Phase Equilibrium

Phase Rule

Phase Diagram
Makaopuhi Lava Lake

Magma samples recovered from various depths beneath solid crust

From Wright and Okamura, (1977) USGS Prof. Paper, 1004.
Makaopuhi Lava Lake

Thermocouple attached to sampler to determine temperature

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Temperature of sample vs. percent glass

Fig. 6-1. From Wright and Okamura, (1977) USGS Prof. Paper, 1004.
Minerals that form during crystallization

Olivine decreases below 1175°C

Fig. 6-2. From Wright and Okamura, (1977) USGS Prof. Paper, 1004.
Mineral composition during crystallization

Makaopuhi Lava Lake

Fig. 6-3. From Wright and Okamura, (1977) *USGS Prof. Paper*, 1004.
Crystallization Behavior of Melts

1. Cooling melts crystallize from a liquid to a solid over a range of temperatures (and pressures)
2. Several minerals crystallize over this T range, and the number of minerals increases as T decreases
3. The minerals that form do so sequentially, with remarkable overlap
4. Minerals that involve solid solution change composition as cooling progresses
5. The melt composition also changes during crystallization
6. The minerals that crystallize (as well as the sequence) depend on T and X of the melt
7. Pressure can affect the types of minerals that form and the sequence
8. The nature and pressure of the volatiles can also affect the minerals and their sequence
The Phase Rule

\[ F = C - \phi + 2 \]

(Gibbs, 1928; @chemical equilibrium)

\[ F = \text{# degrees of freedom} \]

The number of intensive parameters that must be specified in order to completely determine the system

\[ \phi = \# \text{ of phases} \]

phases are mechanically separable constituents

\[ C = \text{minimum # of components} \] (chemical constituents that must be specified in order to define all phases)

\[ 2 = 2 \text{ intensive parameters} \]

Usually = temperature and pressure for us geologists

Intensive <-> Extensive variables
1. The system H₂O

Heat – temperature

Divariant fields
Univariant curves
Invariant points

melting (fusion) – precipitation
condensation – vaporization
sublimation – deposition

Negative and positive slopes

Supercritical fluid and sc region

1 - C Systems

2. The system SiO₂

Fig. 6-6. After Swamy and Saxena (1994), J. Geophys. Res., 99, 11,787-11,794. AGU

Divariant fields
Univariant curves
Invariant points

Positive slopes

Crystallization:
granite - rhyolite
2 - C Systems

A. Systems with Complete Solid Solution

2. The Olivine System Fo - Fa
(Mg$_2$SiO$_4$ - Fe$_2$SiO$_4$)

Fig. 6-10. Isobaric T-X phase diagram at atmospheric pressure After Bowen and Shairer (1932), Amer. J. Sci. 5th Ser., 24, 177-213.

C=2

3D, but
P = const.
so T-X
Note the difference between the two types of fields

The blue fields are one phase fields

Any point in these fields represents a true phase composition

The blank field is a two phase field

Any point in this field represents a bulk composition composed of two phases at the edge of the blue fields and connected by a horizontal tie-line
2-C Eutectic Systems

Diopside (Di - CaMgSi$_2$O$_6$) – Anorthite (An - CaAl$_2$Si$_2$O$_6$)

No solid solution, isobaric T-X

Fig. 6-11. Isobaric T-X phase diagram at atmospheric pressure. After Bowen (1915), Amer. J. Sci. 40, 161-185.
Cool to 1455°C (point b)

What happens at b? Pure anorthite forms (point c)

\[
\phi = 2 \\
F = 2 - 2 + 1 = 1
\]

Composition of all phases determined by T
Xliq is really the only compositional variable in this particular system
- Continue cooling as $X_{\text{liq}}$ varies along the liquidus
- **Continuous reaction:** liq$_A \rightarrow$ anorthite + liq$_B$

Lever rule shows less liquid and more anorthite as cooling progresses
at $1274^\circ C \phi = 3$ so $F = 2 - 3 + 1 = 0$ invariant

(P) $T$ and the composition of all phases is fixed

Must remain at $1274^\circ C$ as a discontinuous reaction proceeds until a phase is lost

What happens at $1274^\circ C$? Get new phase

**Pure diopside g** joins liquid d and anorthite h

d is called the **eutectic point**: MUST reach it in all cases
Note the following:

1. The melt crystallizes over a T range up to ~280°C
2. A sequence of minerals forms over this interval
   - And the number of minerals increases as T drops
6. The minerals that crystallize depend upon T
   - The sequence changes with the bulk composition
Augite forms before plagioclase

Hipidiomorphic **texture**

This forms on the **left** side of the eutectic

Gabbro of the Stillwater Complex, Montana
Plagioclase forms before augite

Ophitic texture

This forms on the right side of the eutectic

Diabase dike
Also note:

- The last melt to crystallize in any binary eutectic mixture is the eutectic composition
- **Equilibrium melting** is the opposite of equilibrium crystallization
- Thus the first melt of any mixture of Di and An must be the eutectic composition as well
In a eutectic system increasing pressure will raise the melting point (as predicted).

