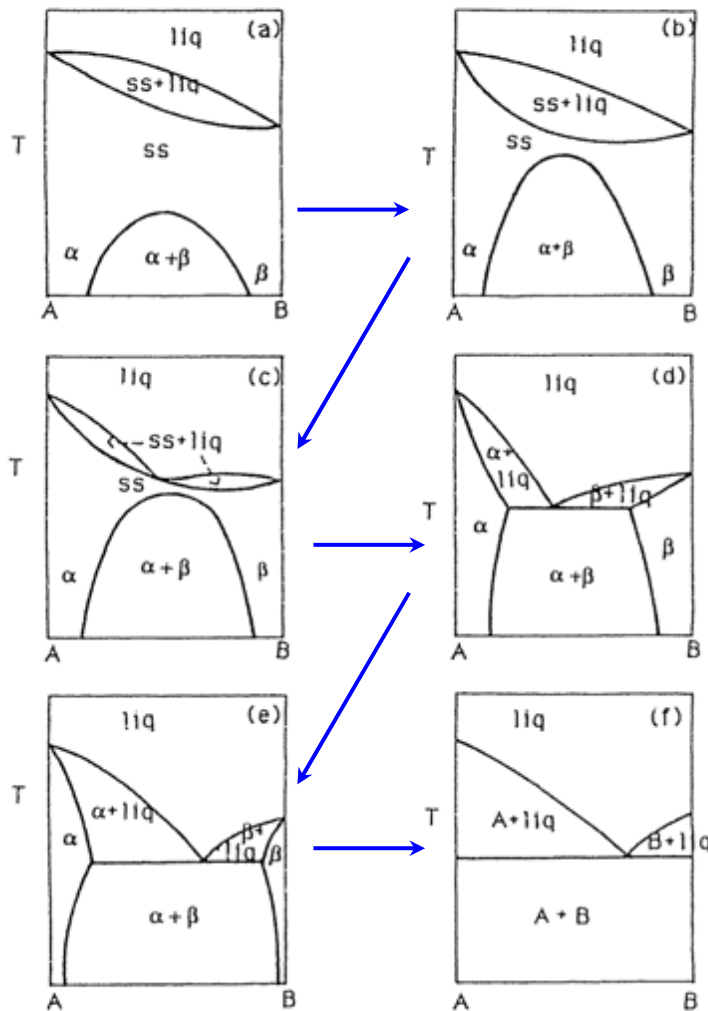


Figure 7.7. Evolution of phase diagram with increasing positive deviation from ideality in the solid in a solid solution forming system.

(Navrotsky, 1994)

solid solution $\rightarrow$ ordering $\rightarrow$ intermediate compound

$$\gamma_i < 1 \rightarrow \gamma_i \ll 1$$

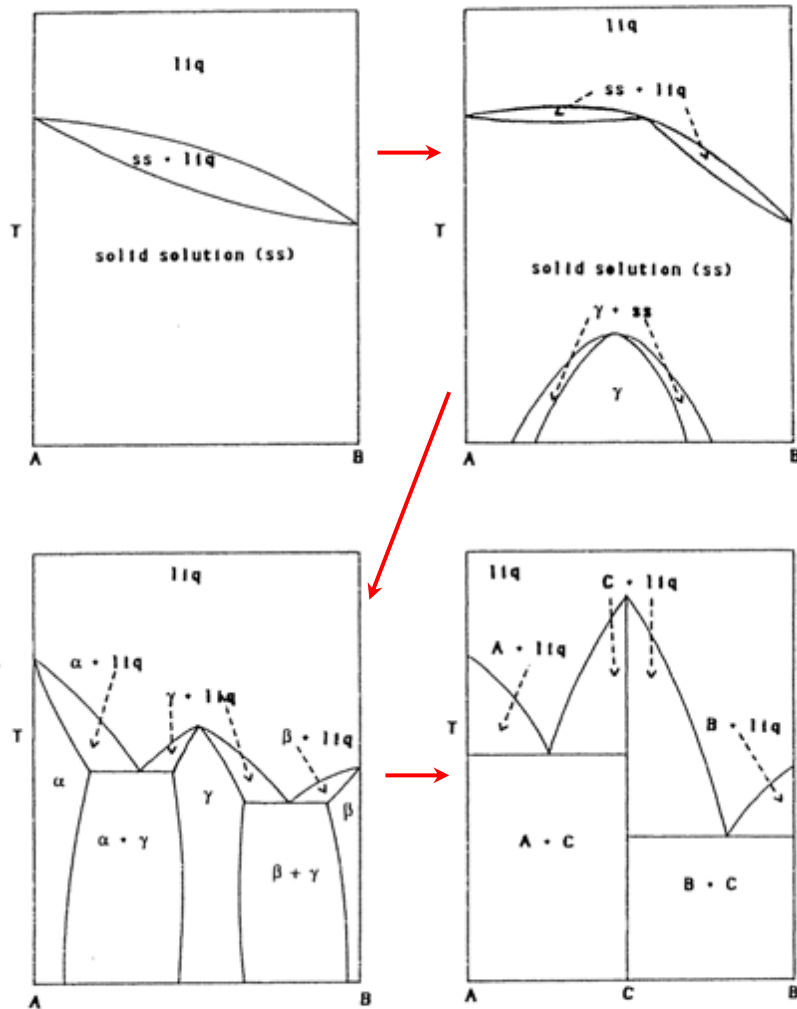


Figure 7.8. Evolution of phase diagram with increasing tendency for forming an ordered solid phase from the solid solution.

(Navrotsky, 1994)

$$\begin{aligned}\mu_i &= \mu_i^0 + nRT \ln a_i \\ &= \mu_i^0 + nRT \ln \gamma_i X_i \\ &= \mu_i^0 + nRT (\ln X_i + \ln \gamma_i)\end{aligned}$$

$\gamma_i = 1$: ideal solution

$$\begin{aligned}\mu_i &= \mu_i^0 + nRT (\ln X_i + \delta \ni \delta = 0) \\ &\Rightarrow \text{complete solid solution}\end{aligned}$$

$$E_{AA} + E_{BB} = 2E_{AB}$$

$\gamma_i > 1$: positive deviation from ideality

$$\begin{aligned}\mu_i &= \mu_i^0 + nRT (\ln X_i + \delta \ni \delta > 0) \\ &\Rightarrow \text{miscibility gap (unmixing)}\end{aligned}$$

$$E_{AA} + E_{BB} < 2E_{AB}$$

$\gamma_i < 1$: negative deviation from ideality

$$\begin{aligned}\mu_i &= \mu_i^0 + nRT (\ln X_i + \delta \ni \delta < 0) \\ &\Rightarrow \text{short-range ordering (compound)}\end{aligned}$$

