METAMORPHIC REACTIONS

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INTRODUCTION

- A metamorphic reaction is a **chemical reaction** that produces, or changes, an assemblage of metamorphic mineral and fluid phases in a rock. The changes affect the compositions of the phases and may also include changes in the phases that are present. Metamorphic processes are those processes that drive metamorphic reactions, by causing a change in the chemical conditions of the rock, such as the pressure or temperature. Metamorphic processes also commonly drive **deformation**.

- In other words , A metamorphic reaction is a chemical reaction that takes place during the geological process of metamorphism wherein one assemblage of minerals is transformed into a second assemblage which is stable under the new temperature/pressure conditions resulting in the final stable state of the observed metamorphic rock.

Reactions among solid and fluid phases can be categorized in several different ways,

Based on **Reaction Effect (**what the reaction does)

Based on **Reaction Progress** (how the reaction progresses)

Based on P**hases Involved (**on the nature of phases involved).

Categorization based on Reaction Effect

NET – TRANSFER REACTIONS

EXCHANGE REACTIONS

Net-transfer Reactions

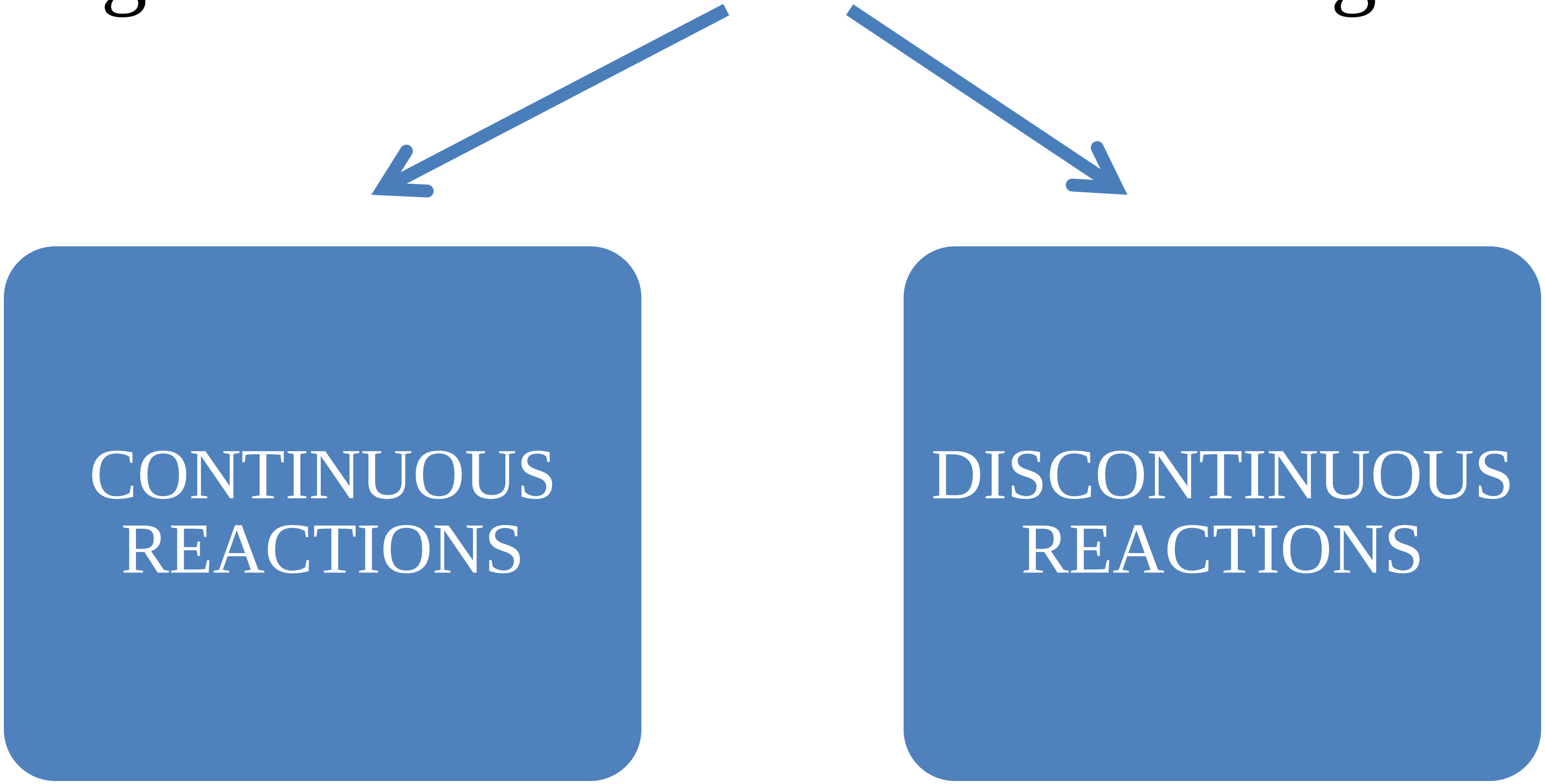
involve chemical components being "transferred" from one phase or set of phases to others (new phases are produced as old ones disappear).
An **example** is : *anorthite = grossular + kyanite + quartz*

