

# Chapter 24. Stable Mineral Assemblages in Metamorphic Rocks

- **Equilibrium Mineral Assemblages**
- At ***equilibrium***, the mineralogy (and the composition of each mineral) is determined by T, P, and X
- “**Mineral paragenesis**” refers to such an equilibrium mineral assemblage
- Relict minerals or later alteration products are excluded unless specifically stated

## Phase equilibrium and Gibbs Phase Rule

- Capable of analyzing 'systems' in a way that allows us to grasp the dynamics of each and to account for the contribution of each chemical constituent to the variations
- Understand how the introduction of additional constituents affects a system – helps us better comprehend new systems and more complex systems in nature

# The Gibbs Phase Rule

$$F = C - \phi + 2$$

**F = # degrees of freedom**

The number of independently **intensive** parameters that must be specified in order to completely determine the system at *equilibrium conditions*

Consist of properties of the substances that compose a system (e.g., mineral assemblage)

Examples: Pressure, Temperature, density, molar volume

# The Gibbs Phase Rule

$$F = C - \phi + 2$$

F = # degrees of freedom

The number of independently intensive parameters that must be specified in order to completely determine the system system at *equilibrium conditions*

$\phi$  = # of phases

phases are **mechanically separable** constituents

Examples: Mineral, liquid, gas, or an amorphous solid such as glass

# The Gibbs Phase Rule

$$F = C - \phi + 2$$

F = # degrees of freedom

The number of dependently intensive parameters that must be specified in order to completely determine the system at *equilibrium conditions*

$\phi$  = # of phases

phases are mechanically separable constituents

C = minimum # of components (chemical constituents that must be specified in order to define all phases)

Example: H<sub>2</sub>O – treat as one component, not two (H, O)

Plagioclase – normally described as two components – **Albite** & **Anorthite**

# The Gibbs Phase Rule

$$F = C - \phi + 2$$

F = # degrees of freedom

The number of independently intensive parameters that must be specified in order to completely determine the system

$\phi$  = # of phases

phases are mechanically separable constituents

C = minimum # of components (chemical constituents that must be specified in order to define all phases)

2 = 2 intensive parameters

Usually = temperature and pressure for us geologists

## The Phase Rule in Metamorphic Systems

If  $F \geq 2$  is the most common situation, then the phase rule may be adjusted accordingly:

$$F = C - \phi + 2 \geq 2$$

$$\phi \leq C \text{ (Eq 24.1)}$$

Goldschmidt's mineralogical phase rule, or simply the **mineralogical phase rule**

## The Phase Rule in Metamorphic Systems

Suppose we have determined  $C$  for a rock  
Consider the following three scenarios:

a)  $\phi = C$

The standard divariant situation

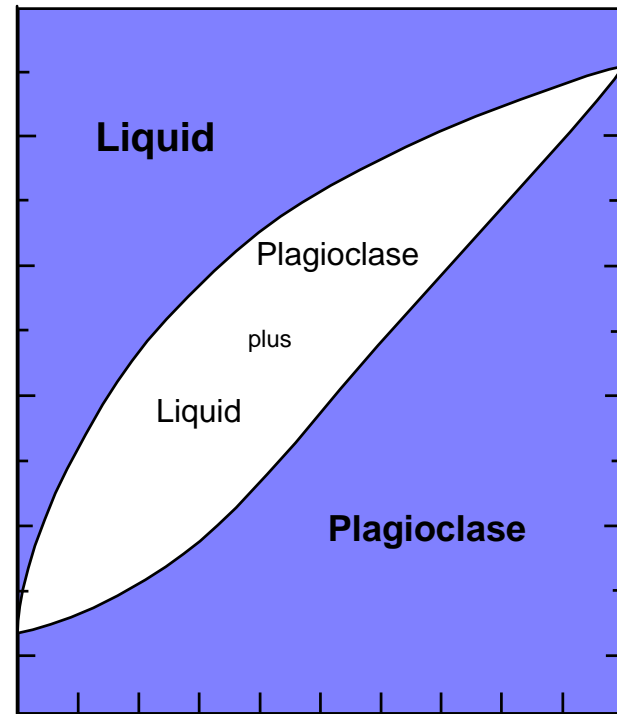
The rock probably represents an equilibrium mineral assemblage from within a metamorphic zone



# The Phase Rule in Metamorphic Systems

b)  $\phi < C$

Common with mineral systems that exhibit **solid solution**



# The Phase Rule in Metamorphic Systems

c)  $\phi > C$

A more interesting situation, and at least one of three situations must be responsible:

1)  $F < 2$

The sample is collected from a location right on a univariant reaction curve (isograd) or invariant point

# The Phase Rule in Metamorphic Systems

Consider the following three scenarios:

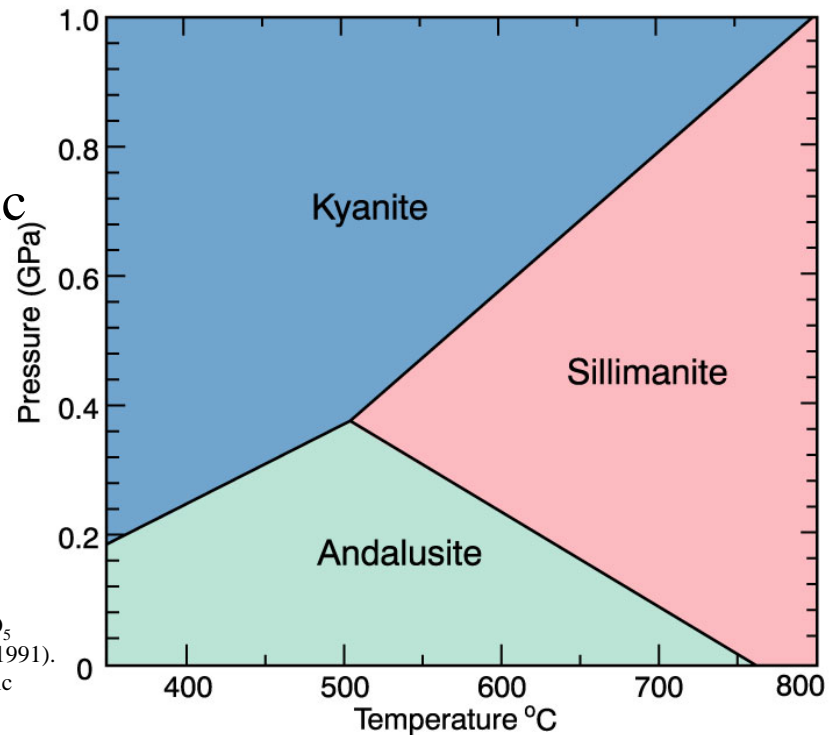
$$C = 1$$

$\phi = 1$  common

$\phi = 2$  rare

$\phi = 3$  only at the specific  
P-T conditions of the  
invariant point

(~ 0.37 GPa and  
500°C)



**Figure 21.9.** The P-T phase diagram for the system  $\text{Al}_2\text{SiO}_5$  calculated using the program TWQ (Berman, 1988, 1990, 1991). Winter (2010) An Introduction to Igneous and Metamorphic Petrology. Prentice Hall.