$$E_{AA} + E_{BB} > 2E_{AB}$$

eutectic $\rightarrow$ peritectic $\rightarrow$ intermediate compound

$$\gamma_i^{liq} < 1 \rightarrow \gamma_i^{liq} \ll 1$$

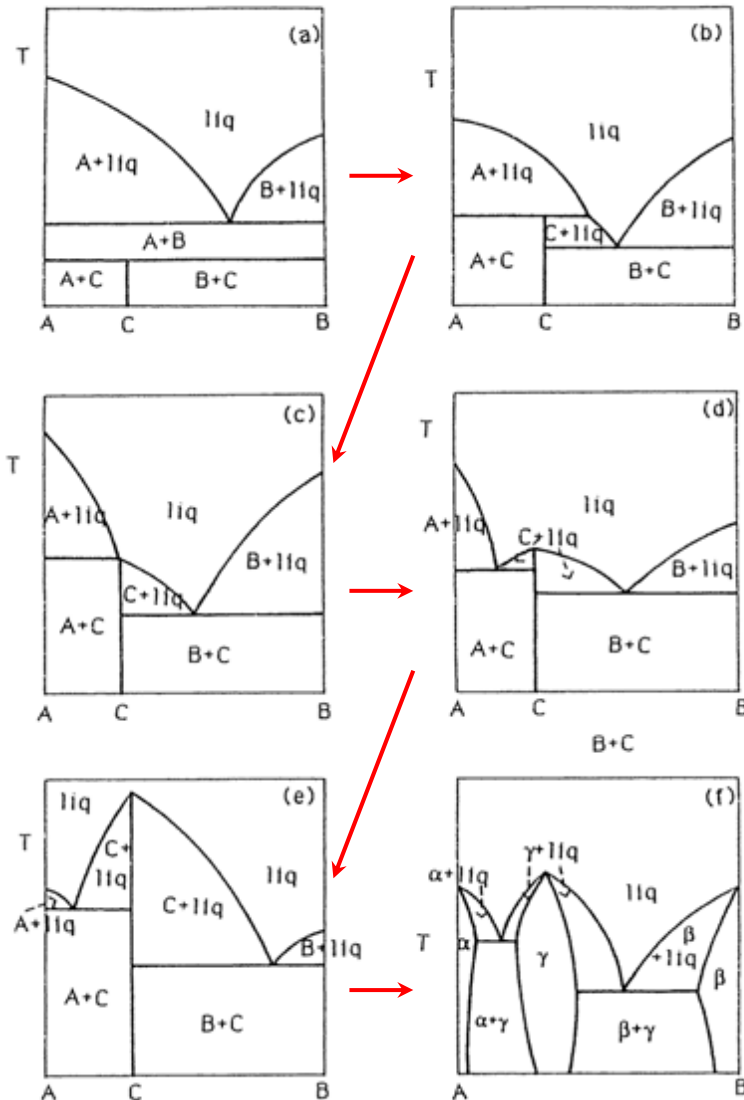


Figure 7.9. Evolution of phase diagram in a system showing negative deviations from ideality in the liquid phase indicative of compound formation.

(Navrotsky, 1994)

$$\begin{aligned}\mu_i &= \mu_i^0 + nRT \ln a_i \\ &= \mu_i^0 + nRT \ln \gamma_i X_i \\ &= \mu_i^0 + nRT (\ln X_i + \ln \gamma_i)\end{aligned}$$

$\gamma_i = 1$: ideal solution

$$\mu_i = \mu_i^0 + nRT (\ln X_i + \delta \ni \delta = 0)$$

$\Rightarrow$ complete solid solution

$$E_{AA} + E_{BB} = 2E_{AB}$$

$\gamma_i > 1$: positive deviation from ideality

$$\mu_i = \mu_i^0 + nRT (\ln X_i + \delta \ni \delta > 0)$$

$\Rightarrow$ miscibility gap (unmixing)

$$E_{AA} + E_{BB} < 2E_{AB}$$

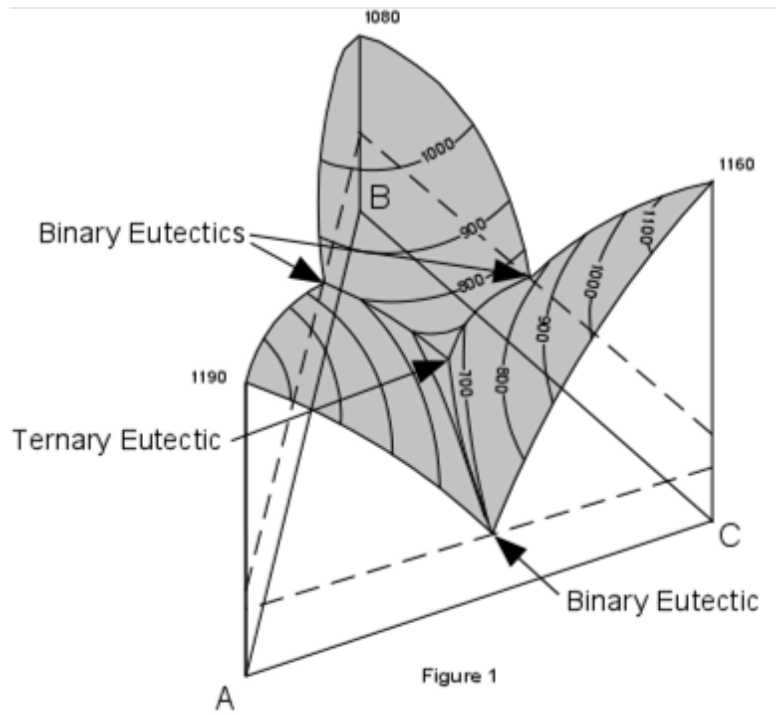
$\gamma_i < 1$: negative deviation from ideality

$$\mu_i = \mu_i^0 + nRT (\ln X_i + \delta \ni \delta < 0)$$

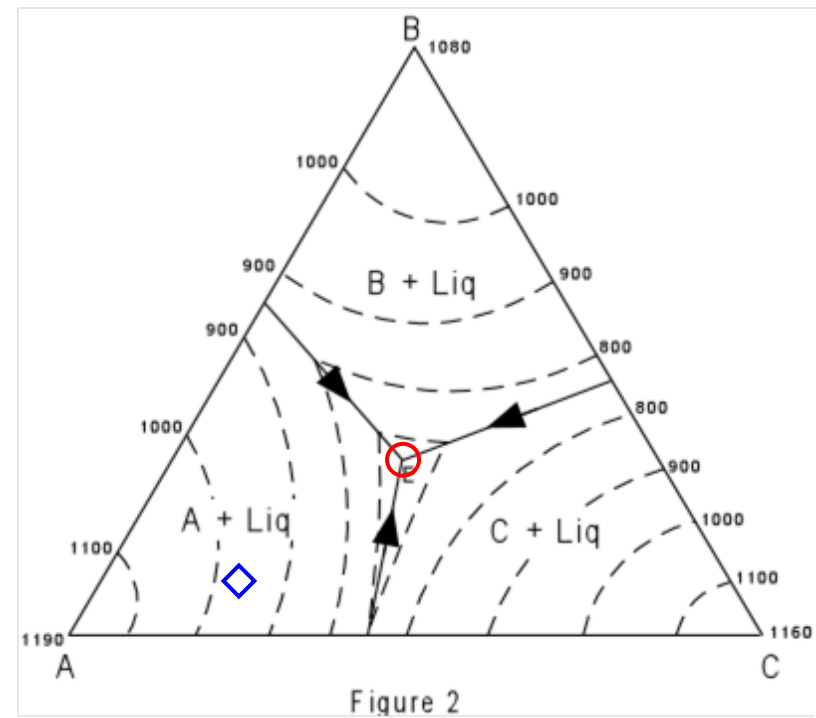
$\Rightarrow$ short-range ordering (compound)

$$E_{AA} + E_{BB} > 2E_{AB}$$

Ternary where all binaries are eutectics



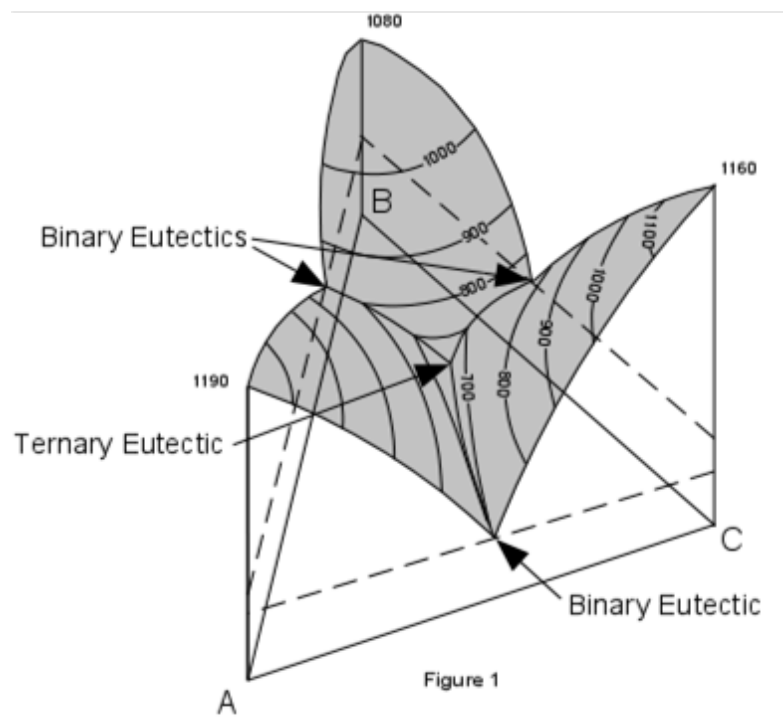
(S. A. Nelson)



