

The Gibbs Phase Rule

- The phase rule allows one to determine the number of degrees of freedom (F) or variance of a chemical system. This is useful for interpreting phase diagrams.

$$F = 2 + C - P$$

Where F is the number of degrees of freedom, C is the number of chemical components and P is the number of phases in the system. The number two is specified because this formulation assumes that both T and P can be varied.

Thermodynamics of Solutions

- **Phases:** Part of a system that is chemically and physically homogeneous, bounded by a distinct interface with other phases and physically separable from other phases.
- **Components:** Smallest number of chemical entities necessary to describe the composition of every phase in the system.
- **Solutions:** Homogeneous mixture of two or more chemical components in which their concentrations may be freely varied within certain limits.

Mole Fractions

$$X_A \equiv \frac{n_A}{\sum n} = \frac{n_A}{(n_A + n_B + n_C + \dots)},$$

where X_A is called the “mole fraction” of component A in some phase.

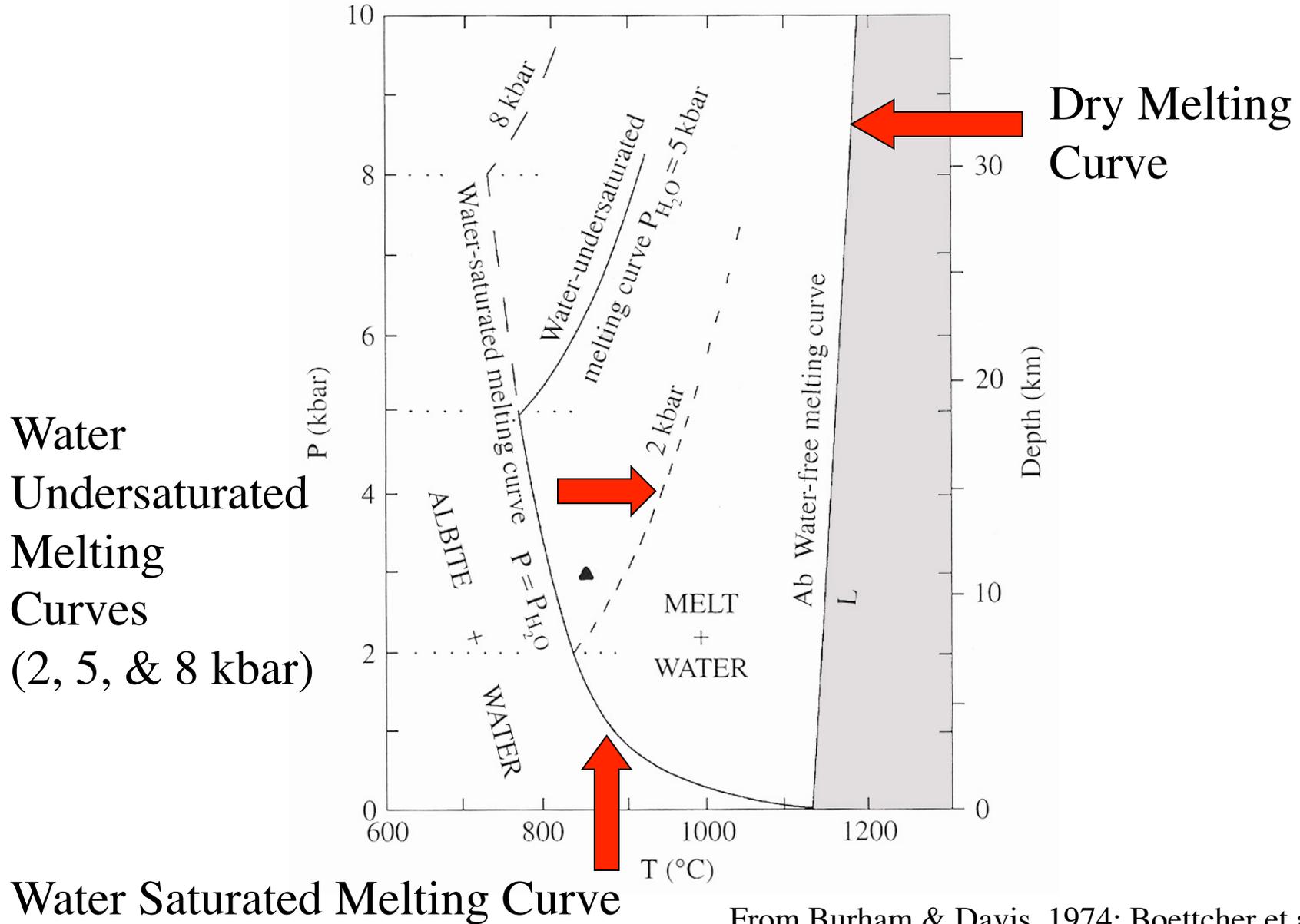
If the same component is used in more than one phase, Then we can define the mole fraction of component A in phase i as X_A^i