# The Phase Rule in Metamorphic Systems

## 2) Equilibrium has not been attained

The phase rule applies only to systems at **equilibrium**, and there could be any number of minerals coexisting if equilibrium is not attained

# The Phase Rule in Metamorphic Systems

## 3) We didn't choose the # of components correctly

Some guidelines for an appropriate choice of C

- Begin with a 1-component system, such as  $\text{CaAl}_2\text{Si}_2\text{O}_8$  (anorthite), there are 3 common types of major/minor components that we can add

### a) Components that generate a new phase

Adding a component such as  $\text{CaMgSi}_2\text{O}_6$  (diopside), results in an additional phase: in the binary Di-An system diopside coexists with anorthite below the solidus

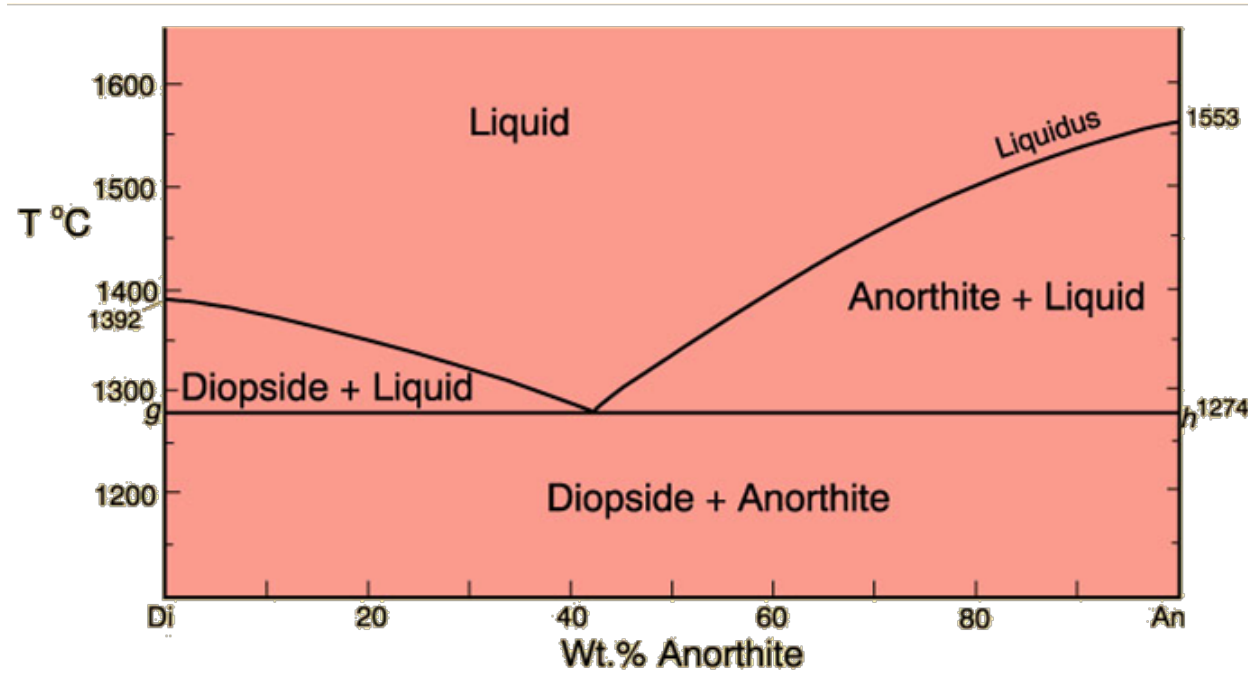


Fig. 6.11. Isobaric T-X phase diagram at atmospheric pressure. After Bowen (1915), Amer. J. Sci. 40, 161-185.

# The Phase Rule in Metamorphic Systems

## 3) We didn't choose the # of components correctly

### b) Components that substitute for other components

- Adding a component such as  $\text{NaAlSi}_3\text{O}_8$  (albite) to the 1-C anorthite system would dissolve in the anorthite structure, resulting in a **single solid-solution mineral** (plagioclase) below the solidus
  - Fe and Mn commonly substitute for Mg
  - Al may substitute for Si
  - Na may substitute for K

# The Phase Rule in Metamorphic Systems

## 3) We didn't choose the # of components correctly

### c) "Perfectly mobile" components

- Mobile components are either a freely mobile fluid component or a component that dissolves readily in a fluid phase and can be transported easily
- The chemical activity of such components is commonly controlled by factors **external** to the local rock system
- They are commonly ignored in deriving C for metamorphic systems



# The Phase Rule in Metamorphic Systems

Consider the very simple metamorphic system, MgO-H<sub>2</sub>O

- Possible natural phases in this system are **periclase** (MgO), **aqueous fluid** (H<sub>2</sub>O), and **brucite** (Mg(OH)<sub>2</sub>)
- How we deal with H<sub>2</sub>O depends upon whether water is perfectly mobile or not
- A **reaction** can occur between the potential phases in this system:



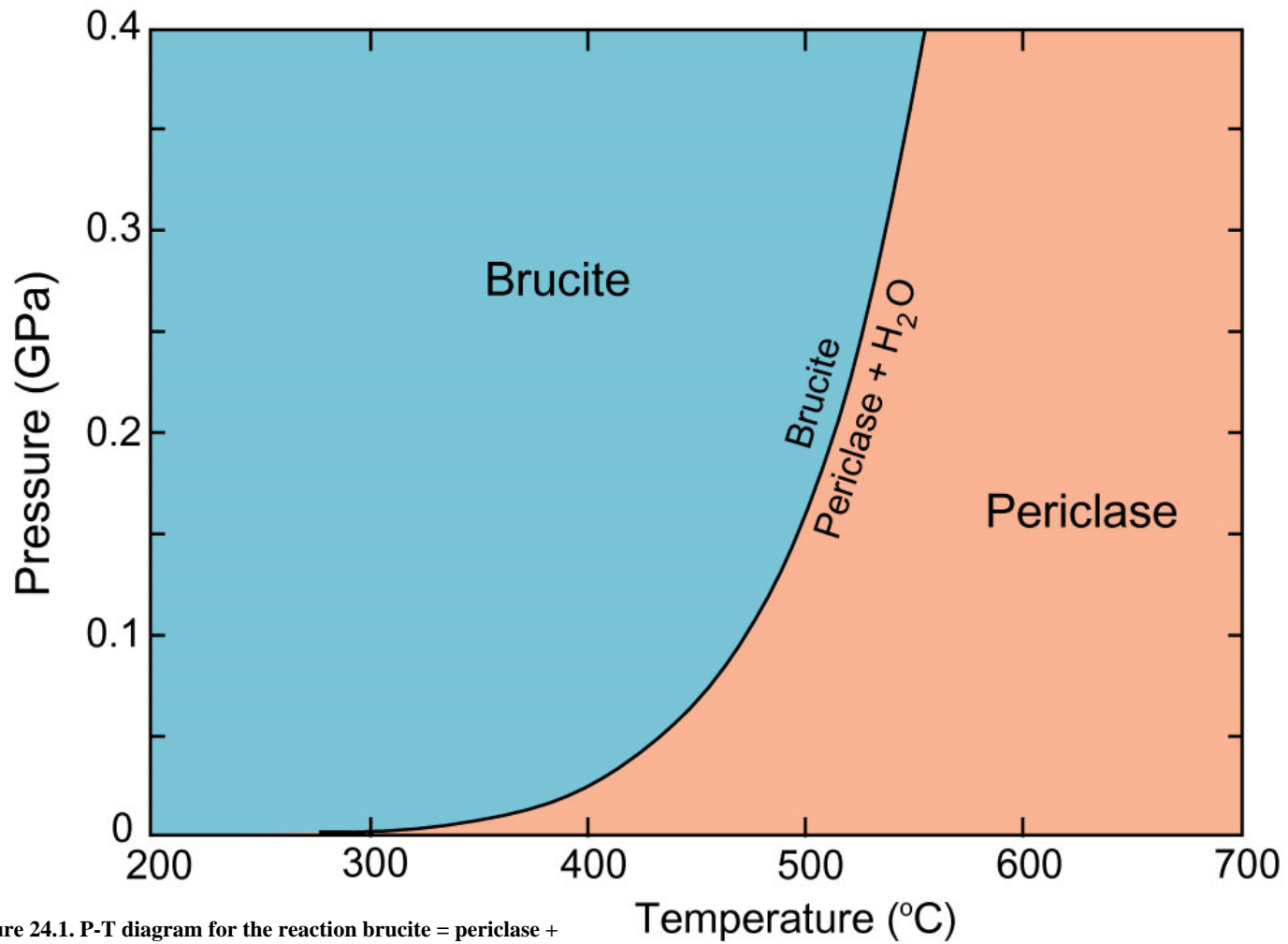


Figure 24.1. P-T diagram for the reaction brucite = periclase + water. From Winter (2010). *An Introduction to Igneous and Metamorphic Petrology*. Prentice Hall.

# The Phase Rule in Metamorphic Systems

## How do you know which way is correct?

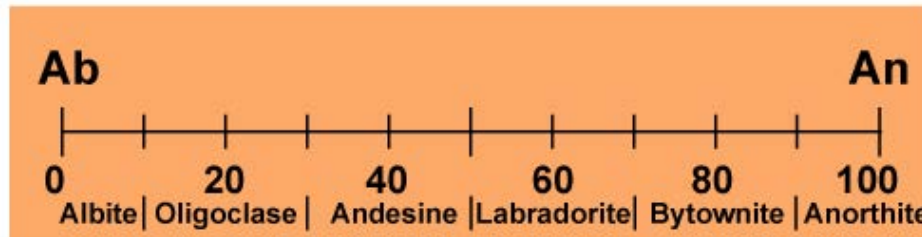
The rocks should tell you

- Phase rule = **interpretive** tool, **not predictive**
- If only see low- $\phi$  assemblages (e.g. Per **or** Bru in the MgO-H<sub>2</sub>O system) → some components may be mobile
- If many phases in an area it is unlikely that all is right on univariant curve, and may require the number of components to include otherwise mobile phases, such as H<sub>2</sub>O or CO<sub>2</sub>, in order to apply the phase rule correctly

# Chemographic Diagrams

**Chemographics** refers to the graphical representation of the chemistry of mineral assemblages

A simple example: the plagioclase system as a linear  $C = 2$  components plot:



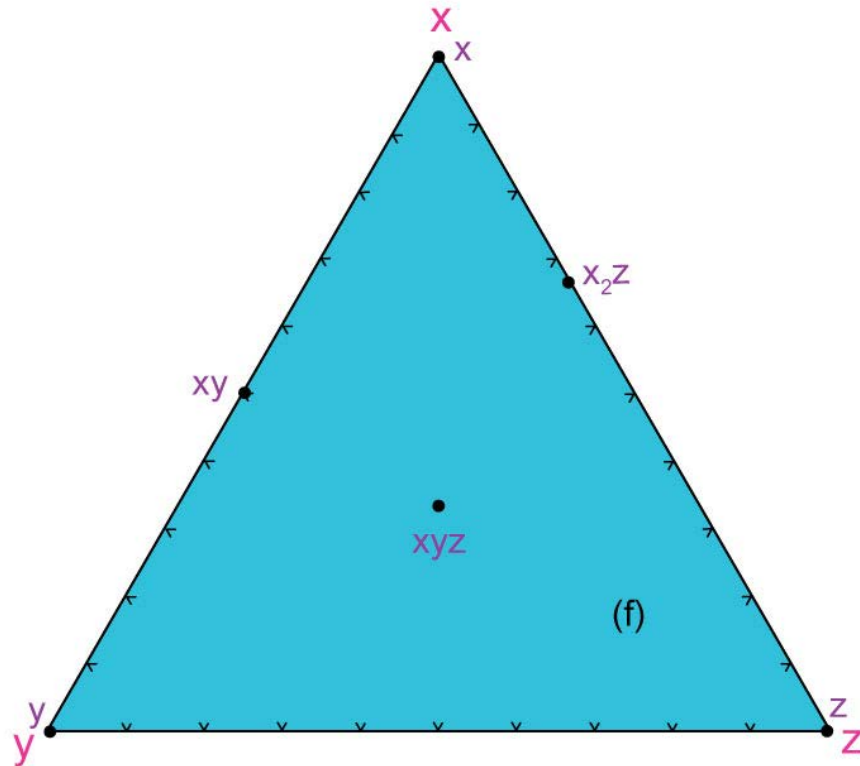
= 100

$An/(An+Ab)$

# Chemographic Diagrams

3-C mineral compositions are plotted on a triangular chemographic diagram as shown in Fig. 24.2

$x$ ,  $y$ ,  $z$ ,  $x_2z$ ,  $xyz$ , and  $xy$



Suppose that the rocks in our area have the following 5 assemblages:

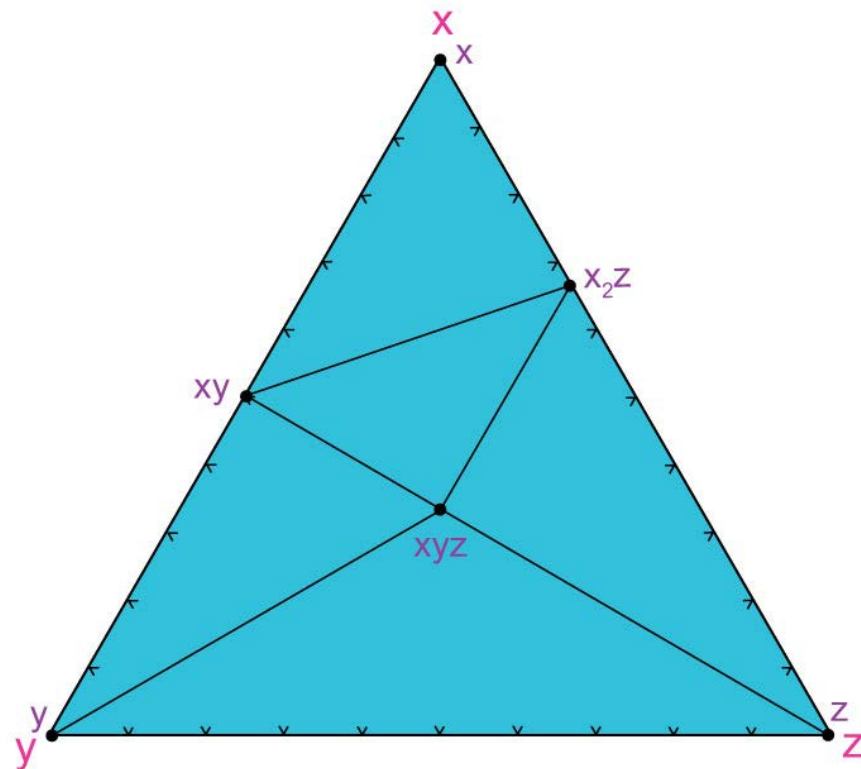
$x - xy - x_2z$

$xy - xyz - x_2z$

$xy - xyz - y$

$xyz - z - x_2z$

$y - z - xyz$



**Figure 24.2.** Hypothetical three-component chemographic compatibility diagram illustrating the positions of various stable minerals. Minerals that coexist compatibly under the range of P-T conditions specific to the diagram are connected by tie-lines. After Best (1982) *Igneous and Metamorphic Petrology*. W. H. Freeman.