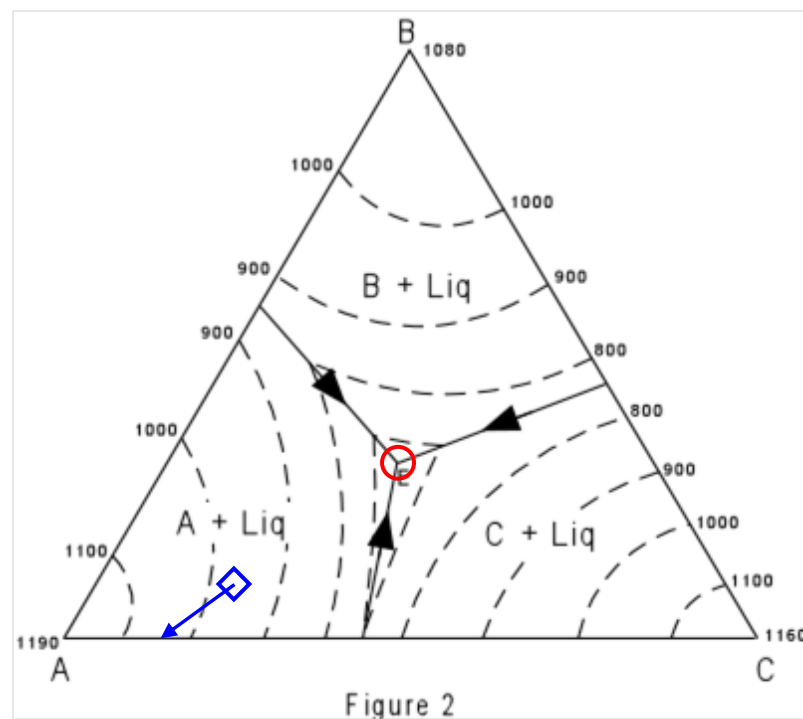
heating of initial solid composition

appearance of first melt at ternary ABC eutectic

Ternary where all binaries are eutectics

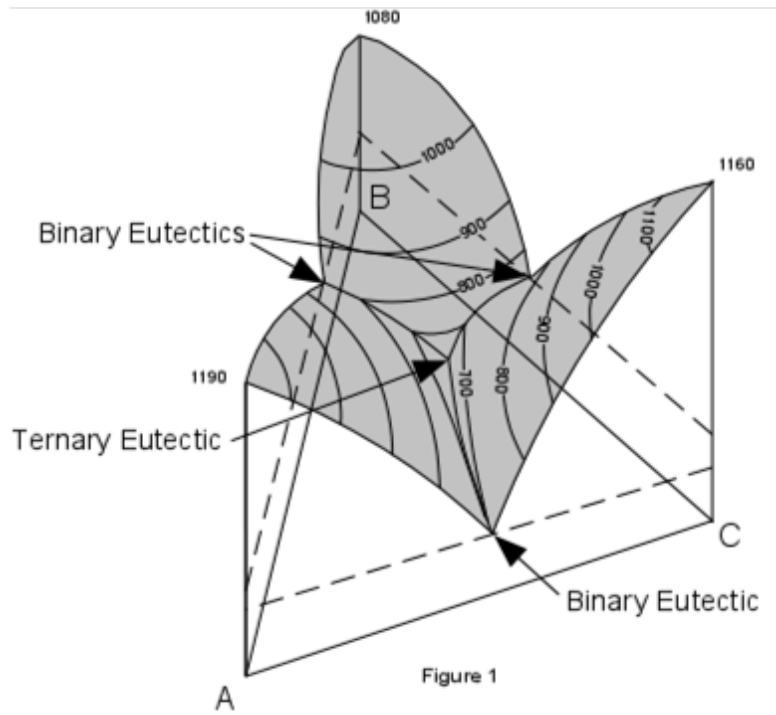


(S. A. Nelson)

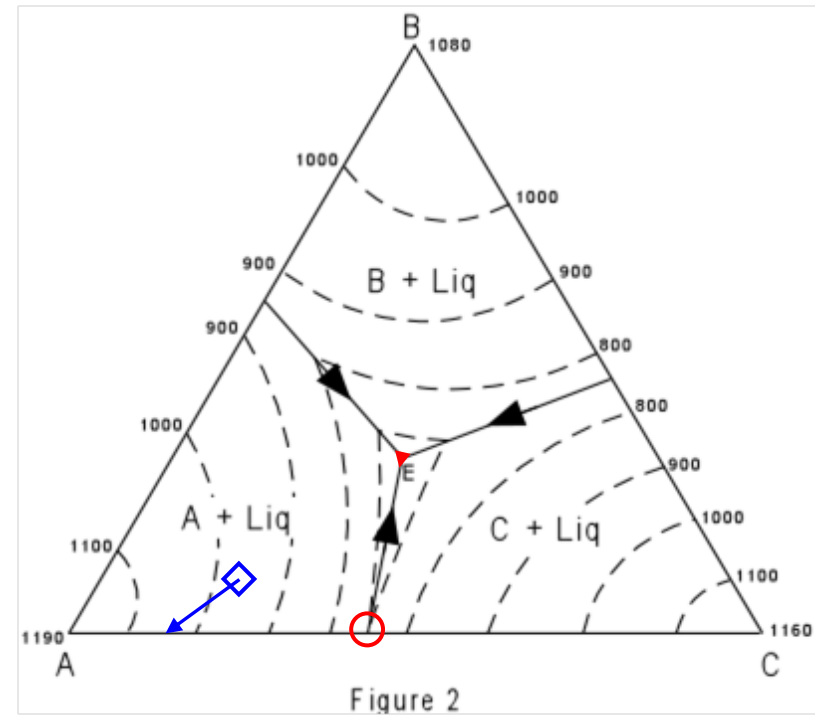


generation of melt at ternary ABC eutectic
migration of solid composition away from ternary eutectic

