EENS 2120	Petrology
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Metamorphic Mineral Assemblages	

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The mineral assemblages that occur in metamorphic rocks depend on four factors:

- The bulk chemical composition of the original rock.

- The pressure reached during metamorphism.

- The temperature reached during metamorphism.

- The composition of any fluid phase that was present during metamorphism.

If a rock is taken to some higher pressure and temperature then the mineral assemblage that develops should represent stable chemical equilibrium if the conditions are held for a long enough period of time that equilibrium can be achieved. Since metamorphism usually involves long periods of geologic time, most metamorphic rocks represent an equilibrium mineral assemblage.

The Phase Rule for Metamorphism

Recall that the phase rule states that

$$F = C + 2 - P$$

where F = the variance of the system or number of degrees of freedom,

C = the number of components in the system,

and P = the number of phases present.

the 2 stands for the two independent variables, Pressure and Temperature.

If you think about it, in metamorphic rocks where temperature and pressure can both vary during metamorphism, the most likely case would be to find a divariant (F=2) assemblage of phases. A univariant assemblage (F=1) would be less likely to occur, and an invariant assemblage (F=0) would represent equilibrium at a fixed point in temperature and pressure, and would thus be even less likely to occur.

So, for F=2, C=P, the number of phases present in a rock for the more common divariant assemblage will be equal to the number of components. If P is greater than C, then one of three possibilities exist for the mineral assemblage.

1. The assemblage represents a non-equilibrium assemblage (perhaps due to incomplete chemical reactions or due to the presence of retrograde minerals that developed during cooling, uplift, or unroofing of the metamorphic rock).

2. The assemblage represents univariant or invariant equilibrium, as discussed above.

3. The number of components have not been chosen correctly.

If possibility (1) is the reason for the lack of correspondence with the phase rule, it can usually be determined by close inspection of the rock. Reaction textures present in the rock might indicate incomplete reaction. Known retrograde minerals, i.e. those stable at lower pressures and temperatures than the rest of the minerals in the rock, could be identified. These retrograde phases could then be subtracted from the number of phases being considered and the phase rule could be reapplied to only the phases known to be in equilibrium. (For example, the presence of chlorite in amphibolite and granulite facies rocks would be indicative that the chlorite is a retrograde mineral or mineral produced during weathering, and thus would not be considered in the application of the phase rule.)

Possibility 2 could always occur, and if the number of components is chosen correctly and retrograde minerals are not considered, then this may be the case.

The number of components, as stated in the phase rule, must be chosen so as to represent the minimum number necessary to form all phases possible in the rock. Recall that the number of components is not strictly the number of oxide components or the number of elements as reported in a chemical analysis of the rock. If we just consider the major phases that make up metamorphic rocks and consider that some ions freely substitute for one another in solid solutions, then the number of components can often be reduced to 7 or 8. For example:

1. $K_2O \cdot Al_2O_3$ (based on the ratio of K to Al in the alkali feldspars)

2. $(Ca,Na_2)O \cdot Al_2O_3$ (based on the ratio of Ca and Na to Al in the plagioclase)

3. $(Si,Ti)O_2$ - based on the common substitution of Ti into tetrahedral sites in most silicates)

4. $(Fe,Mn)O$ - based on the common substitution of Mn for Fe in minerals.

5. MgO - usually needed because Fe-Mg solid solution compositions are both temperature and pressure dependent. (although sometimes these two are combined, which would reduce the total number of components by 1).

6. $(Al,Fe^{+3})_2O_3$ - based on the commonly observed substitution of Fe^{+3} for $Al^{+3}Al$ in minerals.

7. H_2O - usually present in a fluid phase, but also an important component of hydrous minerals.

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8. CO_2 - also usually present in a fluid phase, but also an important component in carbonate minerals.

If H_2O and CO_2 are assumed to be always present and available to form hydrous and carbonate minerals, then the number of components can be reduced to 5 or 6. Thus for a divariant assemblage (F=2) we would expect to find 5 or 6 different mineral phases present in a metamorphic rock, or up to 8 phases if the assemblage is invariant.