Note that this subdivides the chemographic diagram into 5 sub-triangles, labeled (A)-(E)

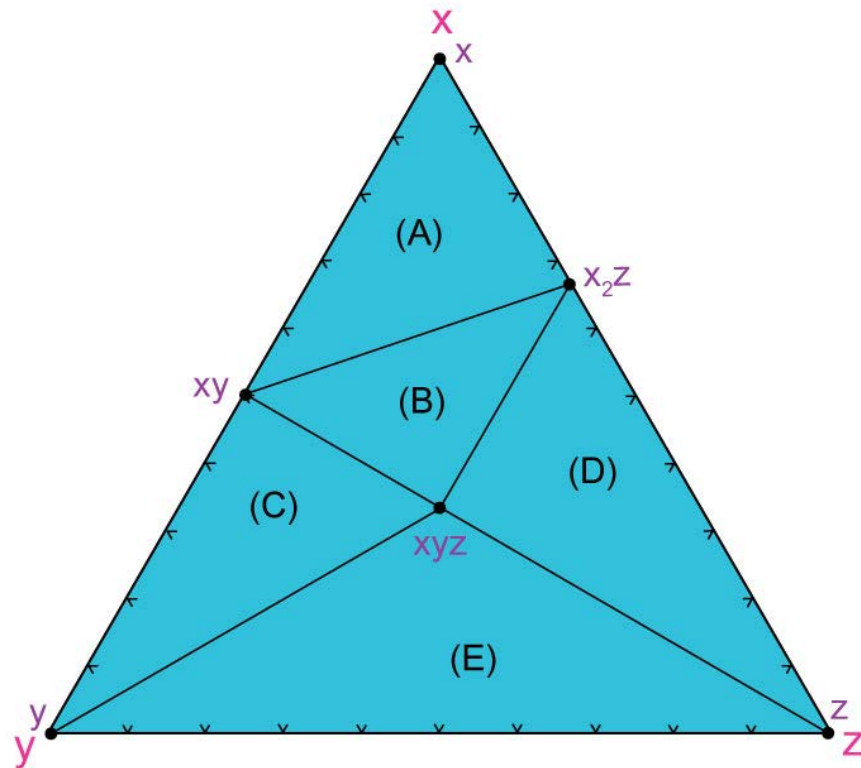
$x - xy - x_2z$

$xy - xyz - x_2z$

$xy - xyz - y$

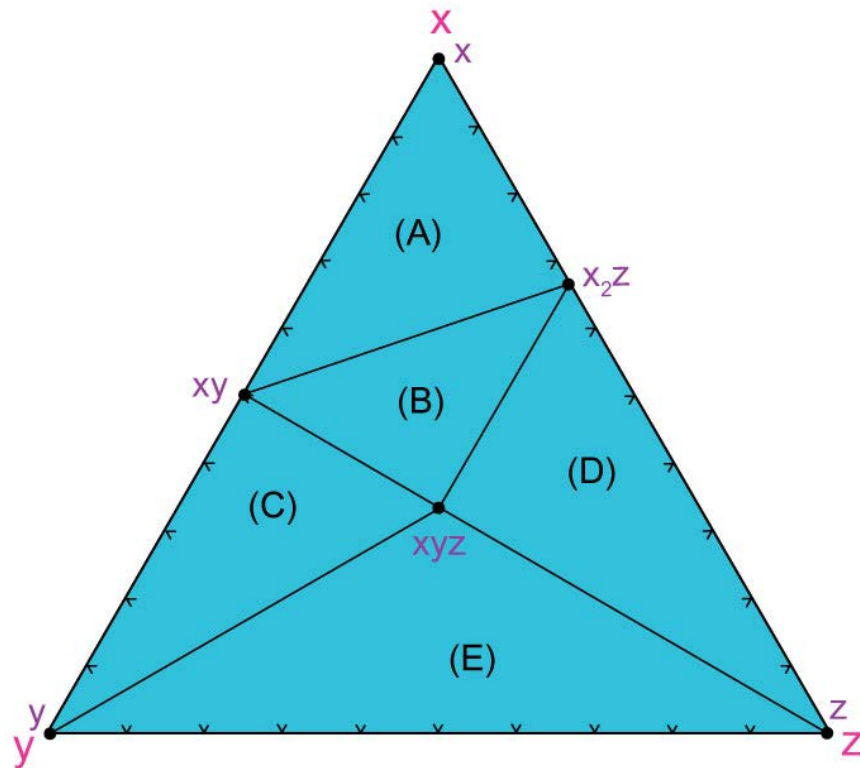
$xyz - z - x_2z$

$y - z - xyz$



Common point corresponds to 3 phases, thus  $\phi = C$

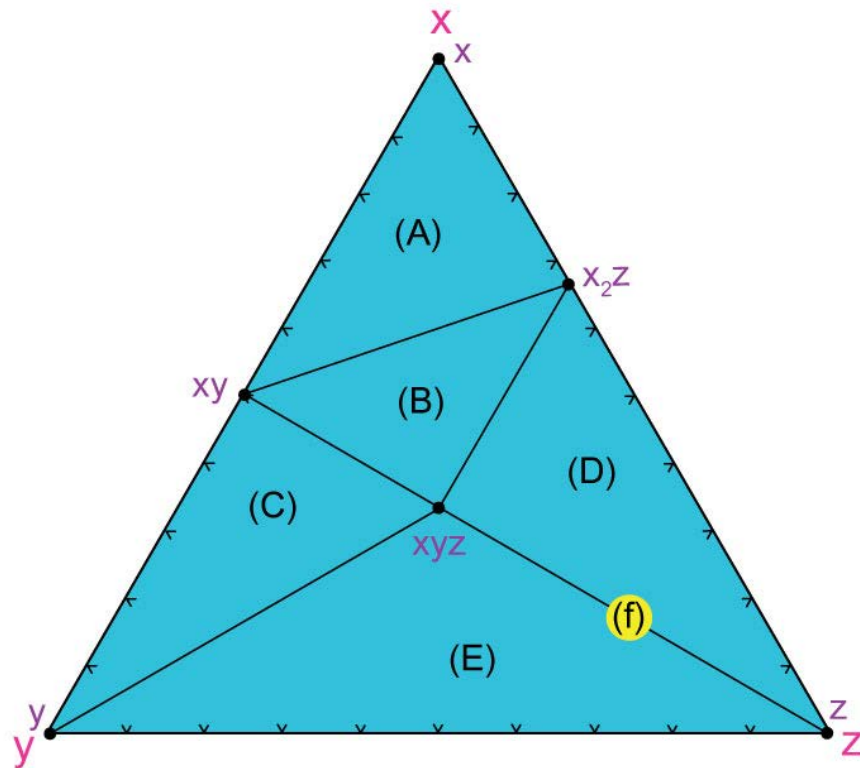
**Figure 24.2.** Hypothetical three-component chemographic compatibility diagram illustrating the positions of various stable minerals. Minerals that coexist compatibly under the range of P-T conditions specific to the diagram are connected by tie-lines. After Best (1982) *Igneous and Metamorphic Petrology*. W. H. Freeman.