Net-transfer reactions may be terminal reactions or tie-line flip reactions (discussed later)

Exchange Reactions

involve chemical components being exchanged between phases, so compositions change, but modes remain the same (no phases disappear and no new phases are produced). An **example** is:
Fe (in garnet) + Mg (in biotite) = Mg (in garnet) + Fe (in biotite)

Categorization based on Reaction Progress



CONTINUOUS REACTIONS

DISCONTINUOUS REACTIONS

Continuous Reactions

are those which take place over a range of P and T as a result of solid solution in one or more of the phases involved. Accordingly, in the model system, such reactions are characterized by assemblages that are at least divariant. Unlike discontinuous reactions, reactants and products can coexist over an range of P and T, but where at least one of the phases constantly changes its composition.

In Other words, Continuous reactions involve phases that may vary in composition. Such reactions are more common than discontinuous reactions because compositional variation, of either fluid or solid phases, is typical for geological materials.
Continuous reactions occur over a range of conditions, so the products and reactants coexist stably over a range of conditions (but the compositions of the phases changes systematically as conditions change).

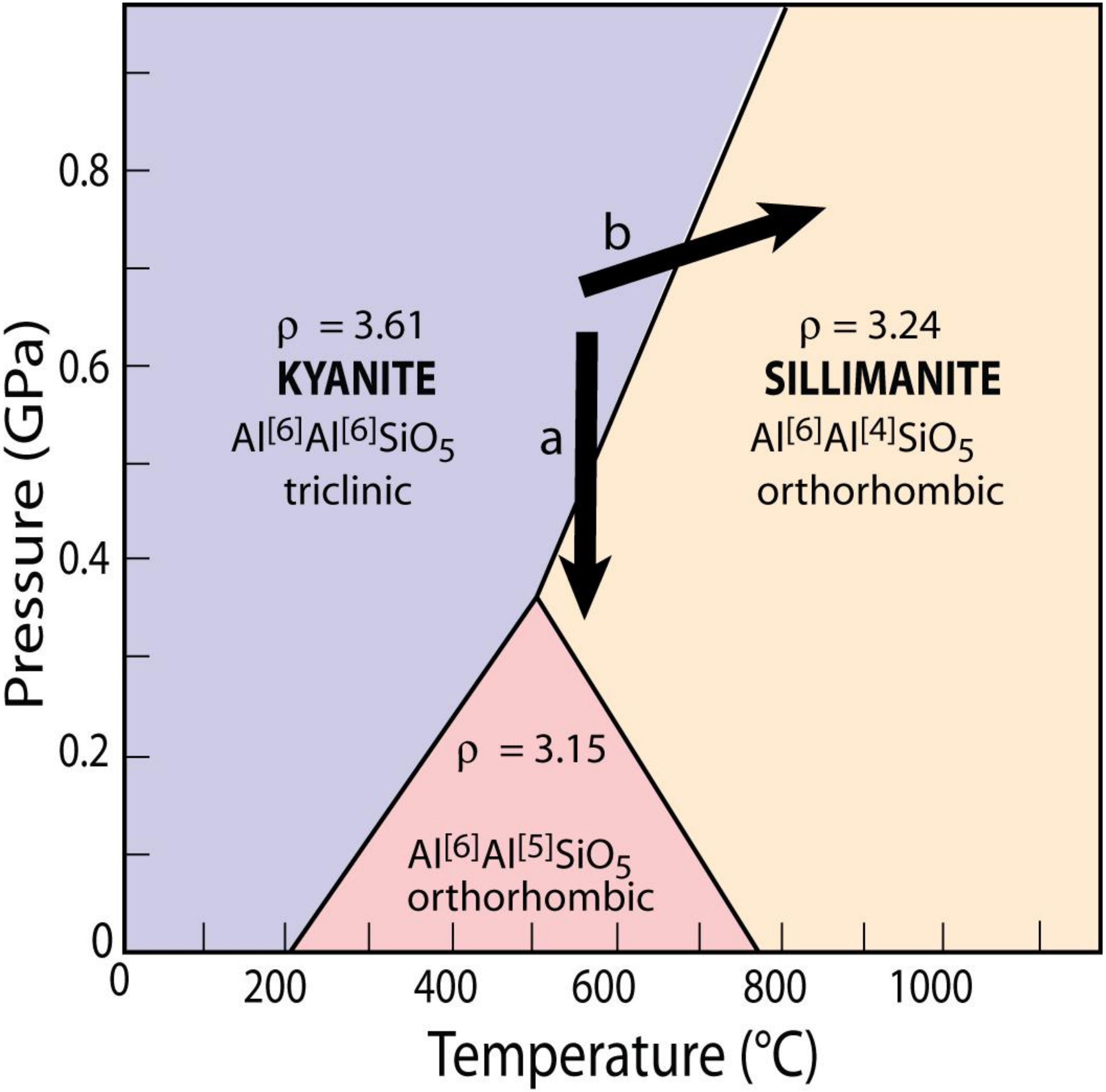
Continuous reactions may be **net-transfer reactions** or **exchange reactions**.