For a simple binary system, $X_A + X_B = 1$

Phase Rule Significance for Phase Diagrams

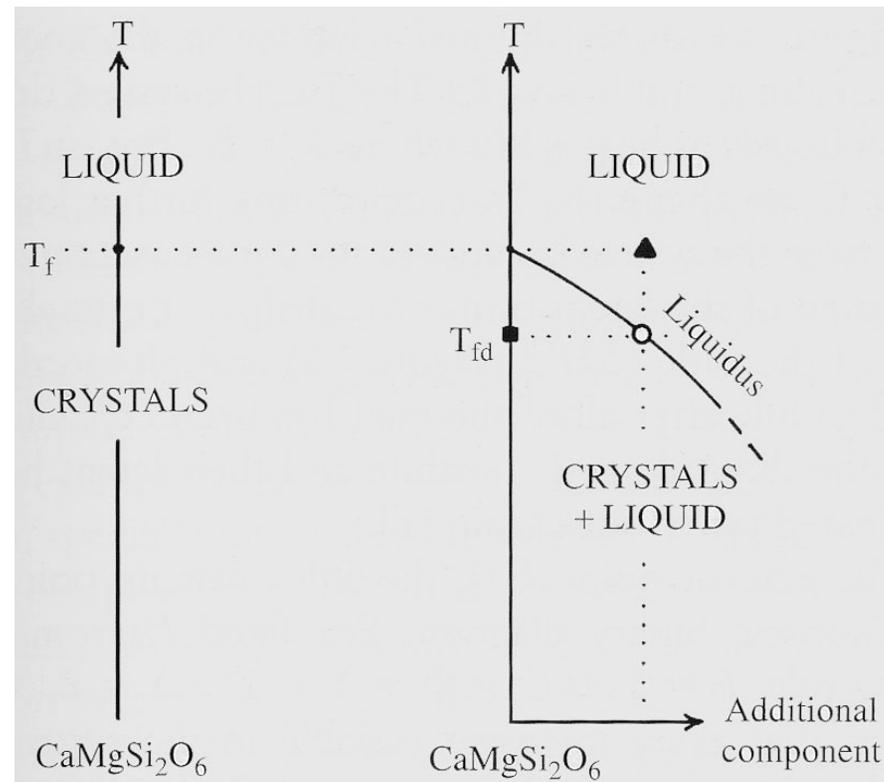
- For two dimensional phase diagrams:
 - **Stability fields:** Areas (T-P, T-X, P-X space) where a phase or phase assemblage (more than one phase) is stable.
 - **Equilibrium boundary lines:** These define the limits of stability fields. These represent values of parameters where phases in adjacent fields coexist.
 - **Triple points:** Points where equilibrium boundary lines meet. All phases in the adjacent stability fields must coexist.

