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

\[ F = C - \phi + 2 \]

\( F = \# \text{ degrees of freedom} \)

The number of independently \textit{intensive} parameters that must be specified in order to completely determine the system at \textit{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 at \textit{equilibrium conditions}.

\( \phi \) = # of phases

phases are \textit{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: \( H_2O \) – 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  
\( \text{The number of independently intensive parameters that} \)  
\( \text{must be specified in order to completely determine the} \)  
\( \text{system} \)  
\( \phi = \) # of phases  
\( \text{phases are mechanically separable constituents} \)  
\( C = \) minimum # of components (chemical constituents that must  
\( \text{be specified in order to define all phases} \)  
\( 2 = \) 2 intensive parameters  
\( \text{Usually = temperature and pressure for us geologists} \)
The Phase Rule in Metamorphic Systems

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

\[
F = C - \phi + 2 \geq 2
\]

\[
\phi \leq C \quad \text{(Eq 24.1)}
\]

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

(\(~0.37\ \text{GPa and } 500^\circ\text{C}\))

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 CaAl$_2$Si$_2$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 CaMgSi$_2$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 NaAlSi$_3$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-H₂O

- Possible natural phases in this system are periclase (MgO), aqueous fluid (H₂O), and brucite (Mg(OH)₂).
- How we deal with H₂O depends upon whether water is perfectly mobile or not.
- A reaction can occur between the potential phases in this system:

  \[ \text{MgO} + \text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 \quad \text{Per} + \text{Fluid} = \text{Bru} \]
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-φ assemblages (e.g. Per or Bru in the MgO-H₂O 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 H₂O or CO₂, 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:

\[
\frac{\text{An}}{\text{An} + \text{Ab}} = 100
\]

An/(An+Ab)
Chemographic Diagrams

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

$x, y, z, x_2z, xyz, \text{ and } xy$
Suppose that the rocks in our area have the following 5 assemblages:

\[
\begin{align*}
&x - xy - x_2Z \\
&xy - xyz - x_2Z \\
&xy - xyz - y \\
&xyz - z - x_2Z \\
&y - z - xyz
\end{align*}
\]

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 \textit{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: SiO$_2$, Al$_2$O$_3$, K$_2$O, CaO, Na$_2$O, FeO, MgO, MnO and H$_2$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)
The ACF Diagram

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

\[
A = \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 - \text{Na}_2\text{O} - \text{K}_2\text{O} \\
C = \text{CaO} - 3.3 \text{P}_2\text{O}_5 \\
F = \text{FeO} + \text{MgO} + \text{MnO}
\]
The ACF Diagram

\[ A = \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 - \text{Na}_2\text{O} - \text{K}_2\text{O} \]

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

\[ C = \text{CaO} - 3.3 \ P_2O_5 \]

\[ F = \text{FeO} + \text{MgO} + \text{MnO} \]
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 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 CaAl$_2$Si$_2$O$_8$

\[ A = 1 + 0 - 0 - 0 = 1, \quad C = 1 - 0 = 1, \quad \text{and} \quad F = 0 \]

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)
The ACF Diagram

Plotting Rules

1. Obtain molecular proportions of oxides comprising the rock or mineral.

2. Component A equals the molecular proportions of Al₂O₃ minus Na₂O minus K₂O. This formulation assumes that plagioclase is present and any K₂O and Na₂O present is in the form of K-feldspar (K₂O • Al₂O₃ • 6SiO₂) and albite (Na₂O • Al₂O₃ • 6SiO₂) dissolved in the plagioclase; note the 1:1 ratios of K₂O and Na₂O to Al₂O₃ in these alkali feldspars. If muscovite or biotite are present, this calculation for A is invalid.

3. Component C equals the molecular proportions of CaO minus \( \frac{10}{3} \) (P₂O₅) minus CO₂. These subtractions allow for the presence of ideal apatite (10CaO • 3P₂O₅) and calcite (CaO • CO₂).

4. Component F equals the molecular proportions of FeO plus MgO. In some cases molecular proportions equal to TiO₂ and Fe₂O₃ may be subtracted to allow for the presence of ideal ilmenite (FeO • TiO₂) and magnetite (FeO • Fe₂O₃).

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)