Discontinuous reactions

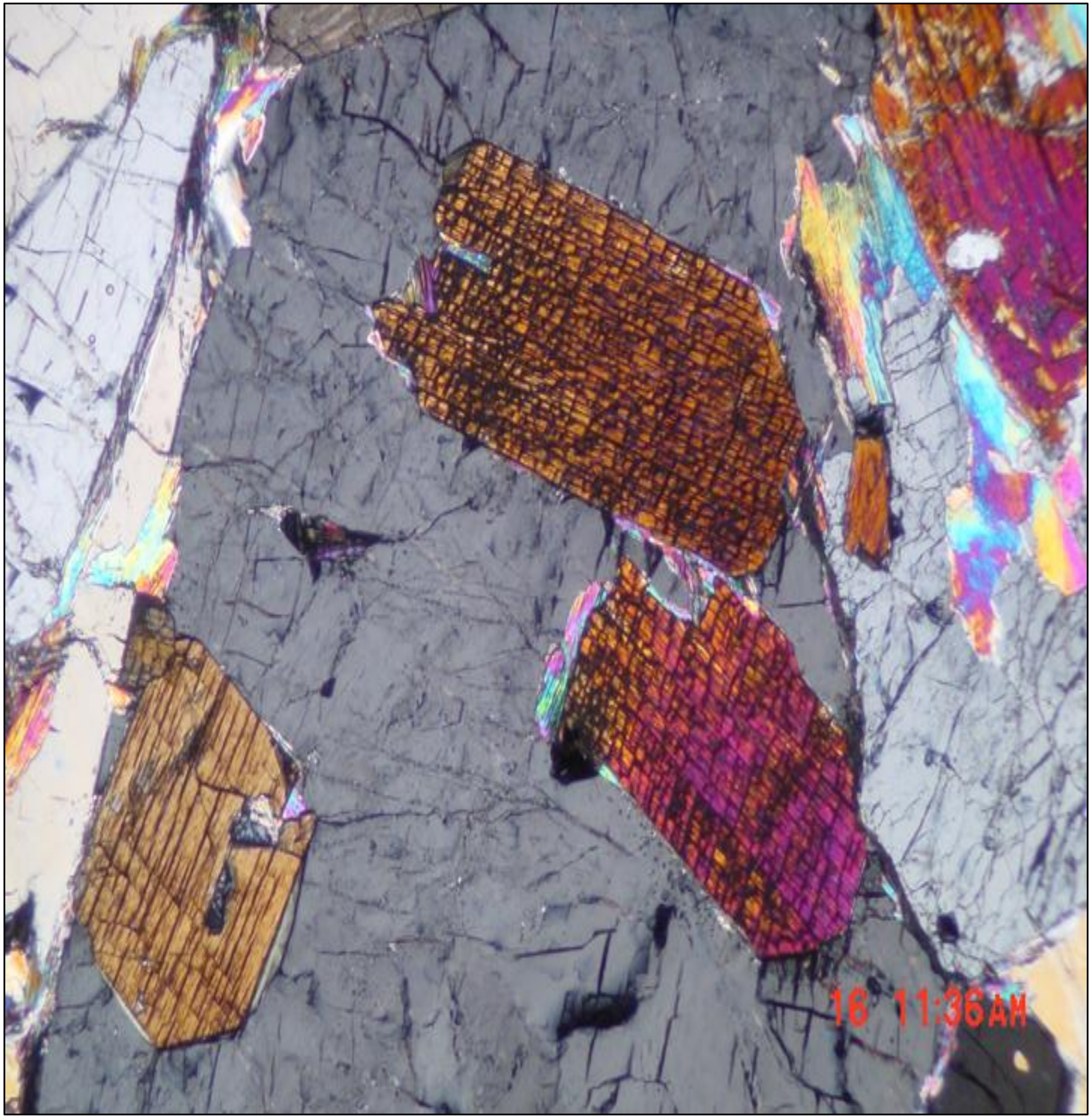
are those which are univariant on P-T diagrams in the "model" system considered. A discontinuous reaction takes place between phases of fixed chemical composition, and will always occur at the same P-T conditions for the compositions defined.

