Chapter 6:
The Phase Rule and One and Two-Component Systems
aka “Phase Equilibria”
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

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

Fig. 6.2. From Wright and Okamura, (1977) USGS Prof. Paper, 1004.
Mineral composition during crystallization

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)
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8. The nature and pressure of the volatiles can also affect the minerals and their sequence
Phase equilibrium and Gibbs Phase Rule

- Capable of analyzing ‘systems’ in a way that allows us to grasp the dynamics of each and to account for the contribution of each chemical constituent to the variations.

- Understand how the introduction of additional constituents affects a system – helps us better comprehend new systems and more complex systems in nature.
The Gibbs Phase Rule

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

\( F = \) # degrees of freedom

The number of \textit{independently intensive parameters} that must be \textit{specified} in order to completely determine the system at \textit{equilibrium conditions}

Consist of properties of the substances that compose a system (e.g., mineral assemblage)

Examples: Pressure, Temperature, density, molar volume
The Phase Rule

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

\( F = \# \text{ degrees of freedom} \)

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

\( \phi = \# \text{ of phases} \)

phases are \textit{mechanically separable} constituents
The Phase Rule

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\( \phi \) = \# of phases

phases are mechanically separable constituents

\( C \) = minimum \# of components (chemical constituents that must be specified in order to define all phases)
**The Phase Rule**

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

- **F** = number of degrees of freedom
  - The number of intensive parameters that must be specified in order to completely determine the system
- **\( \phi \)** = number of phases
  - Phases are mechanically separable constituents
- **C** = minimum number of components (chemical constituents that must be specified in order to define all phases)
- **2** = 2 intensive parameters
  - Usually = temperature and pressure for us geologists
Cross section: sample in red

1 cm

Fig. 6.5. After Boyd and England (1960), J. Geophys. Res., 65, 741-748. AGU
1 - C Systems

1. The system SiO₂

Fig. 6.6. After Swamy and Saxena (1994), J. Geophys. Res., 99, 11,787-11,794. AGU
1 - C Systems

2. The system H$_2$O

A. Systems with Complete Solid Solution

1. Plagioclase (Ab-An, NaAlSi$_3$O$_8$ - CaAl$_2$Si$_2$O$_8$)

Fig. 6.8. Isobaric T-X phase diagram at atmospheric pressure. After Bowen (1913) Amer. J. Sci., 35, 577-599.
Bulk composition $\alpha = \text{An}_{60}$

$= 60 \text{ g An} + 40 \text{ g Ab}$

$X_{\text{An}} = \frac{60}{(60+40)} = 0.60$
F = 2

1. Must specify 2 independent intensive variables in order to completely determine the system
   = a divariant situation

   same as:

2. Can vary 2 intensive variables independently without changing $\phi$, the number of phases
Must specify and or can vary these without changing the number of phases

Now cool to 1475°C (point a) what happens?

Get new phase joining liquid: 0.8

First crystals of plagioclase = 0.87 (point b)

F = ?
Considering an isobarically cooling magma, \( x_{\text{An}}^{\text{liq}} \) and \( x_{\text{plag}} \) are dependent upon \( T \).

\[
F = 2 - 2 + 1 = 1 \quad \text{("univariant")}
\]

Must specify only one variable from among:

\[
T \quad x_{\text{An}}^{\text{liq}} \quad x_{\text{Ab}}^{\text{liq}} \quad x_{\text{An}}^{\text{plag}} \quad x_{\text{Ab}}^{\text{plag}} \quad (P \text{ constant})
\]

The slope of the solidus and liquidus are the expressions of this relationship.
At 1450°C, liquid $d$ and plagioclase $f$ coexist at equilibrium.

A continuous reaction of the type:

$$\text{liquid}_B + \text{solid}_C = \text{liquid}_D + \text{solid}_F$$
The lever principle:

\[
\frac{\text{Amount of liquid}}{\text{Amount of solid}} = \frac{ef}{de}
\]

where \(d\) = the liquid composition, \(f\) = the solid composition, and \(e\) = the bulk composition.
When $X_{\text{plag}} \rightarrow h$, then $X_{\text{plag}} = X_{\text{bulk}}$ and, according to the lever principle, the amount of liquid $\rightarrow 0$

Thus $g$ is the composition of the last liquid to crystallize at $1340^\circ C$ for bulk $X = 0.60$
Final plagioclase to form is $i$ when $X_{An}^{plag} = 0.60$

Now $\phi = 1$ so $F = 2 - 1 + 1 = 2$
Note the following:
1. The melt crystallized over a T range of 135°C *
4. The composition of the liquid changed from b to g
5. The composition of the solid changed from c to h

* The actual temperatures and the range depend on the bulk composition

Numbers refer to the “behavior of melts” observations
Equilibrium **melting** is exactly the opposite

- Heat An$_{60}$ and the first melt is g at An$_{20}$ and 1340$^\circ$C
- Continue heating: both melt and plagioclase change X
- Last plagioclase to melt is c (An$_{87}$) at 1475$^\circ$C
Fractional crystallization:

Remove crystals as they form so they can’t undergo a continuous reaction with the melt

At any \( T \), \( X_{\text{bulk}} = X_{\text{liq}} \) due to the removal of the crystals
Partial Melting:
Remove first melt as forms
Melt $X_{\text{bulk}} = 0.60$ first liquid = $g$
remove and cool bulk = $g \rightarrow$ final plagioclase = $i$
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. The Olivine System

Fo - Fa ($\text{Mg}_2\text{SiO}_4 - \text{Fe}_2\text{SiO}_4$)
also a solid-solution series

Fig. 6.10. Isobaric T-X phase diagram at atmospheric pressure After Bowen and Shairer (1932), Amer. J. Sci. 5th Ser., 24, 177-213.
2-C Eutectic Systems

Example: Diopside - Anorthite

No solid solution

Fig. 6.11. Isobaric T-X phase diagram at atmospheric pressure. After Bowen (1915), Amer. J. Sci. 40, 161-185.
Cool composition \( a \): 
bulk composition = \( \text{An}_{70} \)
Cool to 1455°C (point b)
- Continue cooling as $X_{\text{liq}}$ varies along the liquidus
- **Continuous reaction**: \( \text{liq}_A \rightarrow \text{anorthite} + \text{liq}_B \)
at 1274° C φ = 3 so F = 2 - 3 + 1 = 0  invariant

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

Must remain at 1274° C as a discontinuous reaction proceeds until a phase is lost
Discontinuous Reaction: all at a single T

Use geometry to determine
Left of the eutectic get a similar situation
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

This forms on the left side of the eutectic

Gabbro of the Stillwater Complex, Montana
Plagioclase forms before augite

Ophitic texture

Diabase dike

This forms on the right side of the eutectic
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.