The magnitude of the effect will vary for different minerals:
- Anorthite compresses less than Diopside.
- Thus the elevation of the m. p. is less for An than Di.
- The eutectic thus shifts toward An.

**Figure 7-16.** Effect of lithostatic pressure on the liquidus and eutectic composition in the diopside-anorthite system. 1 GPa data from Presnall *et al.* (1978). Contr. Min. Pet., 66, 203-220.
C. Binary Peritectic Systems

Three phases enstatite $= \text{forsterite} + \text{SiO}_2$

Cool bulk composition $a$ (42 %)

At $a$

\[
\phi_i = 1 \text{ (liquid)}
\]

\[
F = 2 - 1 + 1 = 2
\]

Cool to 1625 °C

Cristobalite forms at $b$

\[
\phi_i = 2
\]

\[
F = 2 - 2 + 1 = 1
\]

\[
X_{\text{liq}} = f(T)
\]

Figure 6-12. Isobaric T-X phase diagram of the system Fo-Silica at 0.1 MPa. After Bowen and Anderson (1914) and Grieg (1927). Amer. J. Sci.
As T lowered Xliq follows path to c: the eutectic
At 1543°C, enstatite forms: d
Now $f = 3$ and $F = 2 - 3 + 1 = 0$

Invariant

Discontinuous reaction:

$$\text{liq} = \text{En} + \text{Crst} \quad \text{colinear}$$

Stay at this T until liq is consumed
Then have En + Crst

$$\phi = 2$$

$$F = 2 - 2 + 1 = 1$$

Univariant

At 1470°C get polymorphic transition Crst -> Trid
Another invariant discontinuous rxn

Figure 6-12. Isobaric T-X phase diagram of the system Fo-Silica at 0.1 MPa. After Bowen and Anderson (1914) and Grieg (1927). Amer. J. Sci.
Next cool \( f = 13 \) wt. % at 1800°C get olivine (Fo) forming
\[
\phi = 2 \\
F = 2 - 2 + 1 = 1
\]
univariant
\[X_{\text{liq}} = f(T)\]

At 1557°C get opx (En) forming
\[
\phi = 3 \\
F = 2 - 2 + 1 = 0
\]
invariant

at 1557: fo+en+liq
\( f = 3, F = ? \)

What is happening? T?, f?
$i$ = “peritectic” point

$1557^\circ C$ have colinear Fo-En-liq

geometry indicates a reaction: $\text{Fo} + \text{liq} = \text{En}$

consumes olivine (and liquid) $\rightarrow$ resorbed textures

When is the reaction finished?

If the bulk X is between Fo and En
the liquid disappears first at the
peritectic temperature
and Fo + En remain as
the final solids

If, on the other hand, the bulk X lies
to the right of En, then Fo is
consumed first and the liquid
continues to evolve toward the
eutectic
at 1557: fo+en+liq
f=3, F=?
What is happening? T?, f?

Figure 6-12. Isobaric T-X phase diagram of the system Fo-Silica at 0.1 MPa. After Bowen and Anderson (1914) and Grieg (1927). Amer. J. Sci.
When is the reaction finished?

The bulk X lies to the right of En, then Fo is consumed first and the liquid continues to evolve toward the eutectic (C).
Incongruent Melting of Enstatite

- Melt of En does not → melt of same composition
- Rather En → Fo + Liq i at the peritectic

Partial Melting of Fo + En (harzburgite) mantle

- En + Fo also → first liq = i
- Remove i and cool
- Result = ?
Cool \( X = n \) Immiscible Liquids

- At 1960°C hit solvus
  - exsolution
  - → 2 liquids o and p
  - \( \phi = 2 \quad F = 1 \)
  - both liquids follow solvus

At 1695°C get Crst also

Reaction?

![Phase diagram showing immiscible liquids at 1960°C and 1695°C](image-url)
Pressure Effects

Different phases have different compressibilities
Thus P will change Gibbs Free Energy differentially

- Raises melting point
- Shift eutectic position (and thus X of first melt, etc.)

Figure 6-15. The system Fo-SiO2 at atmospheric pressure and 1.2 GPa. After Bowen and Schairer (1935), Am. J. Sci., Chen and Presnall (1975) Am. Min.
Pressure Effects

Different phases have different compressibilities
Thus P will change Gibbs Free Energy differentially

- Raises melting point
- Shift eutectic position (and thus X of first melt, etc.)