In Other words, Discontinuous reactions are those that occur at a particular temperature (for a particular pressure). For these, a curve (or line) can be drawn on a pressure-temperature (P-T) diagram. (See the kyanite=sillimanite reaction on the phase diagram shown below.) On either side of the curve, a different set of phases is stable. In a discontinuous reaction, products and reactants can only co-exist stably precisely at the equilibrium reaction conditions (on the reaction line in P-T space).

Discontinuous reactions are always **net-transfer reactions.**



Phase diagram for the Al_2SiO_5polymorphs. The arrows show that kyanite will react to form sillimanite with increasing temperature or with decreasing pressure. Although not labeled, the pink triangular field at the bottom is the stability field for andalusite. *This figure is from Donna Whitney.*



Kyanite inclusions (three tabular grains showing good cleavage and brown-pink interference colors) in andalusite (dark gray interference color, poorly developed cleavage) in a kyanite-andalusite-sillimanite (+ staurolite) quartz vein. This rock was "caught in the act" as kyanite reacted to form andalusite. The photo is from Donna Whitney. This sample is from *Hamadan, Iran, and is discussed by Sepahi et al. (2004, J. Metam. Geology 22, 119-134).*

Categorization based on Phases Involved

- **Solid-solid net transfer reactions** (often just called solid-solid reactions)
- **Polymorphic reactions**
- **Devolatilization reactions**
- **Terminal reactions**
- **Ion-exchange reactions**
- **Tie line flip reactions**

Solid-Solid Net Transfer Reactions

occur among solid phases of differing composition. These phases may include elements found in fluids (H, C), but those elements are conserved in the solid phases so that no fluid phases (H_2O, CO_2) are involved as reactants or products.Solid-solid net transfer reactions can be *continuous* or *discontinuous*, and they may be *terminal*, or *tie-line flip* reactions.

Characteristics:

1- All phases taking part in the reaction are condensed phases (i.e. solids).

2- For the most part, they exhibit very little curvature if any, when plotted on P-T diagrams. (Curvature usually arising from ordering of one of the phases).

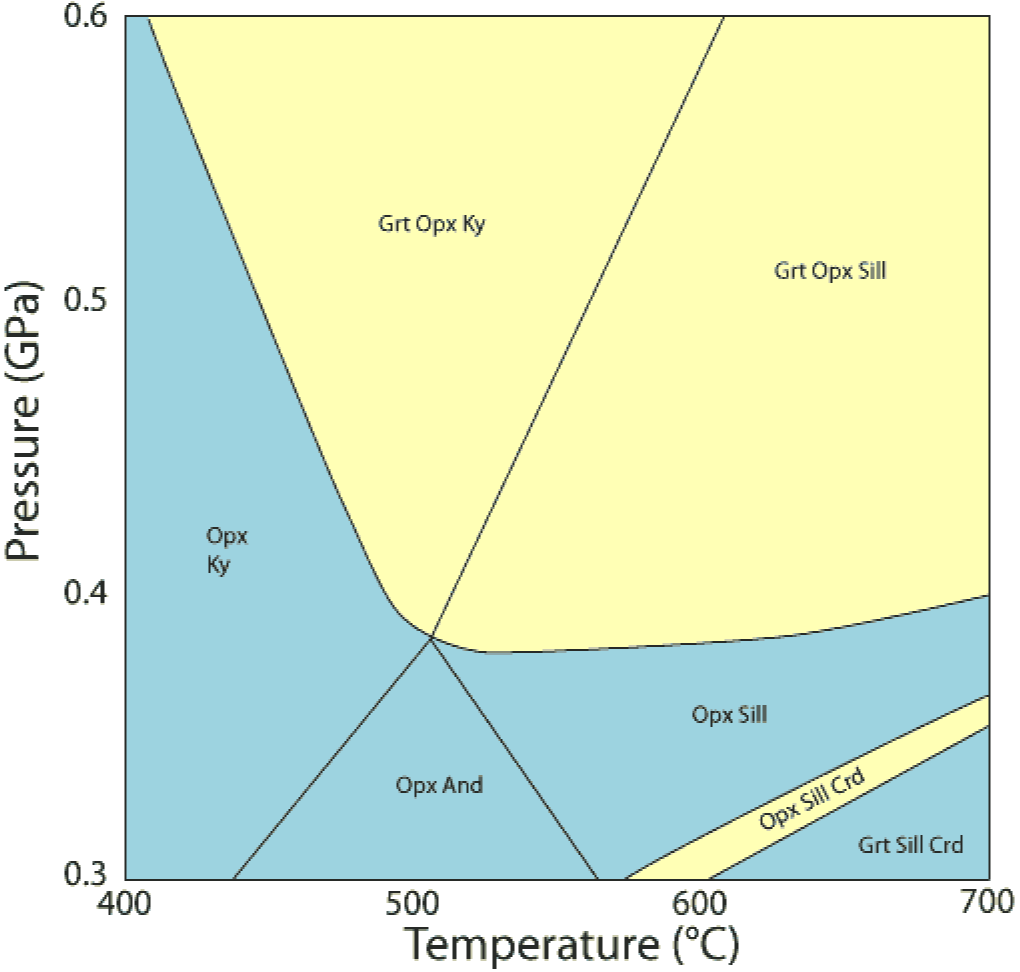
3- They tend to have shallow slopes in P-T space, and are therefore more sensitive to changes in P rather than T. This property makes many such reactions good geobarometers.