Wet and Dry Melting Relations for Albite

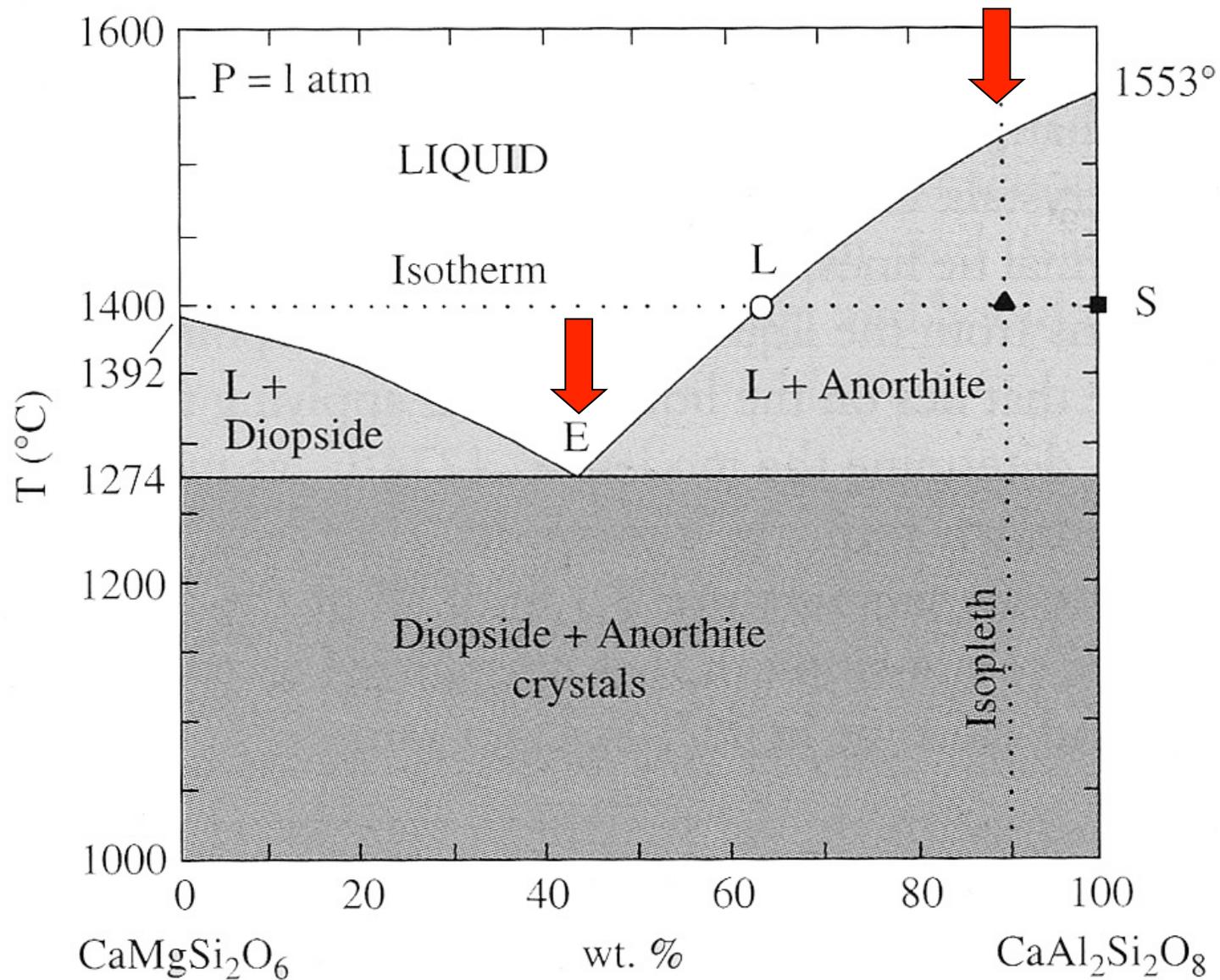


Binary Phase Relations - Definitions

- **Liquidus line:** the line that represents the locus of depressed freezing points as a second component is added to the system. Solid phases are not stable at temperatures above those defined by the liquidus line or surface.



Di-An Binary Eutectic Phase Diagram

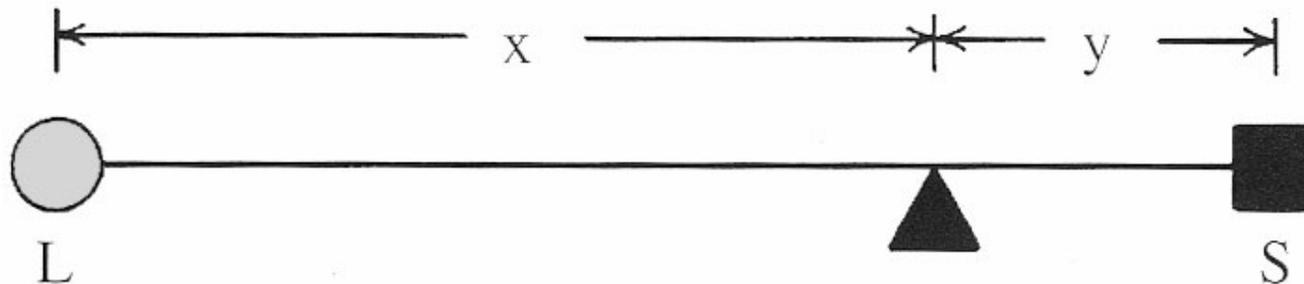


Binary Phase Diagram Definitions

- **Eutectic point:** Lowest T point on the liquidus at which a unique melt of fixed composition is in equilibrium with two or more phases.
- **Isopleth:** line of constant chemical composition.
- **Isotherm:** line of constant temperature
- **Tie line:** portion of isotherm that connects two stable coexisting phases, in this case L (representing the silicate liquid) and S (pure crystalline anorthite feldspar)

The Lever Rule

Follows directly from the Law of Conservation of Mass.
Allows one to calculate either algebraically or graphically the modal abundance of each phase at every temperature.