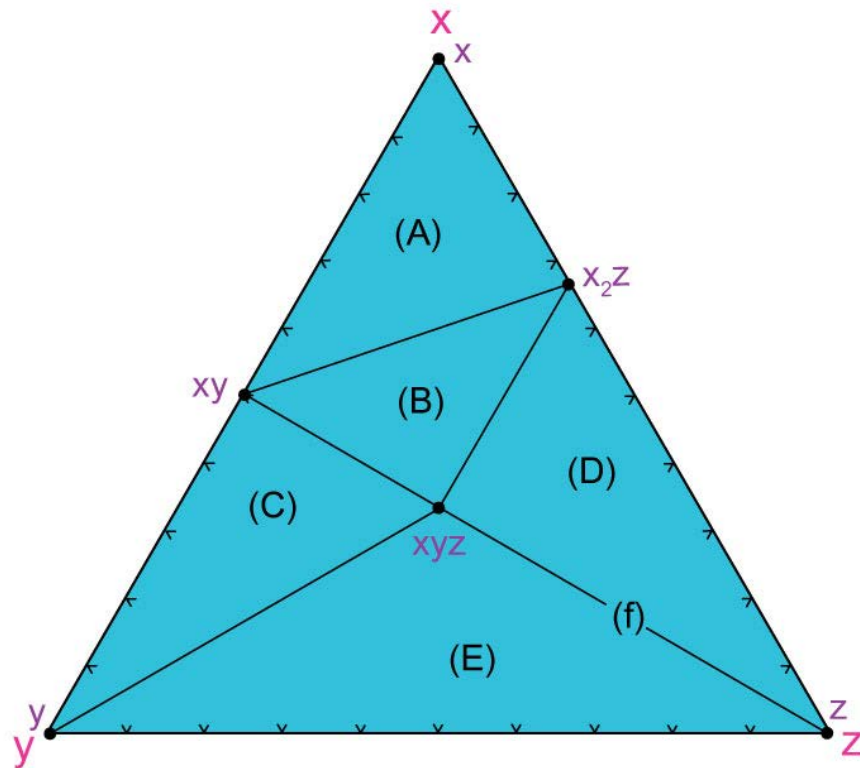
What happens if you pick a composition that falls directly on a tie-line, such as point (f)?

**Figure 24.2.** Hypothetical three-component chemographic compatibility diagram illustrating the positions of various stable minerals. Minerals that coexist compatibly under the range of P-T conditions specific to the diagram are connected by tie-lines. After Best (1982) *Igneous and Metamorphic Petrology*. W. H. Freeman.



In the unlikely event that the bulk composition equals that of a single mineral, such as  $xyz$ , then  $\phi = 1$ , but  $C = 1$  as well

“compositionally degenerate”



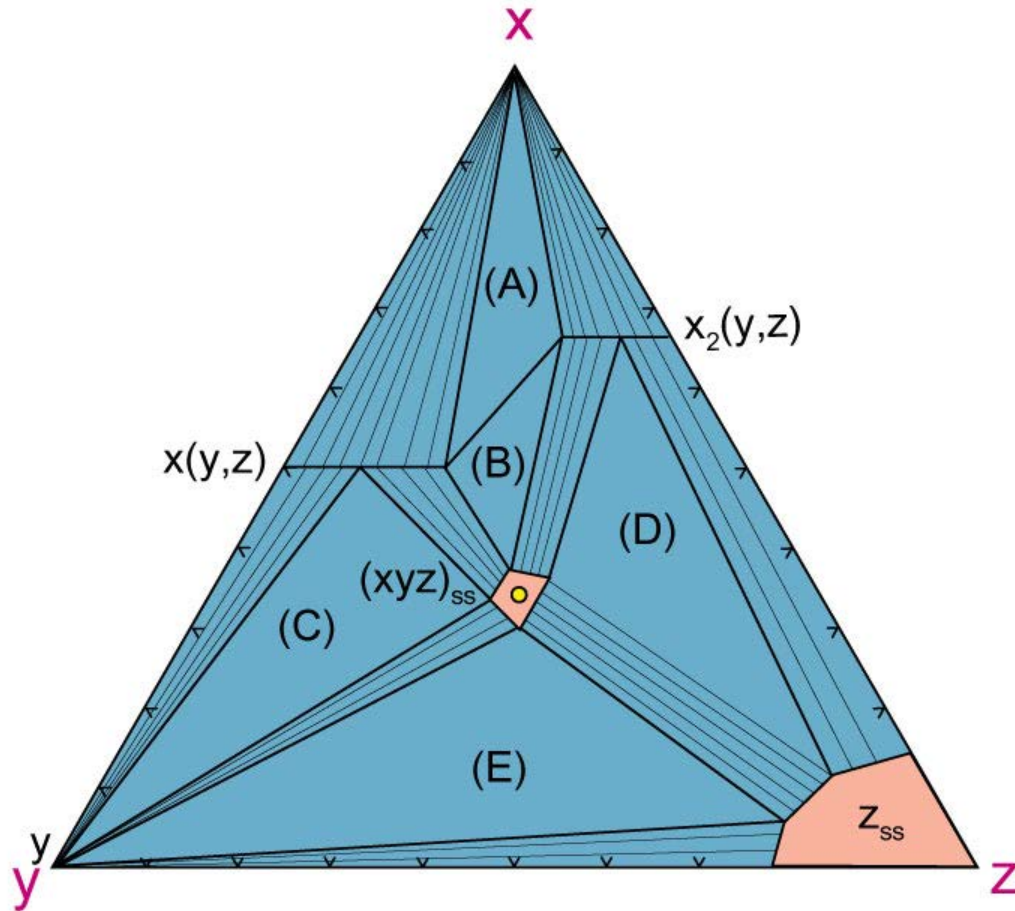
# Chemographic Diagrams

Valid compatibility diagram **must be referenced to a specific range of P-T conditions, such as a zone in some metamorphic terrane**, because the stability of the minerals and their groupings vary as P and T vary

- Previous diagram refers to a P-T range in which the fictitious minerals **x, y, z, xy, xyz, and  $x_2z$**  are all stable and occur in the groups shown
- At different grades the diagrams change
  - Other minerals become stable
  - Different arrangements of the same minerals (different tie-lines connect different coexisting phases)