Most solid-solid reactions plot on a P-T diagram as essentially straight lines. This is because the ΔS and ΔV of reaction do not change much with varying pressure or temperature.

Many solid-solid reactions are **continuous** because they involve phases whose compositions are changing as their modes change. This occurs because the phases contain appreciable solid solution. Specific reactions are difficult to express, but schematically, one would be:

kyanite + orthopyroxene$_1$ *= orthopyroxene*$_2$ *+ garnet*

This reaction is shown on the P-T diagram and in the Al_2O_3-FeO-MgO diagram (next slide). The P-T diagram is a projection – garnet and orthopyroxene compositions change along the reaction curve.



Polymorphic Reactions

are a special type of solid-solid reaction that involves phases of identical composition. Classic examples are the reactions among the aluminum silicates (kyanite-sillimanite-andalusite; see the photomicrograph and phase diagram shown before), the conversion of graphite to diamond at high pressure, and calcium carbonate (calcite-aragonite) equilibria.

Ion-Exchange Reactions

(generally just called "exchange reactions") involve two phases that both share a solid solution exchange such as Na↔K or Fe^{+2} ↔Mg such as garnet, (Fe,Mg)3Al2(SiO4)3 and biotite, K(Fe,Mg)3(Si3Al)O10(OH)2 (both formulas are simplified). Reactions of this type are all continuous, and differ from the others kinds of reactions discussed above in that there is no real product or a reactant. Instead, across the complete range of conditions over which the two minerals are stable, both are changing in composition. Curves for these reactions are straight on a P-T diagram (but can only be plotted for specific compositions) and very steep (because there is essentially no change in volume associated with the reaction.

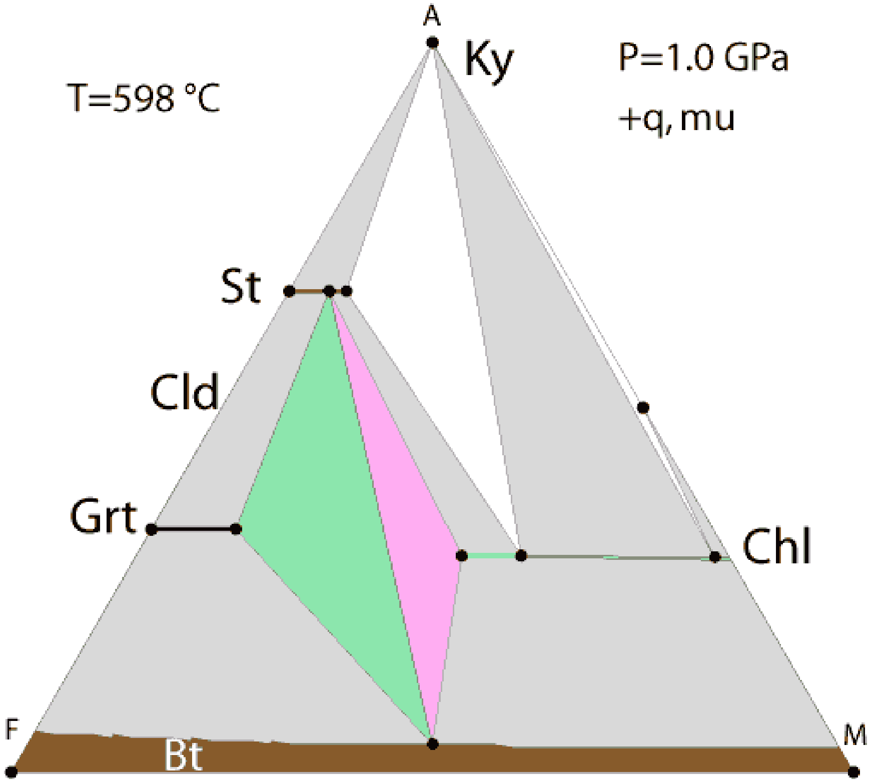
For Fe^{+2} and Mg exchange between garnet and biotite, the reaction can be written:
almandine-in-garnet + *phlogopite-in-biotite* ↔ *pyrope-in-garnet* + *annite-in-biotite*, or:

Fe3Al2(SiO4)3 + KMg3(Si3Al)O10(OH)2↔Mg3Al2(SiO4)3 + KFe3(Si3Al)O10(OH)2.