Ternary where all binaries are eutectics

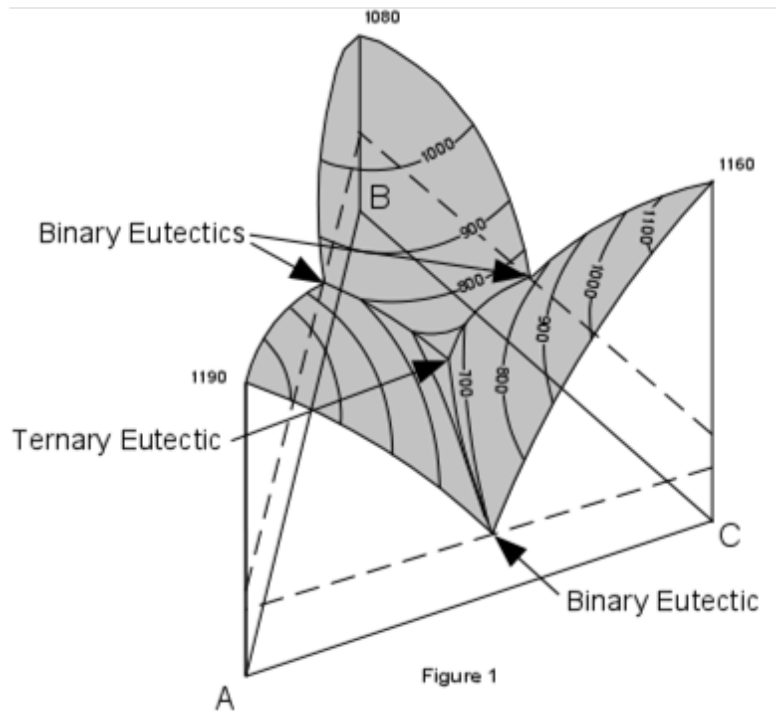


(S. A. Nelson)

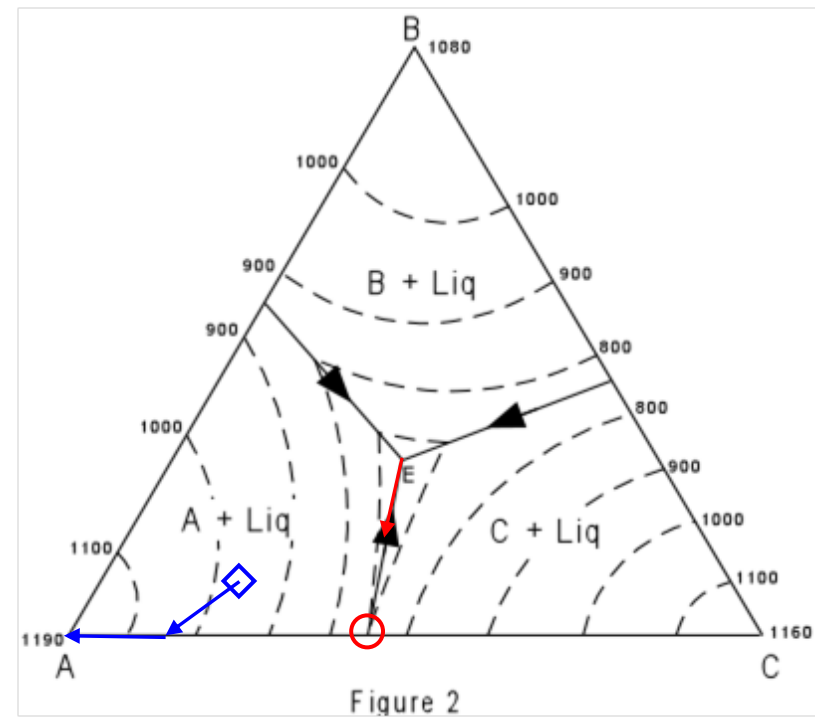


*migration of solid composition away from ternary eutectic,
until all of component B has been extracted from solid
generation of melt at binary AC eutectic*

Ternary where all binaries are eutectics



(S. A. Nelson)

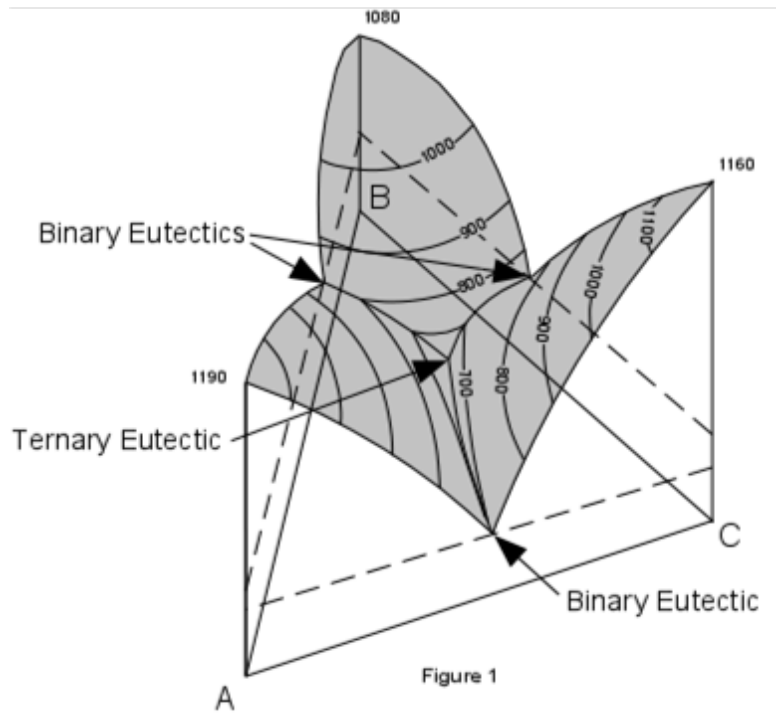


generation of melt at binary AC eutectic

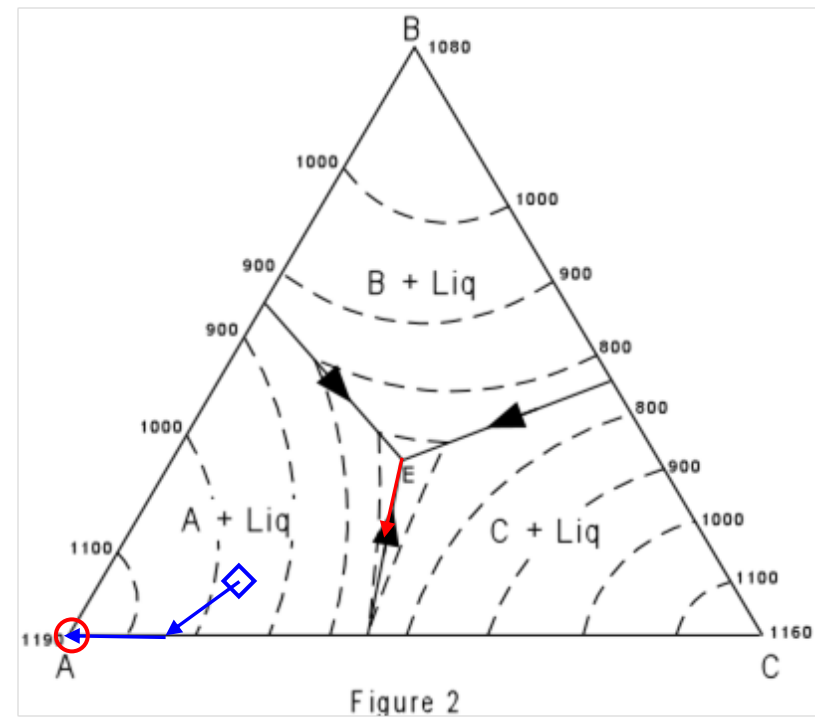
migration of solid composition away from binary eutectic

migration of melt composition toward binary AC eutectic

Ternary where all binaries are eutectics

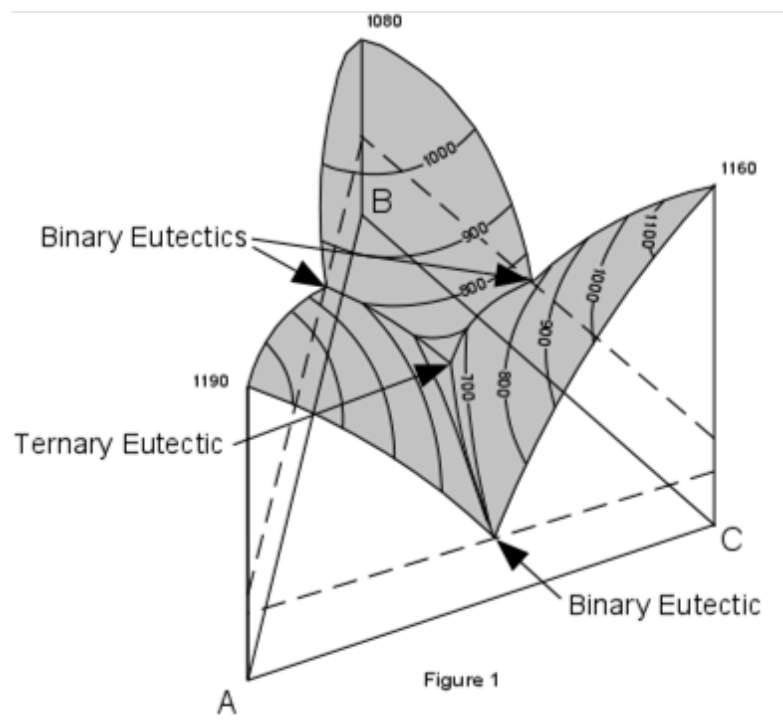


(S. A. Nelson)