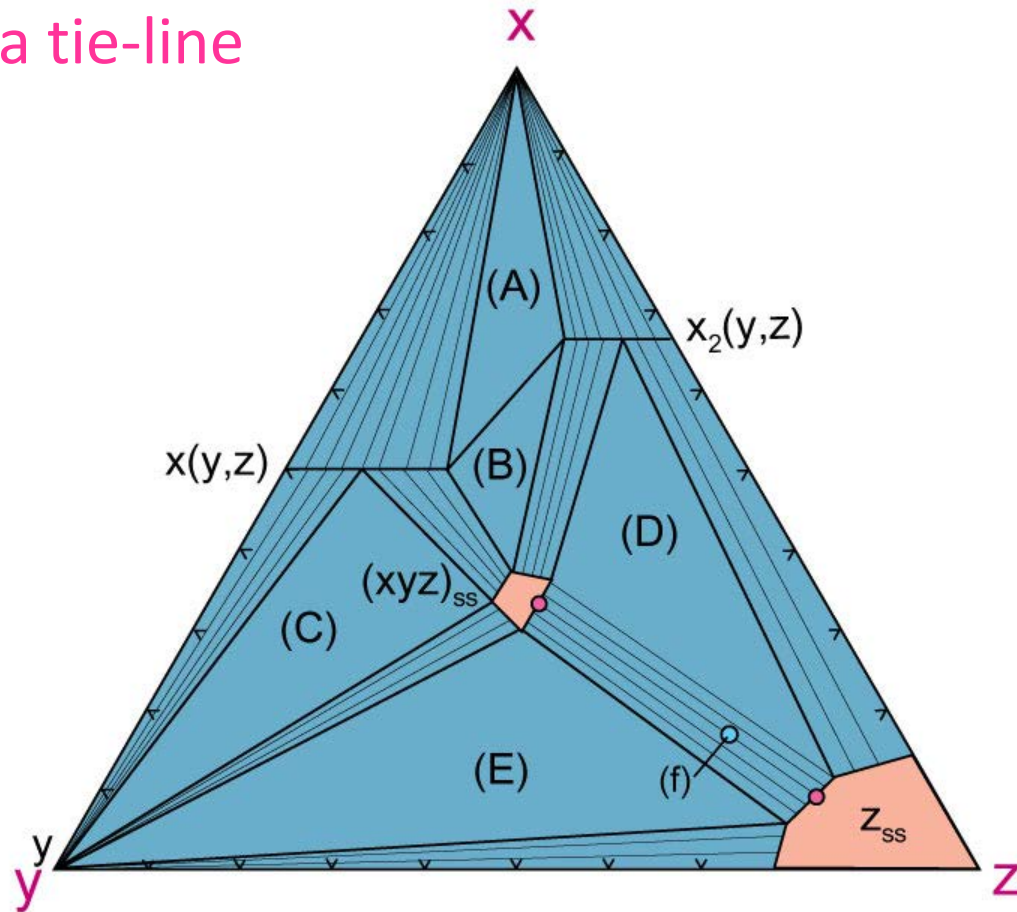
A diagram in which some minerals exhibit **solid solution**

**Figure 24.3.** Hypothetical three-component chemographic compatibility diagram illustrating the positions of various stable minerals, many of which exhibit solid solution. After Best (1982) *Igneous and Metamorphic Petrology*. W. H. Freeman.



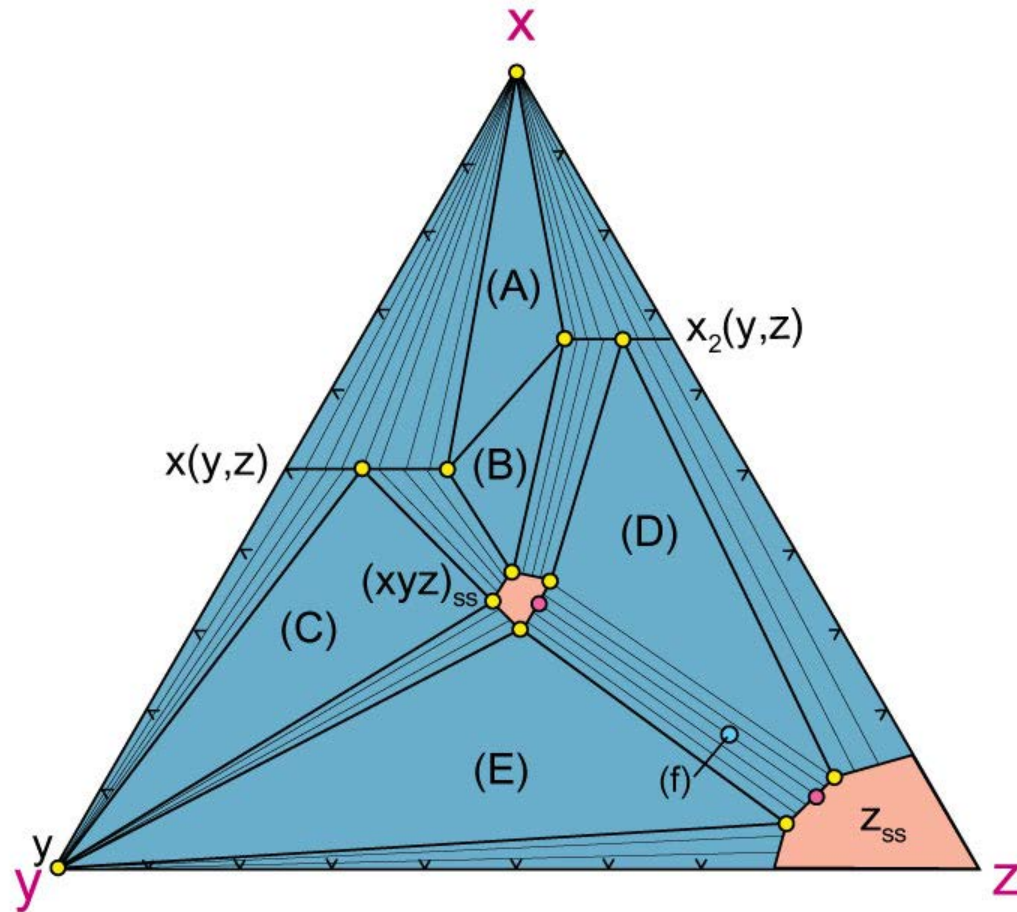
If  $X_{\text{bulk}}$  on a tie-line

**Figure 24.3.** Hypothetical three-component chemographic compatibility diagram illustrating the positions of various stable minerals, many of which exhibit solid solution. After Best (1982) *Igneous and Metamorphic Petrology*. W. H. Freeman.



$X_{\text{bulk}}$  in 3-phase triangles  $F = 2$  (P & T) so  $X_{\text{min}}$  fixed

**Figure 24.3.** Hypothetical three-component chemographic compatibility diagram illustrating the positions of various stable minerals, many of which exhibit solid solution. After Best (1982) *Igneous and Metamorphic Petrology*. W. H. Freeman.



# Chemographic Diagrams for Metamorphic Rocks

- Most common natural rocks contain the major elements:  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{K}_2\text{O}$ ,  $\text{CaO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{FeO}$ ,  $\text{MgO}$ ,  $\text{MnO}$  and  $\text{H}_2\text{O}$  such that  $C = 9$
- **Three** components is the maximum number that we can easily deal with in two dimensions
- What is the “right” choice of components?
- Some simplifying methods:

## 1) Simply “ignore” components

- Trace elements
- Elements that enter only a single phase  
(we can drop both the component and the phase without violating the phase rule)
- Perfectly mobile components



## 2) Combine components

Components that substitute for one another in a solid solution: (Fe + Mg)

## 3) Limit the types of rocks to be shown

Only deal with a sub-set of rock types for which a simplified system works

## 4) Use projections

I' ll explain this shortly

The phase rule and compatibility diagrams are rigorously correct when applied to **complete** systems

- A triangular diagram thus applies rigorously only to *true* (but rare) 3-component systems
- If drop components and phases, combine components, or project from phases, we face some issues:
  - Gain by being able to graphically display the simplified system, and many aspects of the system's behavior become apparent
  - Lose a rigorous correlation between the behavior of the simplified system and reality