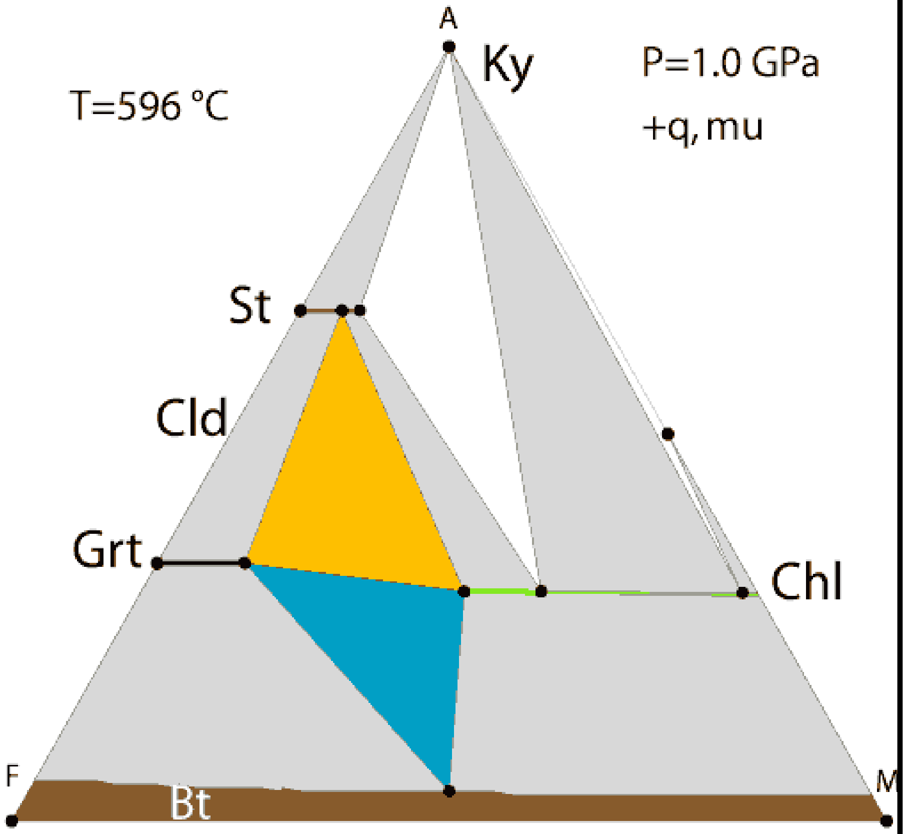
Tie Line Flip Reactions

involve two phases becoming stable together that were previously unstable together, and vice versa. As with terminal reactions, they may be solid-solid reactions or may involve a fluid phase. An example of a tie-line flip reaction is:

chlorite + garnet = biotite + staurolite



Staurolite and biotite are stable together at temperatures above the tie line flip reaction

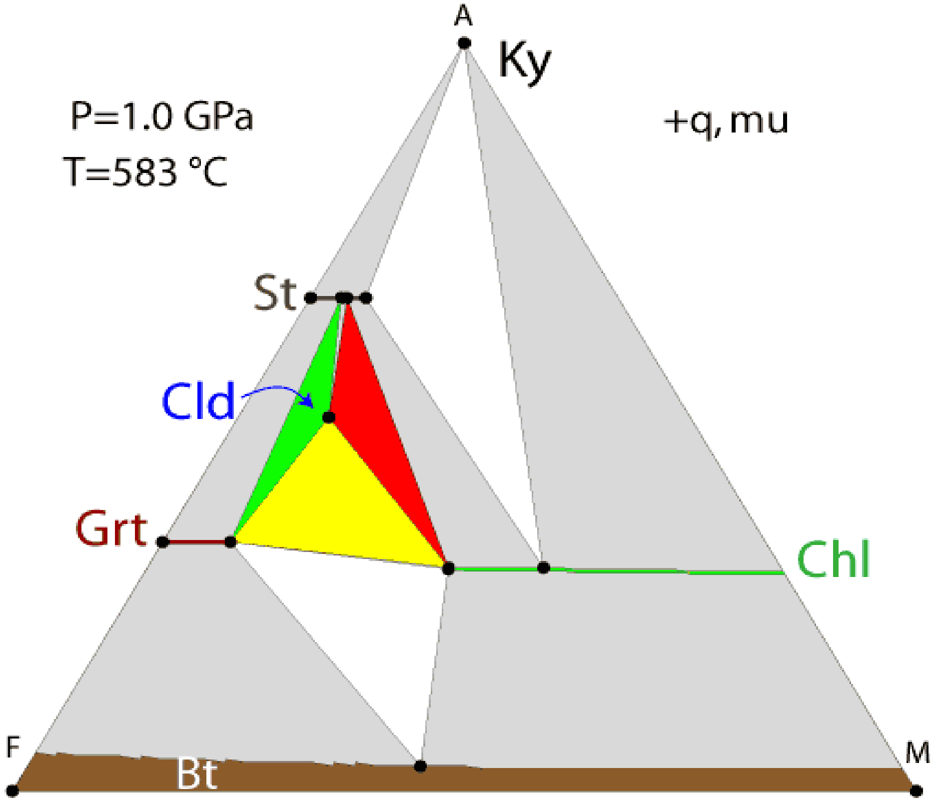


Garnet and chlorite are stable together at temperatures below the tie line flip reaction

