Metamorphic Reactions

- what indicates that metamorphic reactions occur?
- appearance of new minerals (at an isograd)
- but recognize that first appearance of a mineral (e.g., Bt) does not occur by only one reaction; could come from various individual reactions, depending on:
  - reactants available (what minerals are present)
  - rock (system) composition
  - intensive variables (P, T)
Metamorphic Reactions

• If we treat isograds as reactions, we can:

  • understand what physical variables might affect the location of a particular isograd

  • we may also be able to estimate the P-T-X conditions that an isograd represents

• be aware whether we distinguish **field-based isograds** (index minerals) in the classical sense from **reaction-based isograds** (reaction sequence)
Types of reactions

1. polymorphic phase transformations
2. exsolution (Ab-Or, Cc-Dol)
3. solid-solid net-transfer
4. devolatilization
5. continuous (solid solution)
   (Chl + Qtz = Grt + H₂O)
6. ion exchange
7. redox (FMQ, Mt + Qtz = Fa)
## Types of reactions

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<td>Fe-Mg in Ann + Pyr = Phlog + Alm</td>
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I. Phase Transformations

- *Isochemical* phase transformations (the polymorphs of SiO$_2$ or Al$_2$SiO$_5$ or graphite-diamond or calcite-aragonite are the simplest to deal with)
  - we treat them as *unary* phase systems
  - the transformations *depend on T & P only*
  - very useful because the presence of a particular polymorph indicates (hopefully!) P-T of equilibration
I. Phase Transformations

- system CaCO$_3$

- Arag stable at high P (has smaller unit cell volume, by 61%!)

I. Phase Transformations

- system $\text{Al}_2\text{SiO}_5$

- triple point
good to know

Figure 26-15. The P-T phase diagram for the system $\text{Al}_2\text{SiO}_5$ showing the stability fields for the three polymorphs andalusite, kyanite, and sillimanite. Calculated using the program TWQ (Berman, 1988, 1990, 1991).
I. Phase Transformations

- small $\Delta S$ for most polymorphic transformations

- $\rightarrow$ small $\Delta G$ between two alternative polymorphs, even several tens of degrees from the equilibrium boundary

- $\rightarrow$ little driving force for the reaction to proceed, so may find metastable relics persisting outside their stability fields

- coexisting polymorphs may therefore represent non-equilibrium states (overstepped equilibrium curves or polymetamorphic overprints)
3. Solid-Solid Net-Transfer Reactions

- involves solid phases only
- “net transfer” means transfer of matter from one mineral site to another
- differ from polymorphic transformations — involve solids of differing composition, and thus material must diffuse from one site to another for the reaction to proceed
- yields a change in modal proportions of the phases
3. Solid-Solid Net-Transfer Reactions

Examples:

\[ \text{NaAlSi}_2\text{O}_6 + \text{SiO}_2 = \text{NaAlSi}_3\text{O}_8 \]
\[ \text{Jd} \quad \text{Qtz} \quad \text{Ab} \]

\[ \text{MgSiO}_3 + \text{CaAl}_2\text{Si}_2\text{O}_8 = \text{CaMgSi}_2\text{O}_6 + \text{Al}_2\text{SiO}_5 \]
\[ \text{En} \quad \text{An} \quad \text{Di} \quad \text{And} \]

\[ 4 \text{ (Mg,Fe)SiO}_3 + \text{CaAl}_2\text{Si}_2\text{O}_8 = \]
\[ \text{Opx} \quad \text{Plag} \]
\[ \text{(Mg,Fe)}_3\text{Al}_2\text{Si}_3\text{O}_{12} + \text{Ca(Mg,Fe)Si}_2\text{O}_6 + \text{SiO}_2 \]
\[ \text{Grt} \quad \text{Cpx} \quad \text{Qtz} \]
Figure 27-1. Temperature-pressure phase diagram for the reaction: Albite = Jadeite + Quartz calculated using the program TWQ of Berman (1988, 1990, 1991).