BULK COMPOSITION

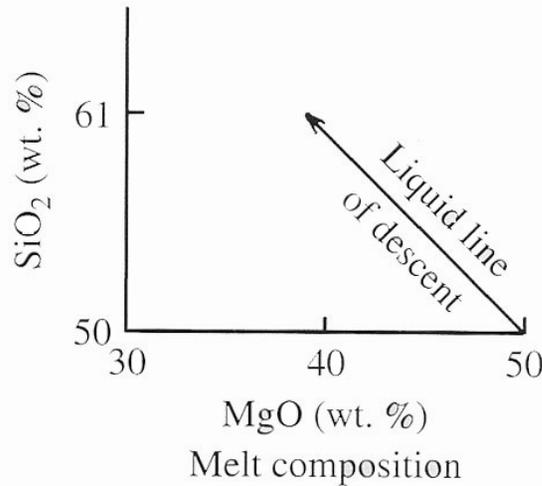
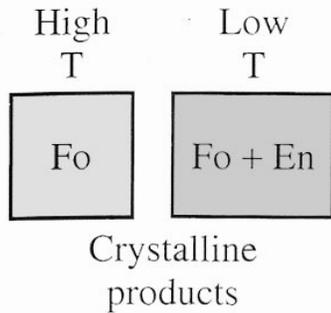
$$L = \frac{y}{(x + y)}$$

MASS OF LIQUID

$$S = \frac{x}{(x + y)}$$

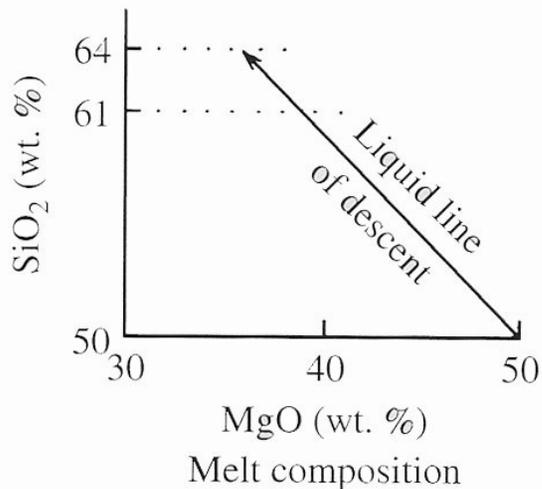
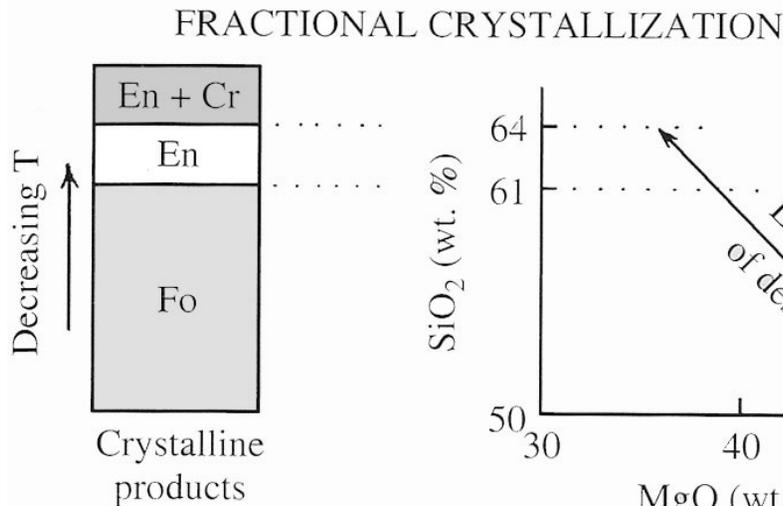
MASS OF SOLID

Equilibrium vs. Fractional Crystallization



Equilibrium Crystallization:

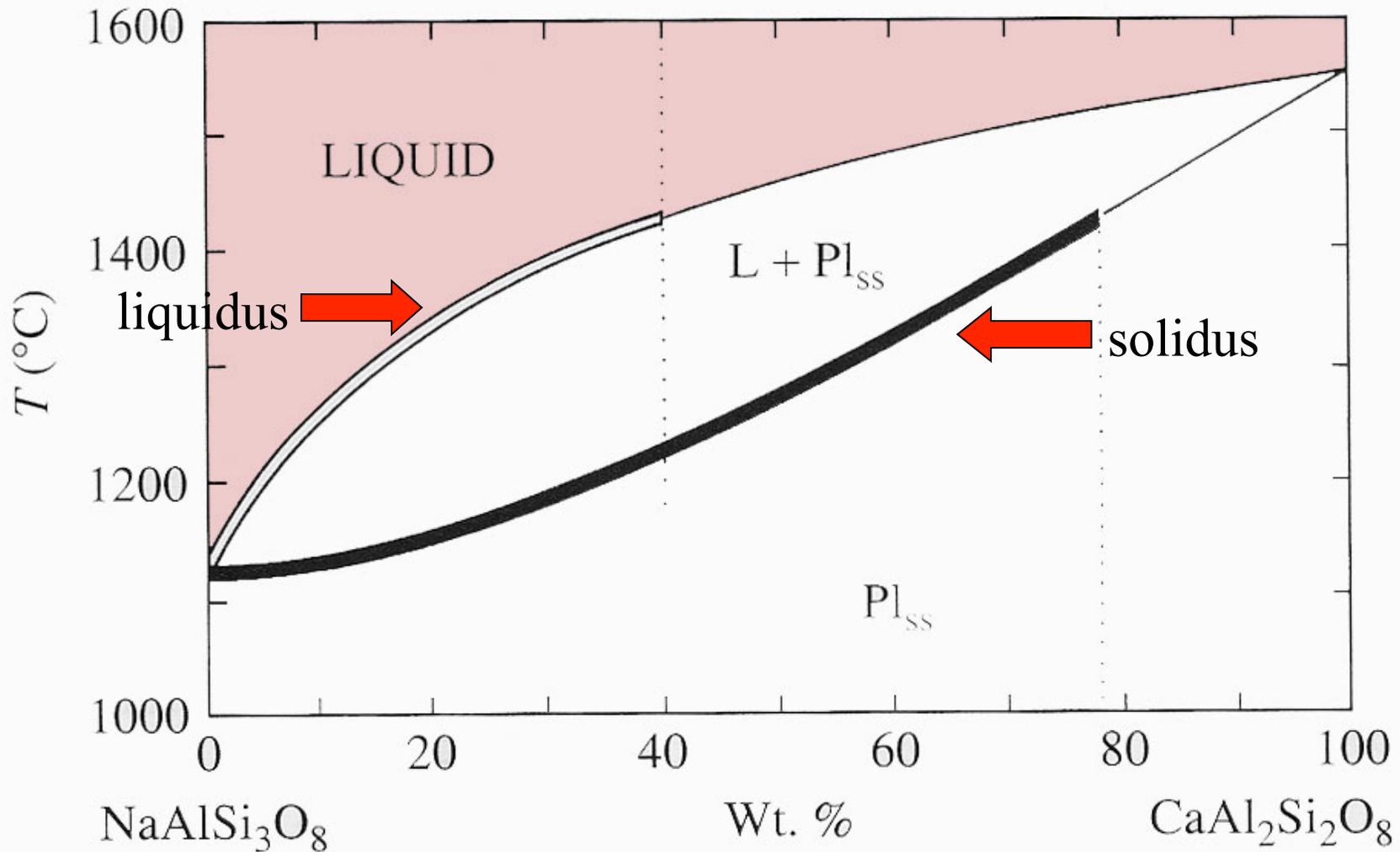
crystals continuously react and re-equilibrate with the melt at P-T-X conditions change. Melt-xtal reactions are *reversible*.



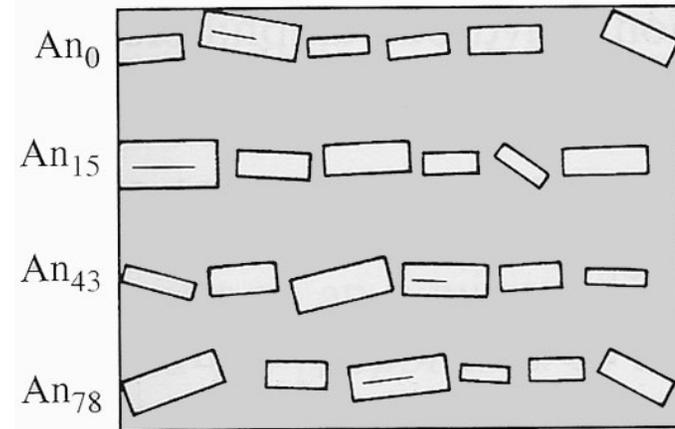
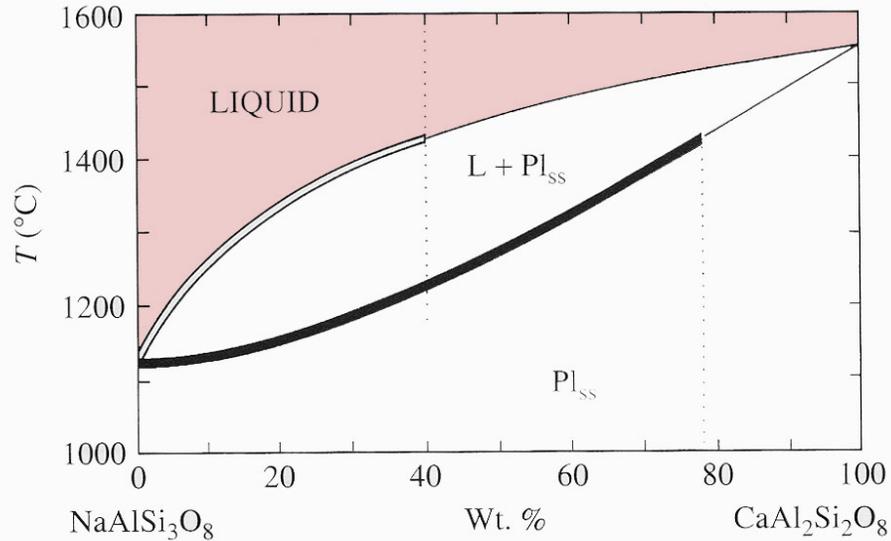
Fractional Crystallization:

Crystals are immediately isolated, removed, or fractionated from the residual melt so that no further reactions can occur. Melt-xtal reactions are *irreversible*.

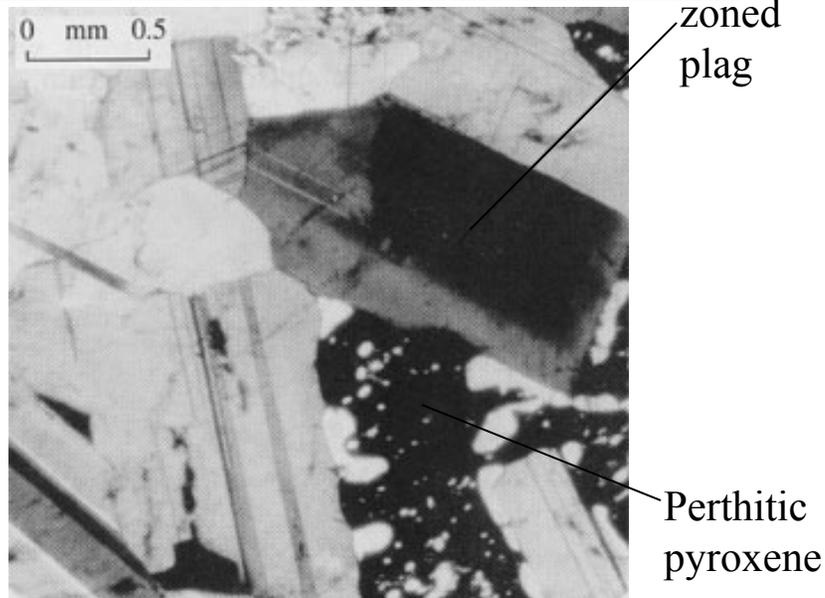