This is the basis for the construction of the AKF and ACF diagrams discussed previously, where the number of components have been reduced to 4, by making assumptions like quartz and alkali feldspar can always be present. Still, you are cautioned that the above analysis is not always generally applicable, and each rock must be considered on a case-by case scenario.

Example of Progressive Metamorphism

Progressive or *prograde metamorphism* occurs as the temperature and pressure are increased on the rock. As the pressure and temperature increase, a rock of a given chemical composition is expected to undergo a continuous series of chemical reactions between its constituent minerals and any fluid phase present to produce a series of new mineral assemblages that are stable at the higher pressures and temperatures. We here illustrate how the mineral assemblages might change in a hypothetical set of rocks, starting with a low grade mineral assemblage as shown in the ACF diagram below.

First, consider the compositions of various types of rocks. Pelitic and quartzo-feldspathic rocks are relatively aluminous, calcareous rocks are relatively rich in the C component, and basic rocks are relative rich in the F component. At some low temperature and pressure typical of low grade metamorphism, pelitic and quartzo feldspathic rocks in this example would consist of epidote, chlorite, andalusite, muscovite, and possibly quartz, k-spar, muscovite, and albite. Calcareous rocks would contain epidote, calcite, actinolite, and possibly quartz, albite, and k-spar. Basic rocks would consist of epidote, chlorite, actinolite, and possibly, quartz, albite, and k-spar. Ultramafic rocks would consist of actinolite, chlorite and talc.

Low Grade Rocks
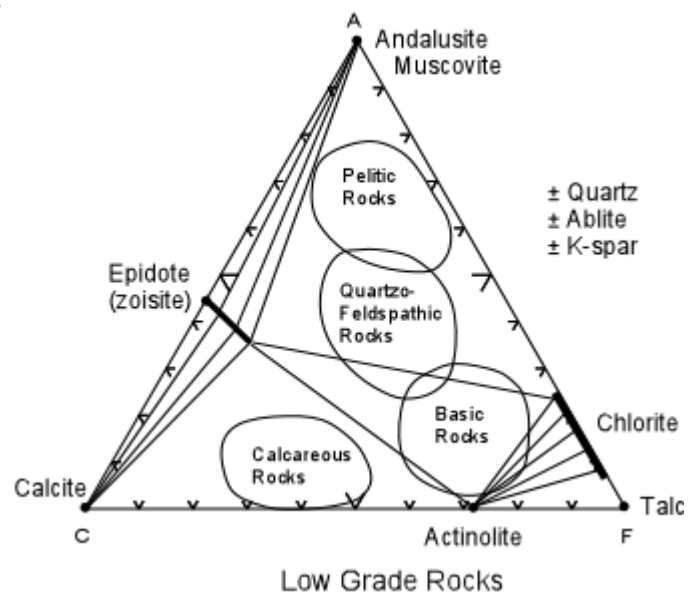
At some higher pressure and temperature the assemblage might change as follows: pelitic rocks would consist of sillimanite, plagioclase, cordierite, muscovite, and possibly quartz and k-spar (the albite is now included in the plagioclase). Quartzo-feldspathic rocks would consist of plagioclase, cordierite, biotite, and likely quartz and k-spar. Calcareous rocks would consist of grossularite, calcite and hornblende. Basic rocks would contain plagioclase, biotite, hornblende, and perhaps quartz and k-spar. Ultramafic rocks would consist of biotite anthopyllite, and hornblende.