(low dp/dT — good barometer)
3. Solid-Solid Net-Transfer Reactions

- if minerals contain volatiles, the *volatiles must be conserved* in the reaction so that no fluid phase is generated or consumed

- for example, the reaction (note mineral types):

\[ \text{Tlc} \quad \text{En} \quad \text{Anth} \]

\[ \text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 + 4 \text{ MgSiO}_3 = \text{ Mg}_7\text{Si}_8\text{O}_{22}(\text{OH})_2 \]

involves hydrous phases, but conserves $\text{H}_2\text{O}$

may therefore be treated as a solid-solid net-transfer reaction
3. Solid-Solid Net-Transfer Reactions

- net-transfer reactions are typically good indicators of $P$, because there is often a notable $\Delta rV$
- for example: $3 \text{An} = \text{Grs} + 2 \text{Ky} + \text{Qtz}$
- the GASP barometer
4. Devolatilization Reactions

- among the *most common metamorphic reactions* with increasing metamorphic grade
- $\text{H}_2\text{O-}\text{CO}_2$ systems are most common, but the principles same for any reaction involving volatiles
- reactions dependent not only upon temperature and pressure, but also very sensitive to the *partial pressure of the volatile species*
4. Devolatilization Reactions

- for example the location on a P-T phase diagram of the dehydration reaction:

\[ \text{KAl}_2\text{Si}_3\text{AlO}_{10}\text{(OH)}_2 + \text{SiO}_2 = \text{KAISi}_3\text{O}_8 + \text{Al}_2\text{SiO}_5 + \text{H}_2\text{O} \]

\[ \text{Ms} \quad \text{Qtz} \quad \text{Kfs} \quad \text{Sil} \]

depends upon the partial pressure of \( \text{H}_2\text{O} \) \( (p_{\text{H}_2\text{O}}) \)

this dependence is easily demonstrated by applying Le Châtelier’s principle to the reaction at equilibrium
4. Devolatilization Reactions

- equilibrium curve represents equilibrium between the reactants and products under water-saturated conditions ($p_{H2O} = P_{lithostatic}$)

- univariant reaction

P-T phase diagram for the reaction $Ms + Qtz = Kfs + Al_2SiO_5 + H_2O$ showing the shift in equilibrium conditions as $p_{H2O}$ varies (assuming ideal H$_2$O-CO$_2$ mixing). Calculated using the program TWQ by Berman (1988, 1990, 1991).
\[ \text{KAl}_2\text{Si}_3\text{AlO}_{10}(\text{OH})_2 + \text{SiO}_2 = \text{KAlSi}_3\text{O}_8 + \text{Al}_2\text{SiO}_5 + \text{H}_2\text{O} \]

| Ms | Qtz | Kfs | Sil | W |

- suppose \( \text{H}_2\text{O} \) is withdrawn from the system at some point on the water-saturated equilibrium curve: \( p_{\text{H}_2\text{O}} < P_{\text{lithostatic}} \)
- according to Le Châtelier’s Principle, removing water at equilibrium will be compensated by the reaction running to the right, thereby producing more water
- this has the effect of stabilizing the right side of the reaction at the expense of the left side
- so as water is withdrawn, the Kfs + Sil + \( \text{H}_2\text{O} \) field expands slightly at the expense of the Ms + Qtz field, and the reaction curve \textit{shifts toward lower temperature}
first, as $p_{\text{H}_2\text{O}}$ goes down, reaction drives to right to produce more volatile

next, as volatile is lost or diluted, equilibrium displaced to lower $T$
4. Devolatilization Reactions

- $p_{H_2O}$ can become less than $P_{Lith}$ by either of two ways:
  - $P_{\text{fluid}} < P_{Lith}$ by *drying out the rock* and reducing the fluid content
  - $P_{\text{fluid}} = P_{Lith}$, but the water in the fluid can become *diluted by adding another fluid component*, such as $CO_2$ or some other volatile phase
4. Devolatilization Reactions

- an important consequence: the T of an isograd based on a devolatilization reaction is **sensitive to the partial pressure of the volatile species** involved

- an alternative: **T-**$X_{\text{fluid}}$ phase diagram
  
  - because H$_2$O and CO$_2$ are by far the most common metamorphic volatiles, the $X$ in T-X diagrams is usually the mole fraction of CO$_2$ (or H$_2$O) in H$_2$O-CO$_2$ mixtures
  
  - because pressure is also a common variable, a **T-$X_{\text{fluid}}$ diagram must be created for a specified pressure**
4. Devolatilization Reactions

Figure 26-4. T-X\(_{H_2O}\) phase diagram for the reaction Ms + Qtz = Kfs + Sil + H\(_2O\) at 0.5 GPa assuming ideal H\(_2O\)-CO\(_2\) mixing, calculated using the program TWQ by Berman (1988, 1990, 1991).
4. Devolatilization Reactions

T-X diagrams help visualize T-dependence on X for reaction

\[ T_{rxn} \text{ decreases with dilution of phase, like in melt-crystal equilibria} \]

Figure 26-2. Winter (2001) An Introduction to Igneous and Metamorphic Petrology. Prentice Hall.