Binary Phase Loop with Solid Solution



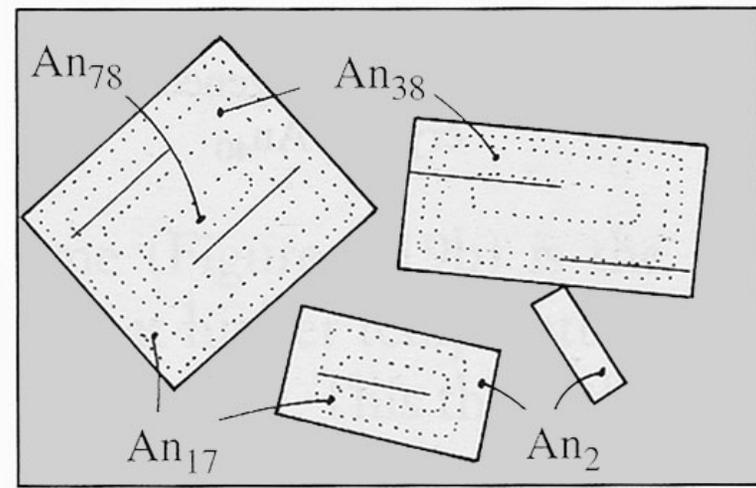
Plagioclase Differentiation Mechanisms



Crystal Settling

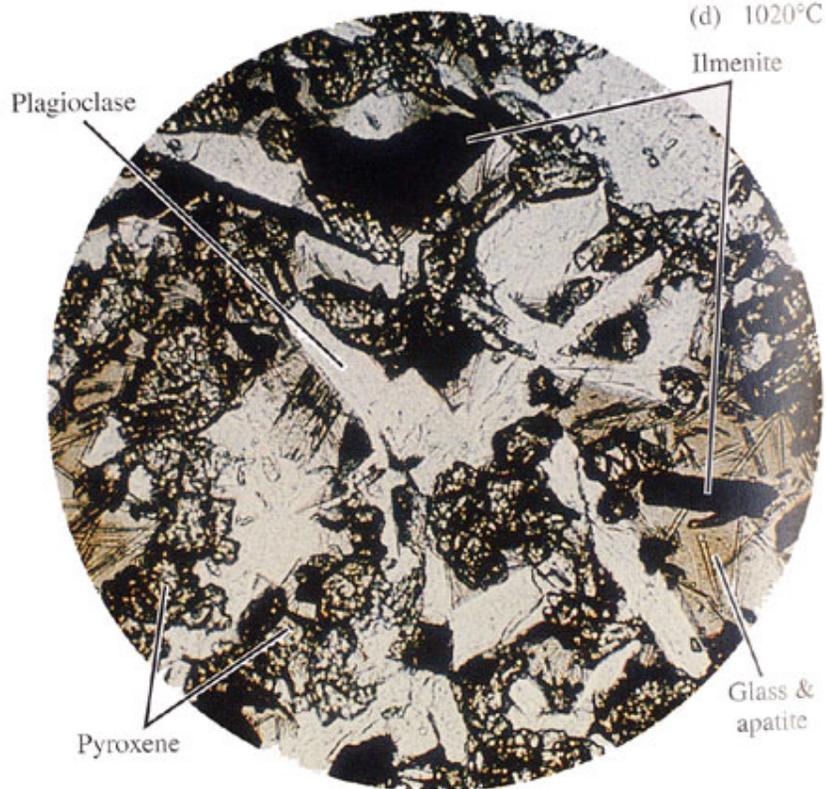
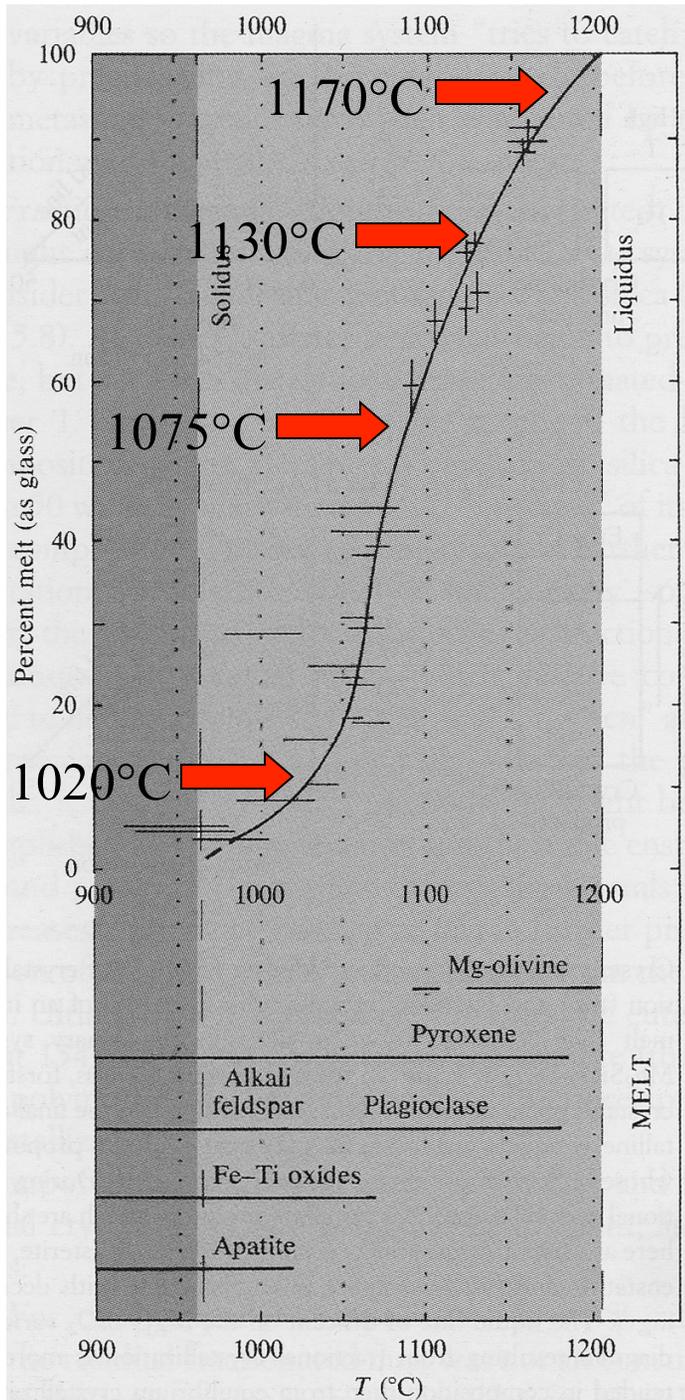