# The ACF Diagram

- Illustrate metamorphic mineral assemblages in mafic rocks on a simplified 3-C triangular diagram
- Concentrate only on the minerals that appeared or disappeared during metamorphism, thus acting as indicators of metamorphic grade

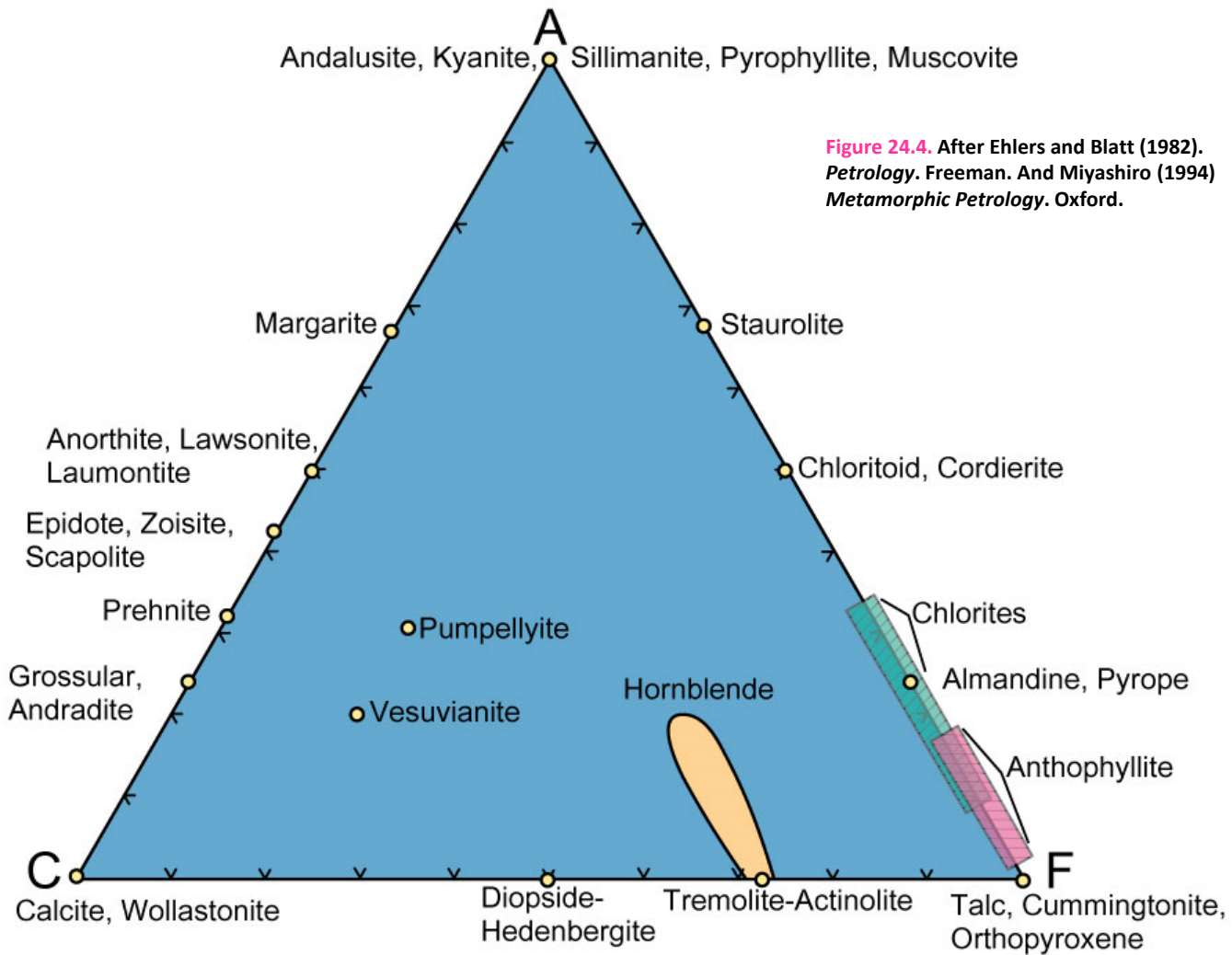


Figure 24.4. After Ehlers and Blatt (1982).  
*Petrology*. Freeman. And Miyashiro (1994)  
*Metamorphic Petrology*. Oxford.

# The ACF Diagram

The three **pseudo**-components are all calculated on a molecular basis:



# The ACF Diagram



Why the subtraction?

- Na and K in the average mafic rock are typically combined with Al to produce Kfs and Albite
- In the ACF diagram, we are interested only in the other Al-bearing metamorphic minerals, and thus only in the amount of  $\text{Al}_2\text{O}_3$  that occurs in excess of that combined with  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  (in albite and K-feldspar)
- Because the ratio of  $\text{Al}_2\text{O}_3$  to  $\text{Na}_2\text{O}$  or  $\text{K}_2\text{O}$  in feldspars is 1:1, we subtract from  $\text{Al}_2\text{O}_3$  **an amount equivalent to  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$**  in the same 1:1 ratio

# The ACF Diagram



# The ACF Diagram

By creating these three pseudo-components, Eskola reduced the number of components in mafic rocks from 8 to 3

- Water is omitted under the assumption that it is perfectly mobile
- Note that  $\text{SiO}_2$  is simply ignored
  - We shall see that this is equivalent to projecting from quartz
- In order for a projected phase diagram to be truly valid, **the phase from which it is projected must be present** in the mineral assemblages represented



# The ACF Diagram

An example:

Anorthite  $\text{CaAl}_2\text{Si}_2\text{O}_8$

$A = 1 + 0 - 0 - 0 = 1$ ,  $C = 1 - 0 = 1$ , and  $F = 0$

Provisional values sum to 2, so we can normalize to 1.0 by multiplying each value by  $\frac{1}{2}$ , resulting in

$$A = 0.5$$

$$C = 0.5$$

$$F = 0$$

Where does Ab plot? Plagioclase?