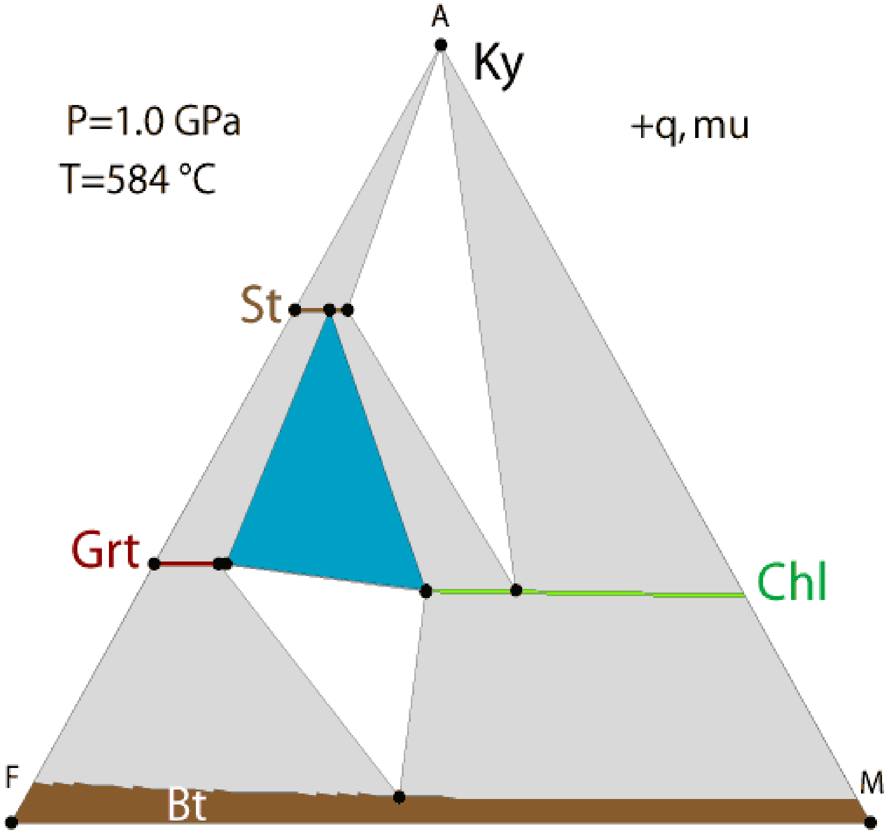
Terminal Reactions

Involve the creation of a new phase from two or three other phases, or (in the other direction) the decomposition of one phase into two or three others. They may be solid-solid reactions or they may involve a fluid phase. An example of a terminal reaction is:

chloritoid = staurolite + garnet + chlorite



At lower temperature (583°), chloritoid is stable for compositions that fall within the red, green and yellow 3-phase fields.



At higher temperature (584°), staurolite, garnet and chlorite are stable together and chloritoid is gone. So, the reaction takes place between 583° and 584° at 1 GPa.

