

Stable Mineral Assemblages

Reference: Winter Chapter 24

The Phase Rule

Phase rule, as applied to systems at equilibrium:

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

ϕ is the number of phases in the system

C is the number of components: the minimum number of chemical constituents required to specify every phase in the system

F is the number of degrees of freedom: the number of independently variable intensive parameters of state (such as temperature, pressure, the composition of each phase, etc.)

The Common Situation, $F \geq 2$

The phase rule is adjusted accordingly:

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

$$\phi \leq C \quad (24-1)$$

This is Goldschmidt's mineralogical phase rule, or simply the mineralogical phase rule

Equilibrium 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 thereby excluded from consideration unless specifically stated

Metamorphic Systems

- Typical metamorphic samples are collected from within a zone, and not from exactly on an isograd
- Likewise, a random point anywhere on a phase diagram is likely within a divariant field and not on a univariant curve or invariant point
- The most common situation is divariant ($F = 2$), meaning that P and T may vary independently without affecting the mineral assemblage

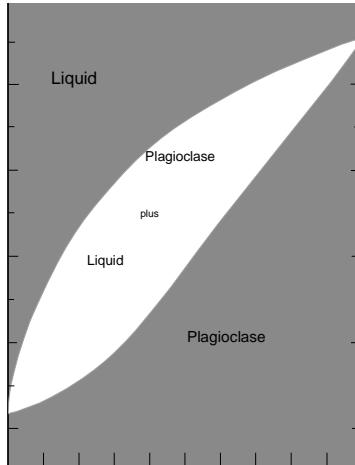
Components and Phases, $\phi = C$

This is the standard divariant situation in metamorphic rocks

Such rocks probably represent an equilibrium mineral assemblage from within a metamorphic zone

If $\phi < C$

This is common with mineral systems that exhibit solid solution



If $\phi > C$

Occurs in one of three possible situations:

1) $F < 2$

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

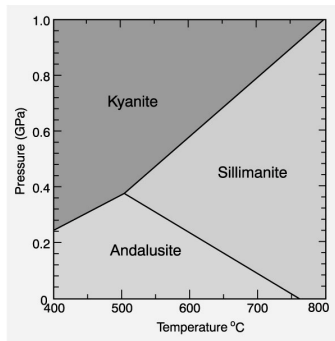
2) Equilibrium was not attained

3) Number of components chosen incorrectly

Consider the following three scenarios:

$C = 1$ (Al_2SiO_5)

- $\phi = 1$ common
- $\phi = 2$ rare
- $\phi = 3$ only at the specific P-T conditions of the invariant point (~ 0.37 GPa and 500°C)



From Winter (2001)

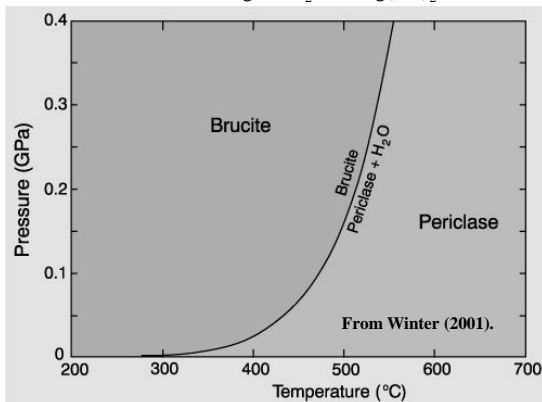
The System $\text{MgO}-\text{H}_2\text{O}$

- Possible natural phases in this system are periclase (MgO), aqueous fluid (H_2O), and brucite ($\text{Mg}(\text{OH})_2$)
- How we deal with H_2O depends upon whether water is perfectly mobile or not
- A reaction can occur between the potential phases in this system:



The retrograde reaction, as written, occurs as the rock cools and hydrates

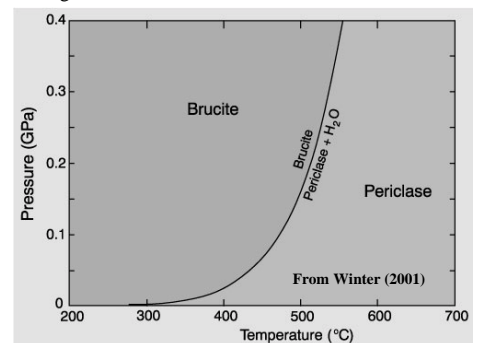
As the system cools to the temperature of the reaction curve, periclase reacts with water to form brucite: $\text{MgO} + \text{H}_2\text{O} \rightarrow \text{Mg}(\text{OH})_2$



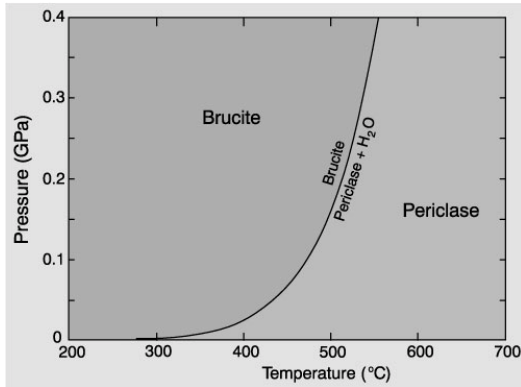
On the reaction line periclase coexists with brucite: $\phi = C + 1$; $F = 1$

To leave the curve, all the periclase must be consumed by the reaction, and brucite remains as the solitary phase:

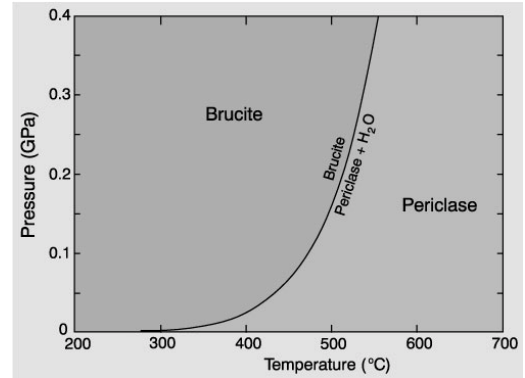
$\phi = 1$ and $C = 1$ again



Once the water is gone, the excess periclase remains stable, together with brucite, as conditions change into the brucite stability field

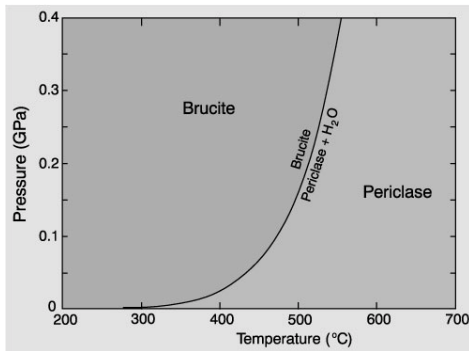


We thus conclude that periclase can be stable anywhere on the whole diagram, provided that the quantity of water is insufficient to permit the reaction to brucite to go to completion



At any point (other than on the univariant curve itself) we could expect to find two phases, not one!

ϕ = brucite + periclase below the reaction curve (if water is limited), or periclase + water above the curve



How can you determine the correct interpretation?

The rocks should tell you.

- The phase rule is an interpretive tool, not a predictive tool, and does not tell the rocks how to behave
- If you only see low- ϕ assemblages (e.g. Per or Bru in the MgO-H₂O system), then some components may be mobile
- If you observe assemblages that have many phases in an area (e.g. periclase + brucite), it is unlikely that so much of the area is right on a 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

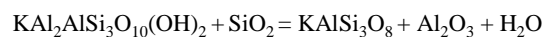
Coupled Reactions

- Involve several minerals
- Appearance or disappearance of key minerals
 - Depends on rock compositions
- Presence or absence of quartz is a factor

Stability of Muscovite

With quartz Mus decomposes at a lower T

Muscovite + Quartz = K-spar + Corundum + water



Without quartz Mus decomposes at a higher T

Muscovite = K-spar + Sillimanite + water



Reactions in Rocks

- More complicated than in theory
- Generally the conditions of metamorphism can be estimated