Higher Grade Rocks
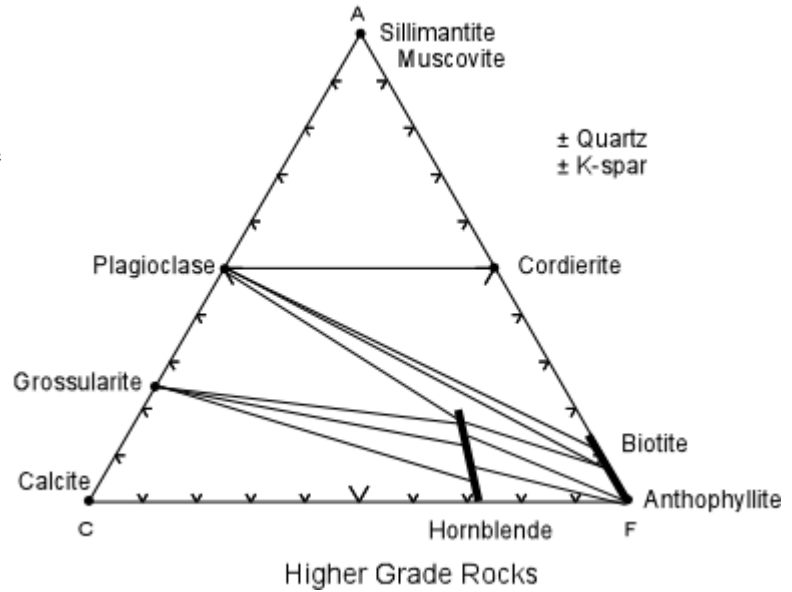
Now let's consider what happened in jumping from the pressure/ temperature conditions of the first diagram to those of the second diagram. First, we list the phases that have disappeared and those that have appeared:

Phases Disappeared	New Phases
andalusite	sillimanite
epidote/zoisite	plagioclase
chlorite	grossularite
talc	cordierite
actinolite	biotite
albite	anthophyllite
	hornblende

Next, let's try to write the chemical reactions that must have occurred between the two sets of pressure/temperature conditions that would explain the new mineral assemblages.
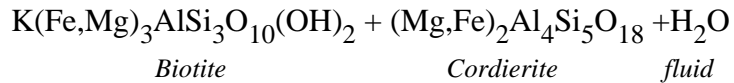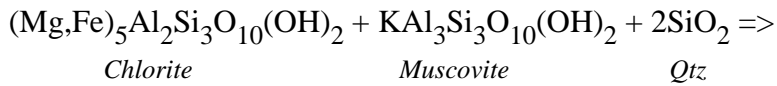
For the disappearance of andalusite and appearance of sillimanite the reaction is simple:

$$Al_2SiO_5 => Al_2SiO_5$$
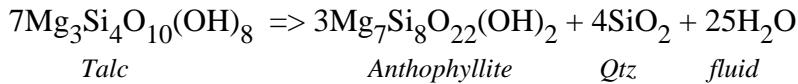*Andalusite   Sillimanite*
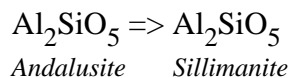
Epidote (zoisite) would break down to produce the anorthite component of plagioclase and grossularite, resulting in the expulsion of water as a fluid phase:

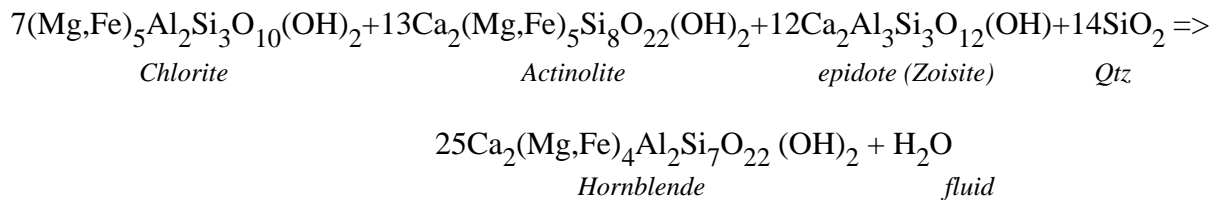$$4Ca_2Al_3Si_3O_{12}(OH) + SiO_2 => 5CaAl_2Si_2O_8 + Ca_3Al_2Si_3O_{12} + 2H_2O$$
Epidote/Zoisite   Qtz   Anorthite (plag) grossularite   fluid