Gabbro - Plane Polarized Light



Plagioclase zoning

Hawaiian Basalt Phase Relations at 1 atm

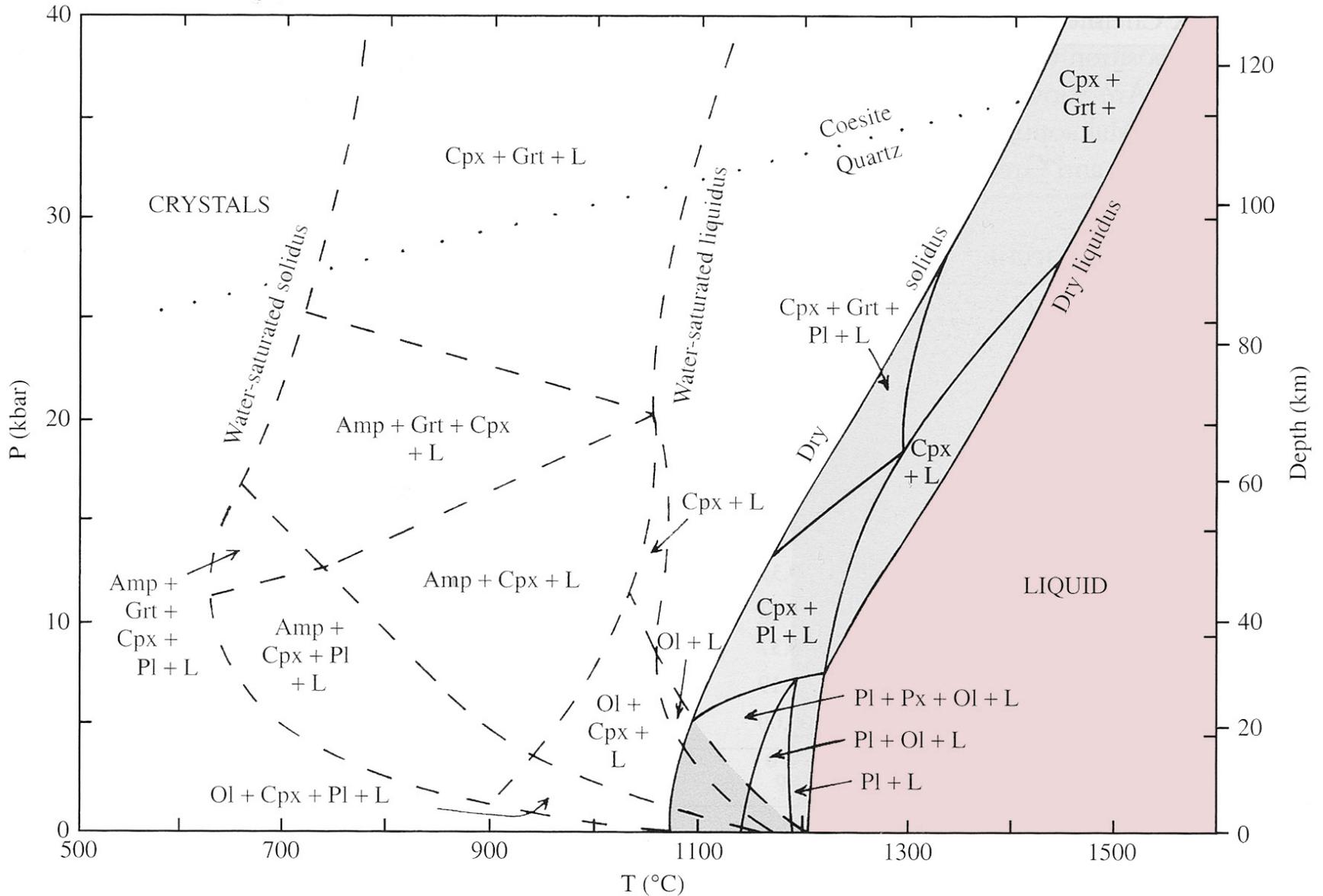


Olivine	5
Pyroxene	51
Plagioclase	30
Fe-Ti oxides	9
Glass	5
Alkali feldspar	trace

Temperatures
measured
in borehole

From Wright & Okamura, 1977

Generalized Basalt Phase Diagram



From Green, 1982