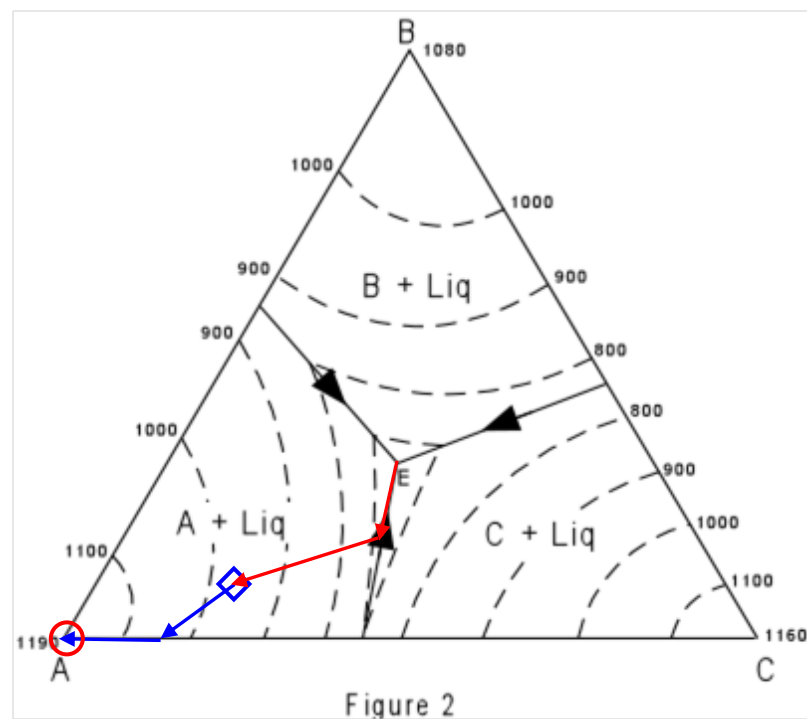


*migration of solid composition away from binary eutectic,
until all of component C has been extracted from solid
generation of melt at A end-member*

Ternary where all binaries are eutectics



(S. A. Nelson)

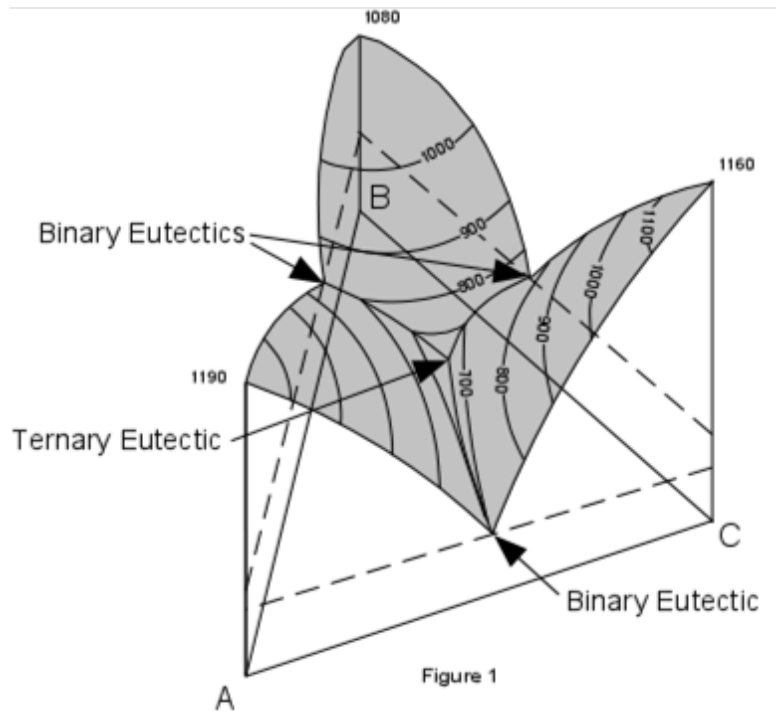


generation of melt at A end-member

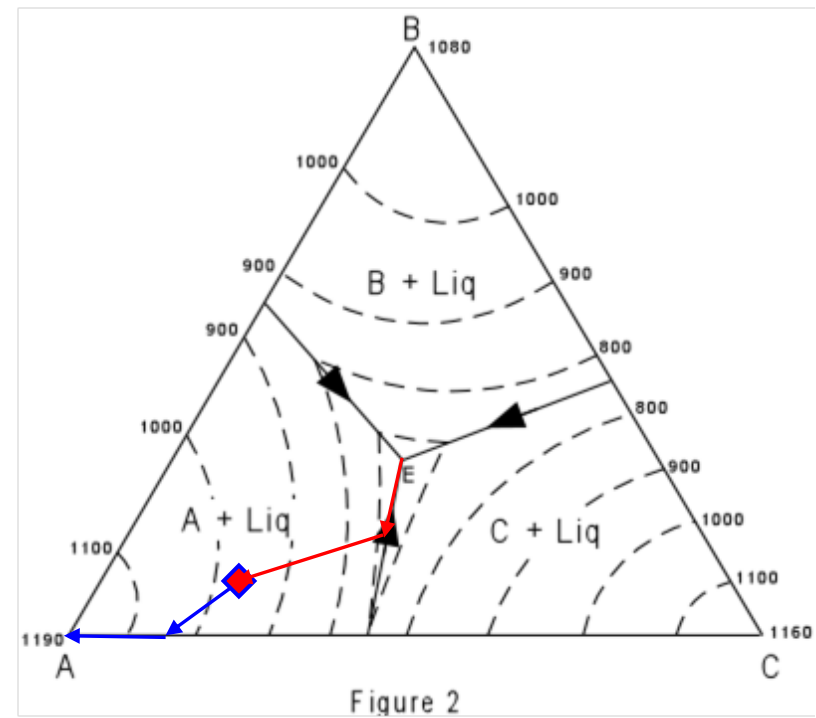
remaining solid composition fixed at A end-member