Chlorite could have reacted with muscovite and quartz to produce biotite, cordierite, and fluid:

$$(Mg,Fe)_5Al_2Si_3O_{10}(OH)_2 + KAl_3Si_3O_{10}(OH)_2 + 2SiO_2 =>$$

     Chlorite   *Muscovite*   *Qtz*

$$K(Fe,Mg)_3AlSi_3O_{10}(OH)_2 + (Mg,Fe)_2Al_4Si_5O_{18} + H_2O$$

          Biotite   *Cordierite*   *fluid*

Talc would break down to produce anthophyllite, quartz, and fluid:

$$7Mg_3Si_4O_{10}(OH)_8 => 3Mg_7Si_8O_{22}(OH)_2 + 4SiO_2 + 25H_2O$$

    Talc   *Anthophyllite*   *Qtz*   *fluid*

and chlorite, actinolite, epidote (zoisite), and quartz would react to produce hornblende and fluid:

$$7(Mg,Fe)_5Al_2Si_3O_{10}(OH)_2 + 13Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2 + 12Ca_2Al_3Si_3O_{12}(OH) + 14SiO_2 =>$$

    Chlorite   *Actinolite*   *epidote (Zoisite)*   *Qtz*

$$25Ca_2(Mg,Fe)_4Al_2Si_7O_{22}(OH)_2 + H_2O$$

       Hornblende   *fluid*

With the exception of the first reaction (andalusite => sillimanite) all of these reactions result in the evolution of H_2O in a fluid phase. Such reactions are called ***dehydration reactions***, and will be discussed further in the next lecture.

Next, let's increase the temperature and pressure so that a new set of minerals develops for each rock.

At these new pressure/temperature conditions, pelitic rocks would contain plagioclase, sillimanite, cordierite, quartz, and k-spar. Quartzo-feldspathic rocks would consist of plagioclase, cordierite, almandine/pyrope garnet, quartz, and k-spar.

Calcareous rocks would consist either of wollastonite, grossularite and diopside, or grossularite, plagioclase, and diopside, or plagioclase, diopside, and biotite, depending on the composition of the initial rock. Basic rocks would consist of plagioclase, diopside, and almandine/pyrope, or plagioclase, hypersthene, and almandine/pyrope. Ultramafic rocks would consist of hypersthene, almandine/pyrope, and diopside.
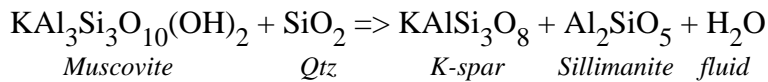

Highest Grade Rocks
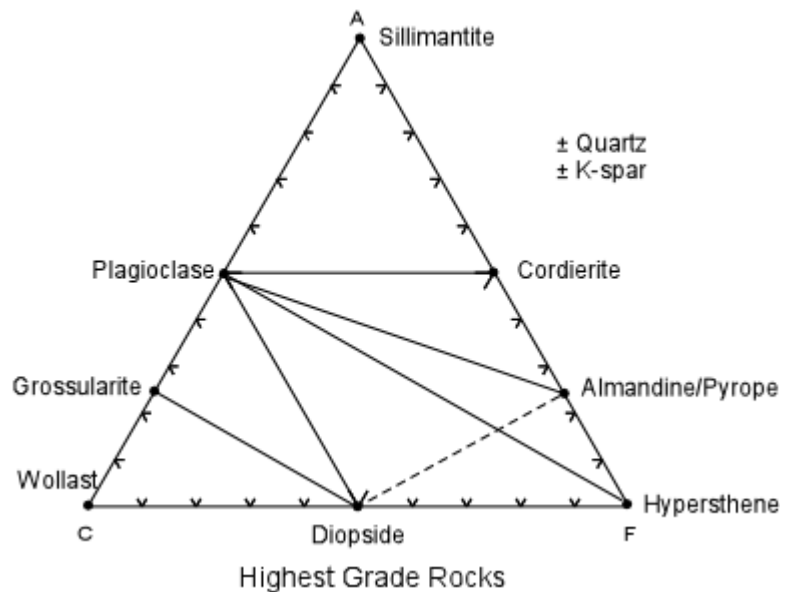
Again, we can make a list of the phases that disappeared and those that appeared at some point between the two pressure/temperature conditions.
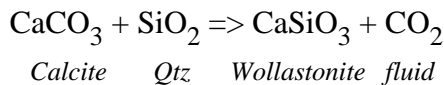
Phases Disappeared	New Phases
muscovite	wollastonite
calcite	diopside
hornblende	hypersthene
anthophyllite	almandine/pyrope
biotite	