Figure 26-4. Winter (2001) An Introduction to Igneous and Metamorphic Petrology. Prentice Hall.
4. Devolatilization Reactions

- shape of most *dehydration curves* on T-X$_{\text{fluid}}$ diagrams are similar (also true for *decarbonation* reactions)
- maximum temperature at the pure H$_2$O end, and slope gently at high X$_{\text{H}_2\text{O}}$, but steeper toward low X$_{\text{H}_2\text{O}}$, becoming near vertical at very low X$_{\text{H}_2\text{O}}$
- reaction temperature can thus be practically *any temperature below the maximum at* $p_{\text{H}_2\text{O}} = P_{\text{lith}}$
- must constrain the fluid composition (if possible) before using a dehydration reaction to indicate metamorphic grade
4. Devolatilization Reactions


Figure 26-5. T-X$_{CO_2}$ phase diagram for the reaction Cal + Qtz = Wo + CO$_2$ at 0.5 GPa assuming ideal H$_2$O-CO$_2$ mixing, calculated using the program TWQ by Berman (1988, 1990, 1991).
6. Ion Exchange Reactions

- reciprocal *exchange of components* between 2 or more minerals (typically cations)

\[ \text{MgSiO}_3 + \text{CaFeSi}_2\text{O}_6 = \text{FeSiO}_3 + \text{CaMgSi}_2\text{O}_6 \]

- expressed as pure end-members, but really involves Mg-Fe (or other) exchange between intermediate solutions

- modal amounts of the phases remains constant!

- exchange is a *diffusion process* — f(T)

- ∴ cation partitioning between two minerals in equilibrium is the basis for many *geothermometers*
6. Ion Exchange Reactions

- sloping tielines related to Fe-Mg exchange, given by values of $K_D$
- rotation of tie-lines on compatibility diagrams

Figure 27-6. AFM projections showing the relative distribution of Fe and Mg in garnet vs. biotite at approximately 500°C (a) and 800°C (b). From Spear (1993) Metamorphic Phase Equilibria and Pressure-Temperature-Time Paths. Mineral. Soc. Amer. Monograph 1. MSA.
Reaction mechanisms

- theoretical balanced reactions are all fine and dandy, but *what really happens???*
- mineral *textures may not indicate* which minerals participated in reactions to produce an observed texture
- products do not always grow next to reactants!
- some reactions involve other “mystery” phases
- Ex. growth of Al-silicates (after Carmichael)...
Figure 26-20. a. Sketch from a photomicrograph showing small crystals of kyanite (purple) and quartz (blue) in a larger muscovite grain (green). Small crystals of fibrolitic sillimanite also occur in the muscovite. Glen Cova, Scotland. b. Sillimanite needles in quartz (blue) embaying muscovite (green). Pink crystals are biotite. Donegal, Ireland. After Carmichael (1969). Contrib. Mineral. Petrol., 20, 244-267.
simple mechanism

- transformation of Ky to Sil by “reversal” of Ms
- requires participation of volatile and free cations

Figure 26-21. A possible mechanism by which the Ky → Sil reaction can be accomplished while producing the textures illustrated in Figure 26-20a and b. The exchange of ions shown between the two local zones is required if the reactions are to occur. After Carmichael (1969). Contrib. Mineral. Petrol., 20, 244-267.
complex mechanism

- several intermediate steps, occurring in different places
- participation growth of other phases (e.g., Bt, Ab)

Figure 26-21. An alternative mechanism by which the reaction Ky → Sil reaction can be accomplished while producing sillimanite needles associated with biotite with plagioclase occupying embayments in the biotite. The exchange of ions shown between the two local zones is required if the reactions are to occur. After Carmichael (1969). Contrib. Mineral. Petrol., 20, 244-267.