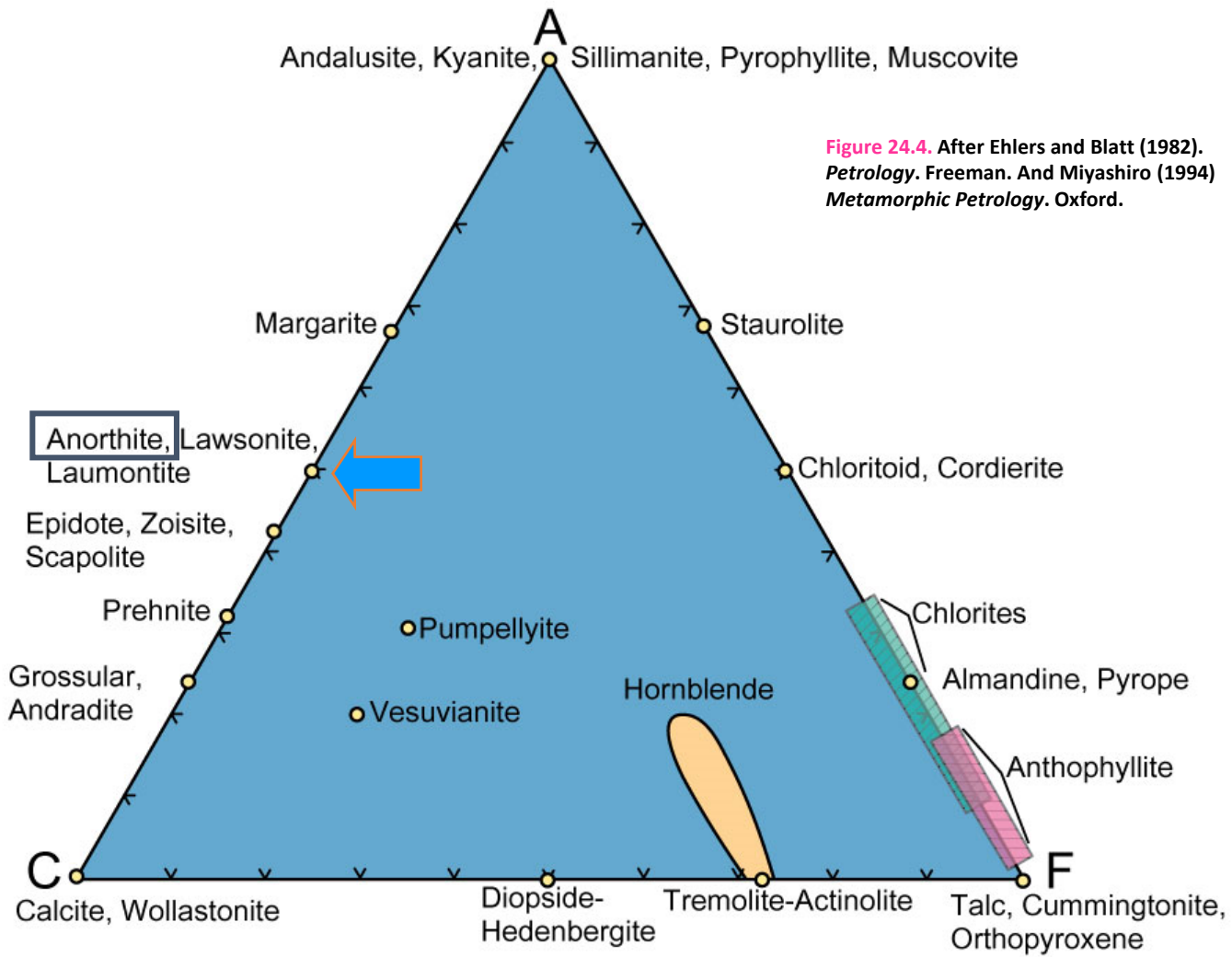


Figure 24.4. After Ehlers and Blatt (1982).  
*Petrology*. Freeman. And Miyashiro (1994)  
*Metamorphic Petrology*. Oxford.

# The ACF Diagram

## Plotting Rules

1. Obtain molecular proportions of oxides comprising the rock or mineral.
2. Component A equals the molecular proportions of  $\text{Al}_2\text{O}_3$  minus  $\text{Na}_2\text{O}$  minus  $\text{K}_2\text{O}$ . This formulation assumes that plagioclase is present and any  $\text{K}_2\text{O}$  and  $\text{Na}_2\text{O}$  present is in the form of K-feldspar ( $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ ) and albite ( $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ ) dissolved in the plagioclase; note the 1 : 1 ratios of  $\text{K}_2\text{O}$  and  $\text{Na}_2\text{O}$  to  $\text{Al}_2\text{O}_3$  in these alkali feldspars. If muscovite or biotite are present, this calculation for A is invalid
3. Component C equals the molecular proportions of  $\text{CaO}$  minus  $\frac{10}{3}(\text{P}_2\text{O}_5)$  minus  $\text{CO}_2$ . These subtractions allow for the presence of ideal apatite ( $10\text{CaO} \cdot 3\text{P}_2\text{O}_5$ ) and calcite ( $\text{CaO} \cdot \text{CO}_2$ ).
4. Component F equals the molecular proportions of  $\text{FeO}$  plus  $\text{MgO}$ . In some cases molecular proportions equal to  $\text{TiO}_2$  and  $\text{Fe}_2\text{O}_3$  may be subtracted to allow for the presence of ideal ilmenite ( $\text{FeO} \cdot \text{TiO}_2$ ) and magnetite ( $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ ).
5. The sum of  $A + C + F$  is found and the percentages of A, C, and F calculated for plotting

A typical ACF compatibility diagram, referring to a specific range of P and T (the kyanite zone in the Scottish Highlands)

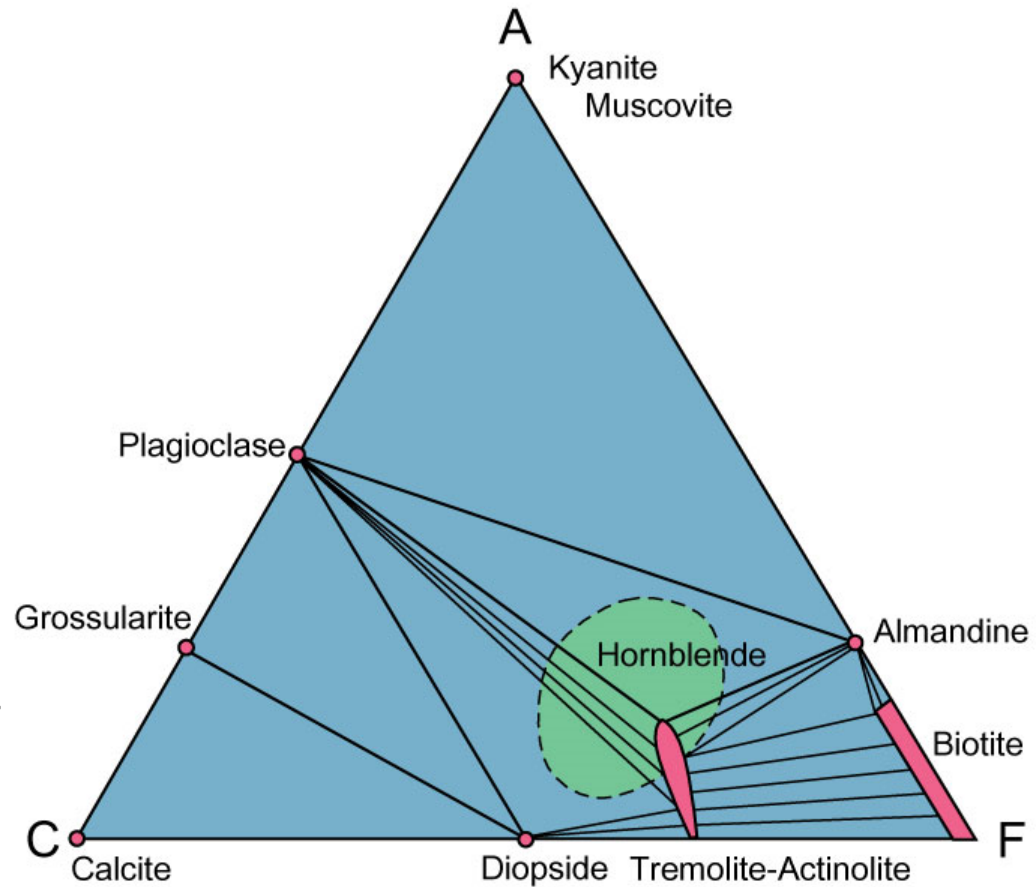


Figure 24.5. After Turner (1981). *Metamorphic Petrology*. McGraw Hill.