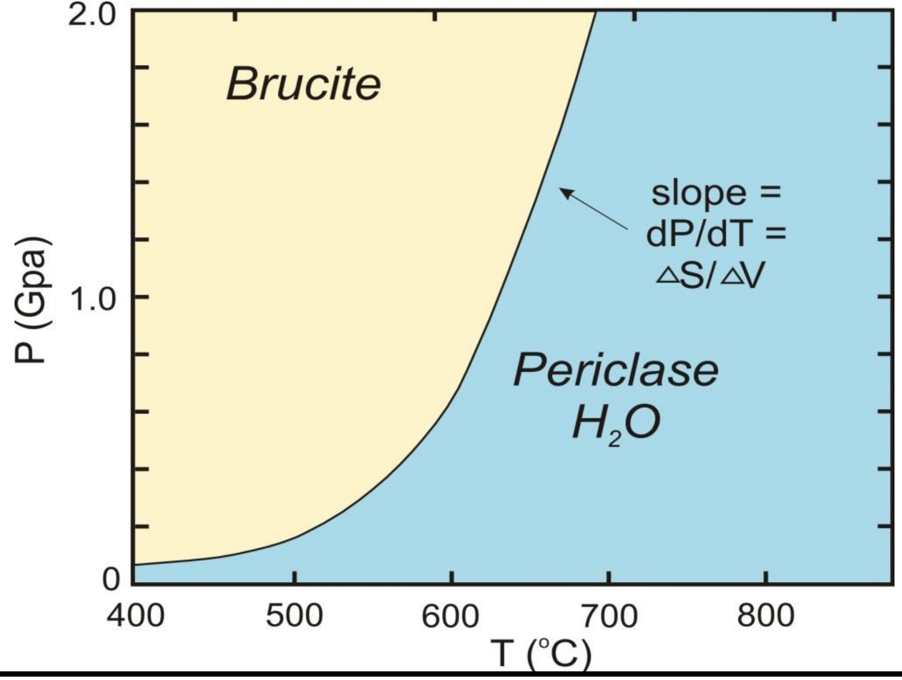
Devolatilization Reactions

are **net-transfer** reactions that involve the liberation of a volatile phase (H_2O for **dehydration reactions** or CO_2 for **decarbonation reactions**). Examples of a dehydration and a decarbonation reaction are:

muscovite + quartz = K-feldspar + sillimanite + H_2O, (dehydration)

calcite + quartz = wollastonite + CO_2 (decarbonation)

Because the entropy of a fluid is generally greater than the entropy of solid phases, fluids appear on the high-temperature side of most such reactions. If the fluid composition is fixed (stays constant), then devolatilization reactions are discontinuous, but if the fluid composition can vary as a result of the liberation of H_2O or CO_2, then the reactions will be continuous.



P-T diagram showing the (dehydration) reaction of brucite to periclase + H_2O. Figure from D. Perkins.

***Curvature*:**

The curves for dehydration or decarbonation reactions on a P-T diagram will have shallow slopes at low pressure because the volume of a fluid phase is much larger than that of solid phases. However, the compressibility of a fluid leads to a rapid decrease in volume as pressure rises, so the slopes steepen with rising pressure, leading to substantial curvature. Some (rare) reactions curve around and gain a negative slope at high pressure.

***Sensitivity to fluid composition*:**

The P-T position of a decarbonation or dehydration reaction changes if fluid composition changes. For a dehydration reaction such as:

muscovite + quartz = K-feldspar + sillimanite + H_2O,

if the rock contains an H_2O-rich fluid, the right-hand side of the reaction will be stable over a smaller range of conditions than if the rock contains an H_2O-poor fluid (either because the fluid is diluted with CO_2, or the rock is "dried out" and not fluid saturated).

Dehydration Reactions:

These are reactions that have H2O (usually) among their higher T products. They are characterized by

1. a "stepwise" nature, where H2O may be released in increments as T increases,
2. a steep P-T slopes and endothermic nature (usually, but not always), and
3. the slopes and P-T locations vary with variations in the fluid compositions (i.e. amounts of components other than H2O in the fluid phase).

Examples:

A good example for a typical dehydration reaction (satisfying the above listed criteria) is:

Muscovite + Qz = Sillimanite + K-spar + H2O

On the other hand, a few reactions may have H2O among their low T reactants, such as:

25 Gln + 6 Cz + 7 Qz + 14 H2O = 6 Tr + 9 Chl + 50 Ab

A third type of dehydration reaction is exothermic, releasing heat and H2O, such as:

Jadeite + H2O = Analcime

Decarbonation Reactions:

These are reactions that release CO2. They are important in the metamorphism of calcareous rocks. Like common dehydration reactions, they have positive steep slopes on P-T diagrams and positive convex upward curves on T-XCO2 diagrams .

Example: CaCO3 + SiO2 = CaSiO3 + CO2.

Oxidation-Reduction Reactions:

These are reactions that involve a change in the oxidation state of one or more of the elements involved. *Examples :*Consider the two component system: Fe - O_2, containing the phases hematite, magnetite and O_2. We can therefore write the reaction:

$$2\ Fe_3O_4 + 1/2\ O_2 = 3\ Fe_2O_3$$

Mixed Volatile Reactions:

These are reactions that involve two fluid phases, such as H_2O and CO_2. There are two types: reactions in which H_2O and CO_2 are on the same side (i.e. either reactants or products) and; reactions in which H_2O and CO_2 are on different sides of the reaction (one reactant, the other a product).An example of the first type, which on T-X_{CO_2} diagrams would plot as *convex upward* curves with maxima the locations of which depend on the stoichiometric reaction coefficients of CO_2 and H_2O, is:

$$Tr + Cc + Qz = Di + 3\ CO_2 + H_2O$$

IDENTIFY THE FOLLOWING REACTIONS

Ky ↔ Sill, Calcite ↔ Aragonite, Graphite ↔ Diamond.

$$\underset{\text{Mg-biotite}}{KMg_3AlSi_3O_{10}(OH)_2} + \underset{\text{Fe-garnet}}{Fe_3Al_2Si_3O_{12}} \leftrightarrow \underset{\text{Fe-biotite}}{KFe_3AlSi_3O_{10}(OH)_2} + \underset{\text{Mg-garnet}}{Mg_3Al_2Si_3O_{12}}$$

Do + Qz + H2O = Tc + Cc + CO2

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THANKS