migration of melt composition toward A end-member

Ternary where all binaries are eutectics



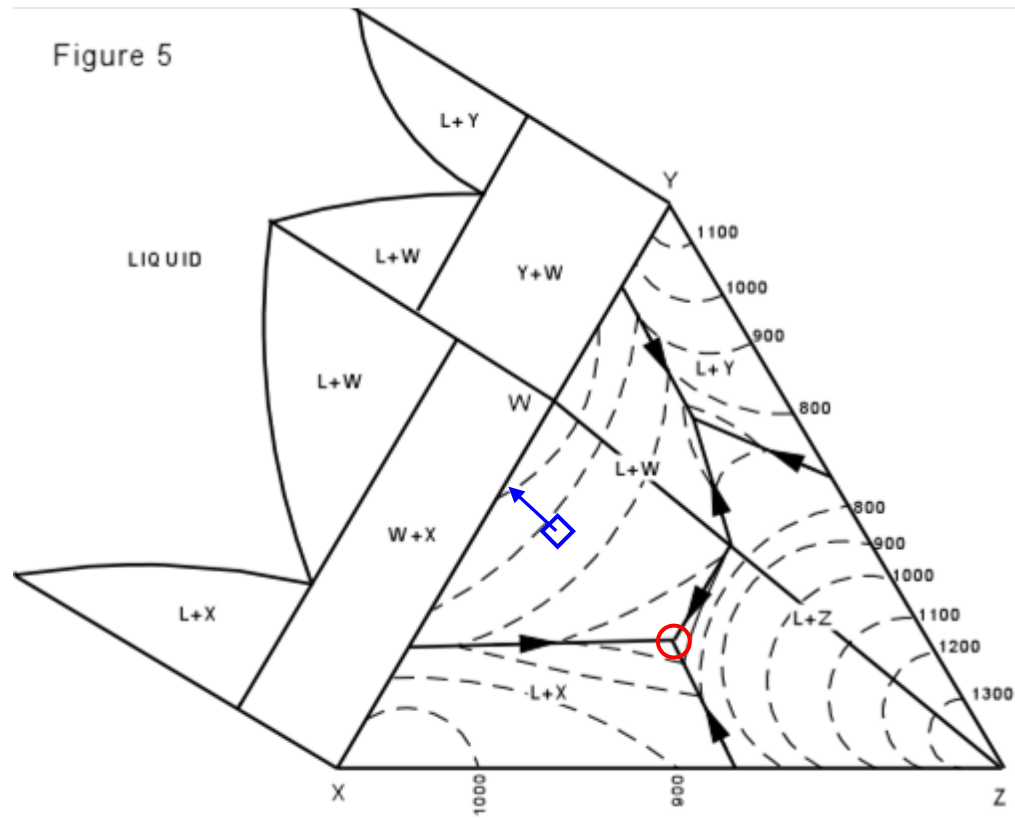
(S. A. Nelson)



*migration of melt composition toward A end-member,
until all remaining solid has been melted
(final melt composition = initial solid composition)*

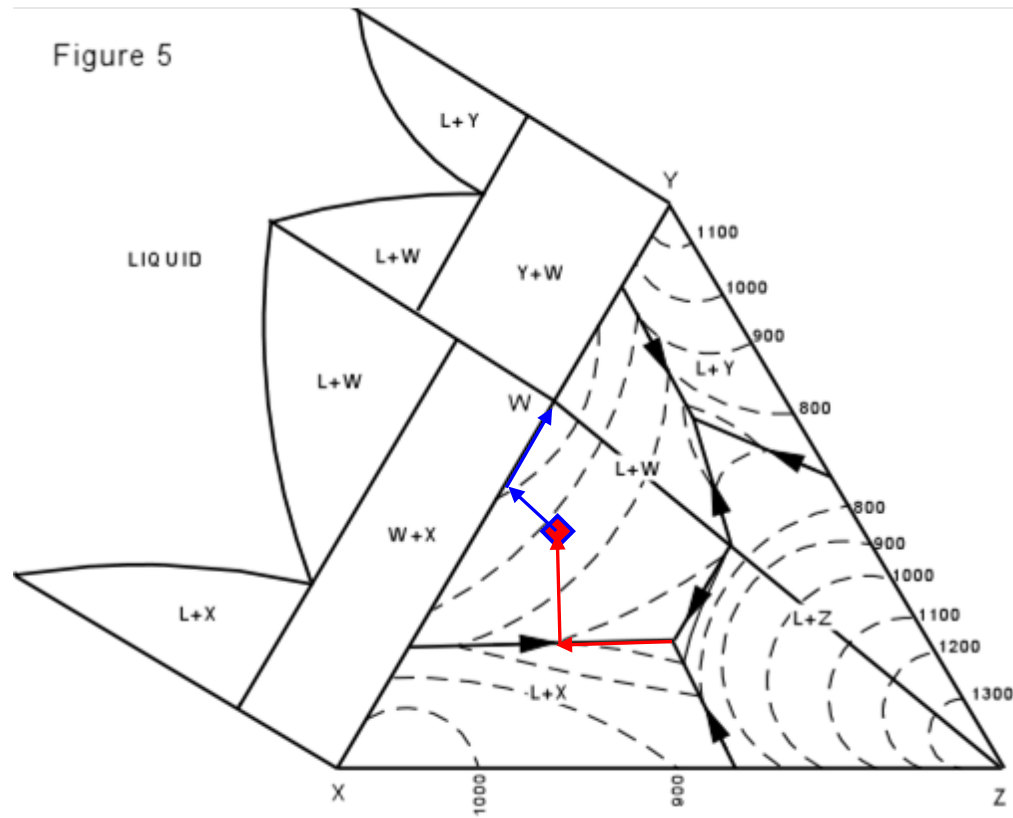
Ternary with congruently melting compound

Figure 5



(S. A. Nelson)

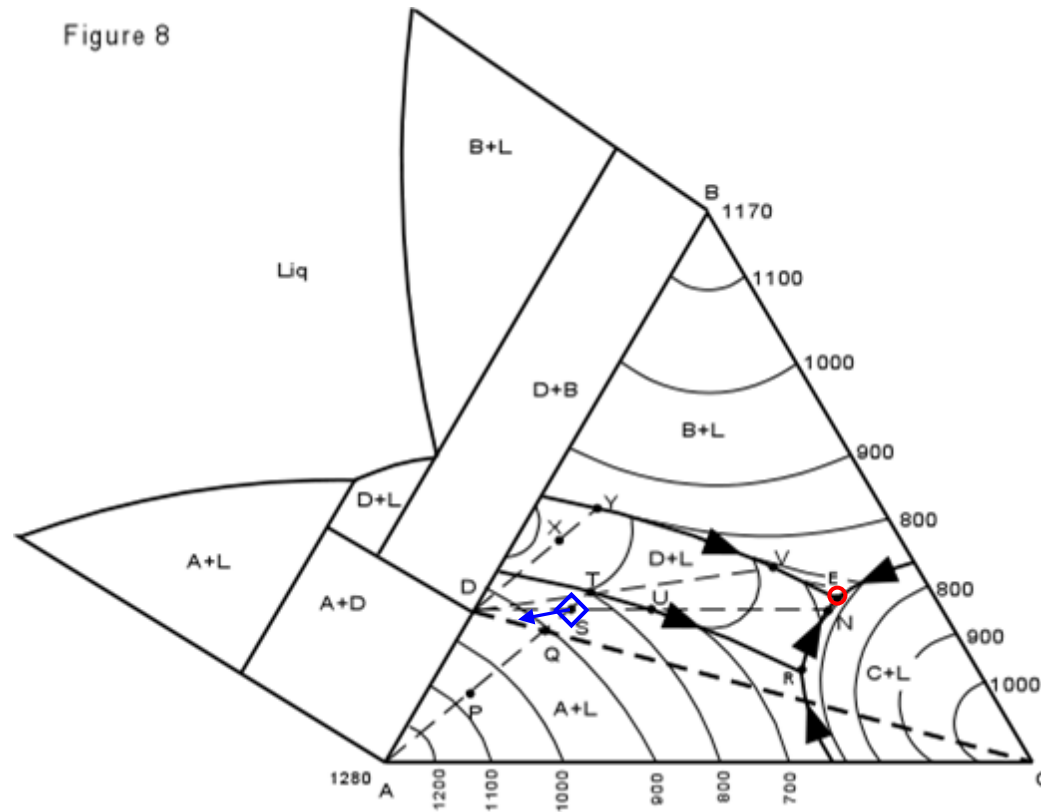
Ternary with congruently melting compound



(S. A. Nelson)