Exploring the reactions that must have taken place to explain the new mineral assemblage, we proceed as follows:

For the disappearance of muscovite we can write:

$$KAl_3Si_3O_{10}(OH)_2 + SiO_2 => KAlSi_3O_8 + Al_2SiO_5 + H_2O$$

Muscovite   Qtz   K-spar   Sillimanite fluid

For the disappearance of calcite and the appearance of wollastonite we can write:

$$CaCO_3 + SiO_2 => CaSiO_3 + CO_2$$

Calcite   Qtz   Wollastonite fluid

Hornblende would break down to diopside, hypersthene, plagioclase, and fluid.:

$$Ca_2Mg_4Al_2Si_7O_{22}(OH)_2 => CaMgSi_2O_6 + 3MgSiO_3 + CaAl_2Si_2O_8 + H_2O$$

Hornblende   Diopside   Hypersthene   Plagioclase   fluid
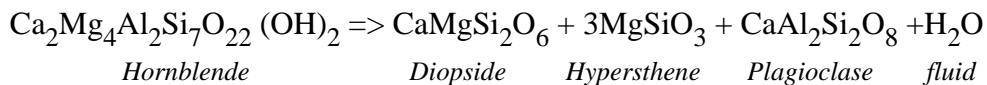
Anthophyllite would break down to hypersthene and quartz:

$$Mg_7Si_8O_{22}(OH)_2 => 7MgSiO_3 + SiO_2 + H_2O$$

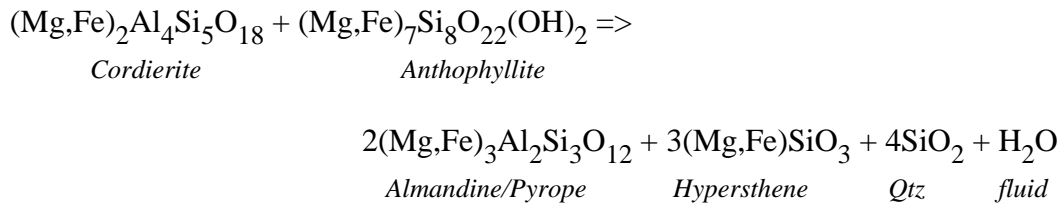*Anthophyllite   Hypersthene   Qtz   fluid*
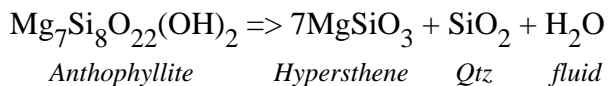
For the breakdown of biotite to form hypersthene and k-spar the following reaction must have occurred:

$$K(Fe,Mg)_3AlSi_3O_{10}(OH)_2 + 3SiO_2 => KAlSi_3O_8 + 3(Mg,Fe)SiO_3 + H_2O$$

Biotite   Qtz   K-spar   Hypersthene   fluid
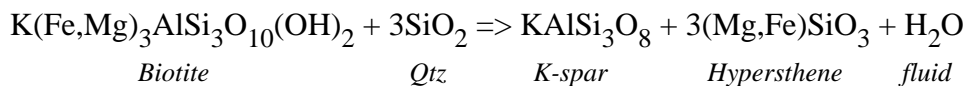
And finally, for the formation of almandine/pyrope from cordierite and anthophyllite, the following reaction could have occurred:

$$(Mg,Fe)_2Al_4Si_5O_{18} + (Mg,Fe)_7Si_8O_{22}(OH)_2 =>$$

  Cordierite   *Anthophyllite*

$$2(Mg,Fe)_3Al_2Si_3O_{12} + 3(Mg,Fe)SiO_3 + 4SiO_2 + H_2O$$

  Almandine/Pyrope   *Hypersthene*   *Qtz*   *fluid*

Again, all of the reactions evolve a fluid phase. The calcite => wollastonite reaction is a decarbonation reaction, and the rest are dehydration reactions. This illustrates very well the concept we have discussed repeatedly throughout this course, that prograde metamorphism involves a series of devolatilization reactions that produce a fluid phase. The fluid phase generally will consist of a mixture of H_2O and CO_2. This results in producing minerals that are less volatile rich with increasing grade of metamorphism. Ultimately, at the highest grade of metamorphism no hydrous or carbonate bearing phases exist.

Retrograde Metamorphism

If retrograde metamorphism were a common process then upon uplift and unroofing metamorphic rocks would progressively return to mineral assemblages stable at lower pressures and temperatures. Yet, high grade metamorphic rocks are common at the surface of the Earth and usually show only minor retrograde minerals. Three factors inhibit retrograde metamorphism, two of which involve the fluid phase.

1. Chemical reactions run faster at higher temperatures. During prograde metamorphism the reaction boundaries are continually being over-stepped to higher temperature. At higher temperature diffusion rates are higher and molecular vibration required to break chemical bonds is higher. Thus, during prograde metamorphism reaction rates are faster. As temperature is lowered on a rock, the reaction boundaries are over-stepped to low temperature, and as a result the reaction rates are much slower.

   Of course, this depends on the rate at which temperature is lowered. It is certainly possible for temperatures to decrease at such a slow rate during uplift and unroofing, that retrograde mineral assemblages would have time to form. Also, a second episode of prograde metamorphism may occur during which temperatures are increased again. Minerals stable at the new temperature may start to grow and overprint the minerals that were formed at higher temperature during the first episode of metamorphism.

2. During prograde metamorphism, as we have just seen, a fluid phase is driven off as a result of the devolatilization reactions. As pressure increases, porosity of rocks also decreases, and thus this fluid phase will likely be driven out of the rock body. In the absence of the fluid phase it is impossible to form hydrous minerals and carbonates, since H_2O and CO_2, two of the key components needed in such reactions, may not be present.

3. The fluid phase also helps to catalyze chemical reactions. Although the net reactions may appear to be solid-solid reactions, in reality there may be more involved. For example the fluid phase could dissolve a mineral in one part of the rock and precipitate a new mineral in another part of the rock, just as happens during diagenesis of sedimentary rocks. If the fluid phase is driven off during prograde metamorphism, then it will not be available to catalyze the reactions to produce the retrograde mineral assemblage as pressure and temperature are lowered.

Given enough time, all metamorphic rocks will eventually change to an assemblage of minerals stable under conditions present near the surface of the Earth.

This process, however, is called weathering, and occurs near the earth's surface..

Next time we will explore in more detail some the factors that govern the chemical reactions that occur during metamorphism.

Examples of questions on this material that could be asked on an exam

1. What faactors are responsible for the mineral assemblages that develop in metamorphic rocks?

2. Given a sequence of triangular diagrams, be able to deduce and write the chemical reactions that must have occurred as the pressure and temperature conditions changed during progressinve metamorphism.

3. Why is retrograde metamorphism less commonly observed than prograde metamorphism?

4. What is the ultimate fate of metamorphic rocks that have reached the surface of the earth and why does this occur?

Return to EENS 2120 Home Page