Ternary with incongruently melting compound

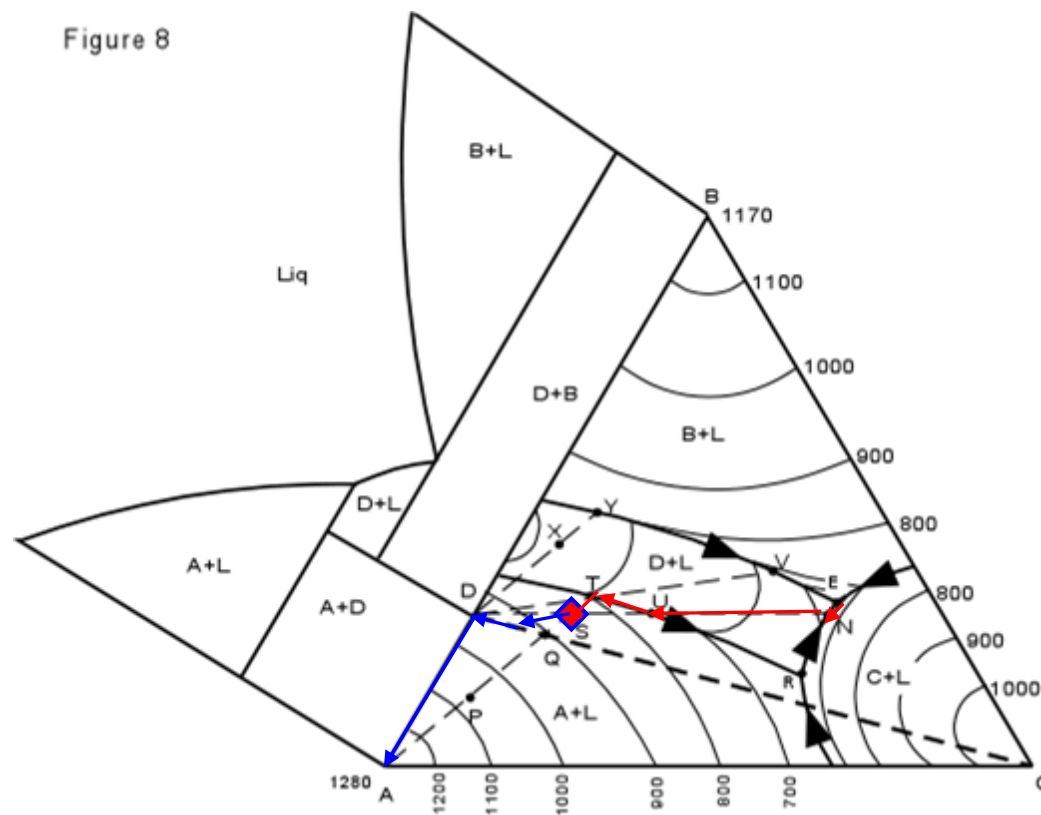
Figure 8



(S. A. Nelson)

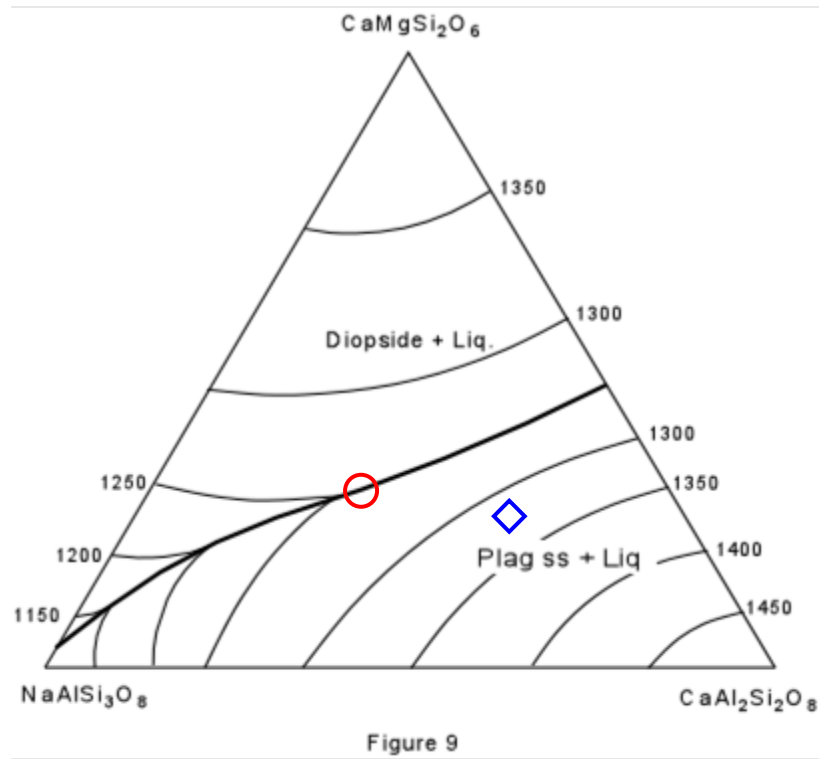
Ternary with incongruently melting compound

Figure 8



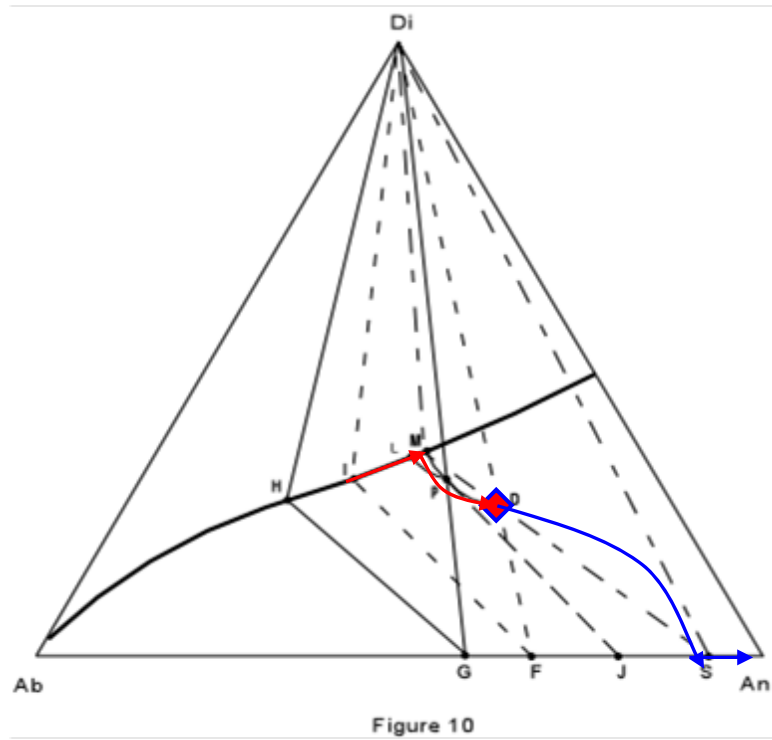
(S. A. Nelson)

Ternary with binary solid solution



(S. A. Nelson)

Ternary with binary solid solution



(S. A. Nelson)

Theoretical Models of Melting

- **Simon, Kraut-Kennedy:** correlations, often linear (*semi-empirical*).
- **Born, May, Jackson & Liebermann, Tallon:** Upon heating, the shear modulus falls, reaching zero for the liquid (*shear instability*).
- **Lindemann, Gilvarry:** Upon heating, atomic vibrations become so large that atomic spheres collide, or the RMS amplitudes of atomic vibrations reach a critical fraction of the separation distance (*vibrational instability*, “shakes itself to pieces” [Frank, 1939]).
- **Lennard-Jones & Devonshire, Frank:** Upon heating, the solid transforms from an ordered to a disordered state (*disorder instability*).
- **Ninomiya, Poirier:** Upon heating, formation of dislocations (linear lattice defects) locally disrupts order, leading to increasing loss of long-range order. The liquid is represented by a solid saturated with dislocation core, allowing approximate treatment of solid-liquid equilibrium (*dislocation-mediated*).

(cf. Poirier, 2000)

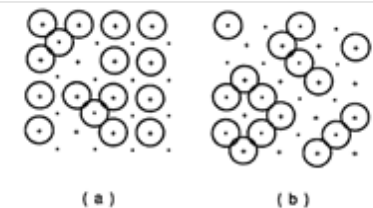
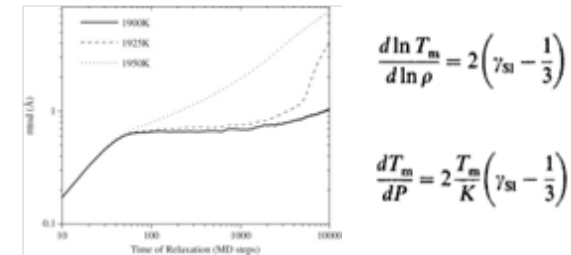
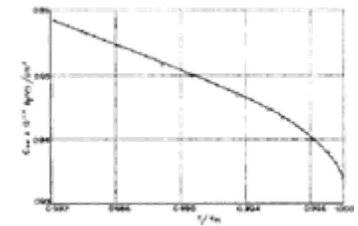


Figure 5.10 Melting by atomic disordering (after Lennard-Jones and Devonshire, 1939). (a) Local displacement of atoms, but long-range order preserved. (b) Long-range order broken: equal number of atoms on regular lattice sites (crosses) and interstitial sites (dots).

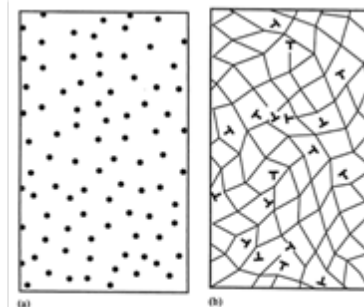


Figure 5.12 Dislocation melting (two-dimensional example): a disordered liquid (a) can be represented by a solid saturated with dislocations (b); the dislocation cores are traditionally represented by “nuclei.”

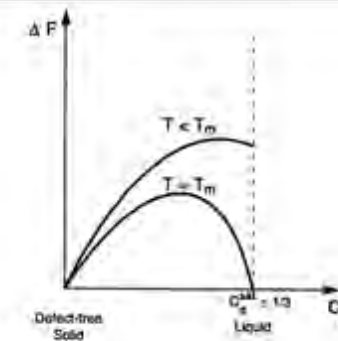


Figure 5.13 Extra free energy of a crystal containing a dislocation concentration C_d . At the melting temperature, $\Delta F = 0$ for $C_d = C_d^*$.

Theoretical Models of Melting

“All melting theories are imperfect because to construct a good theory for the first-order melting transition, one must write that **the free energies of the solid and the liquid are equal at equilibrium**. This would necessitate a better description of the liquid state than the ones currently available – indeed, the structure of the liquid state is a standing problem in physics.”

“It remains that even the best theories of melting, developed for simple solids like solid gases or metals, dismally fail in the case of minerals due to the complexity of the structure of their liquids.”

(Poirier, 2000)

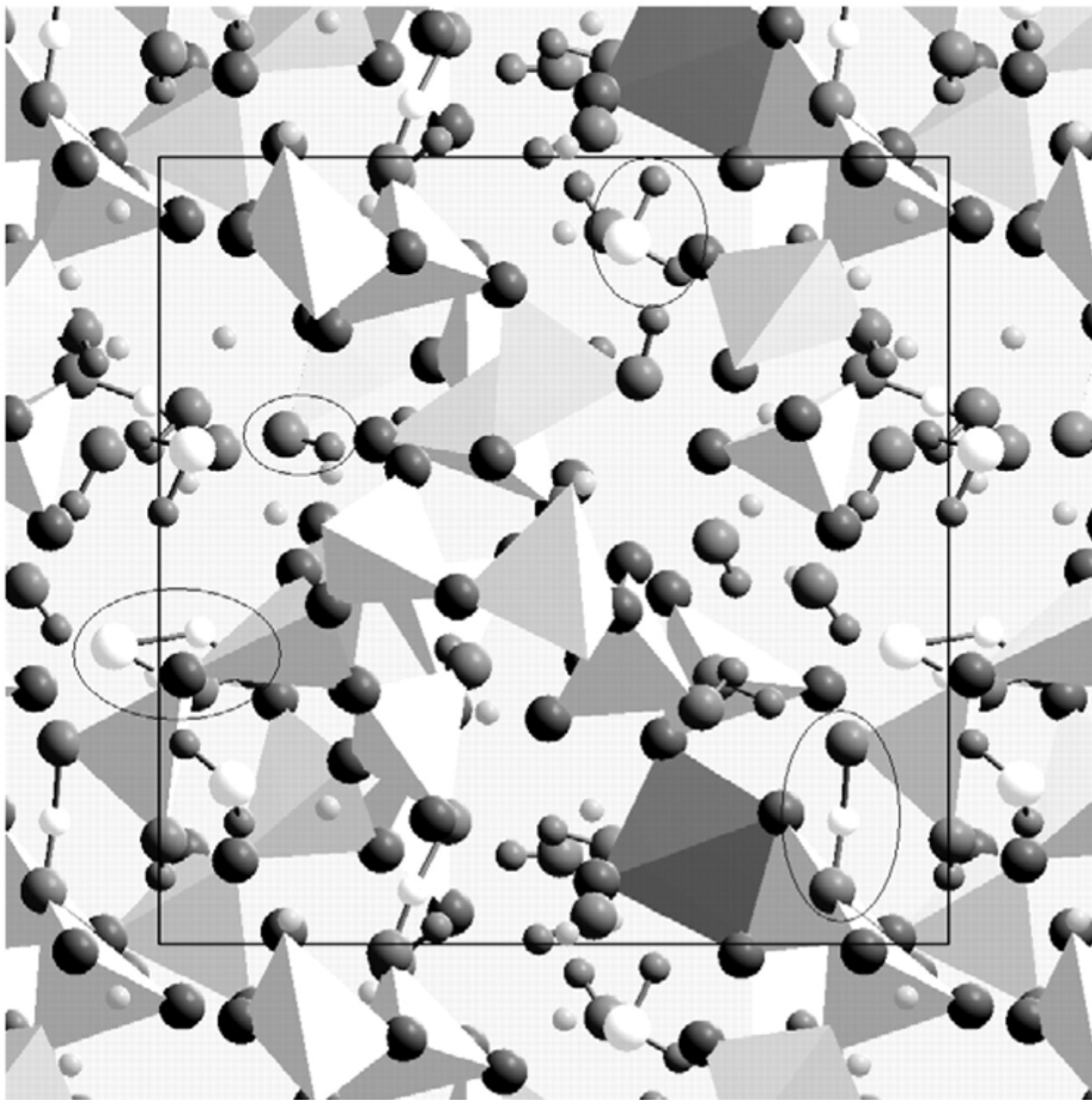


Figure 8. Si-O coordination (polyhedra), and O-H and H-O coordination (spheres) displayed together. The mixed environment represents Si-O coordination polyhedra (4-fold, light; 5-fold, dark) and various forms (marked) of water speciation including hydroxyls (large dark-small dark pairs), water molecules (small dark-large light-small dark triplets), polyhedral bridging (large dark-small light-large dark triplets), and four-atom sequences (such as one in the lower part of the left boundary). The smallest (free) spheres represent Mg atoms. The oxygen atoms (large spheres) bonded to Si atoms are shown at the polyhedral vertices or those to Mg atoms are shown as free spheres.

(Karki, 2010)