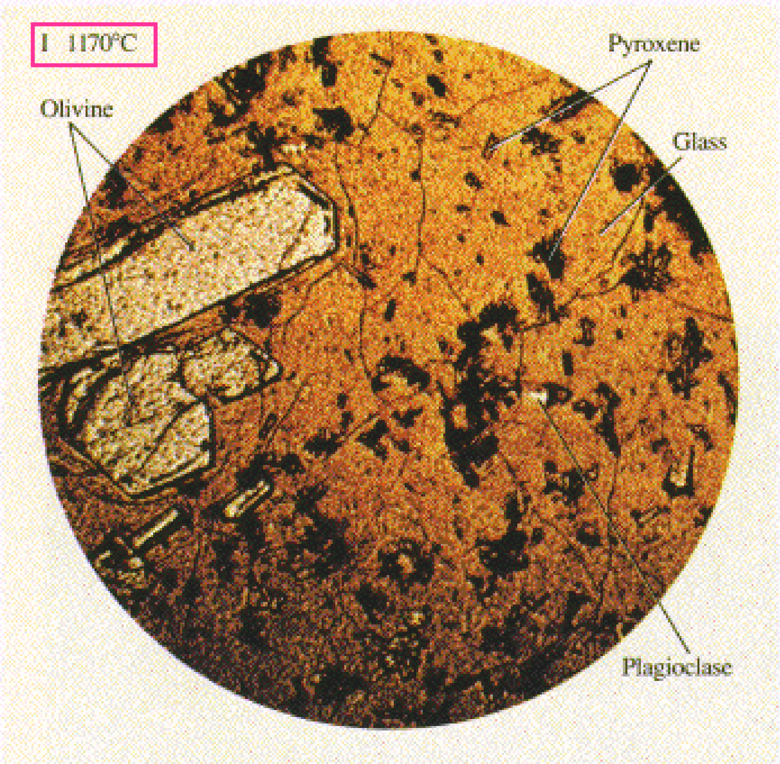
Chapter 6:
The Phase Rule and One and Two-Component Systems
aka “Phase Equilibria”

Makaopuhi Lava Lake

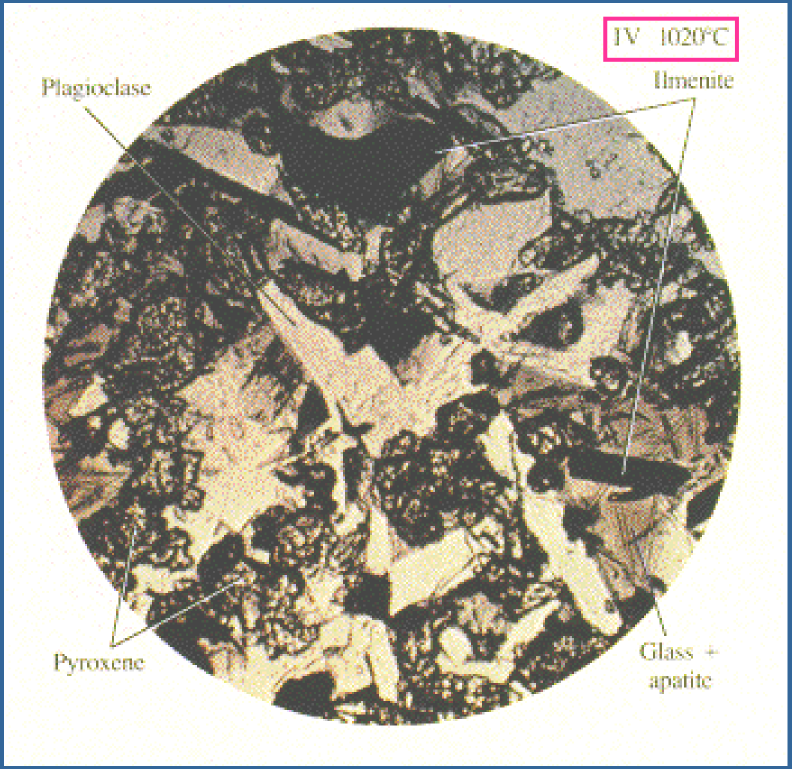
Magma samples recovered from various depths beneath solid crust



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**.

Makaopuhi Lava Lake

- Temperature of sample vs. Percent Glass

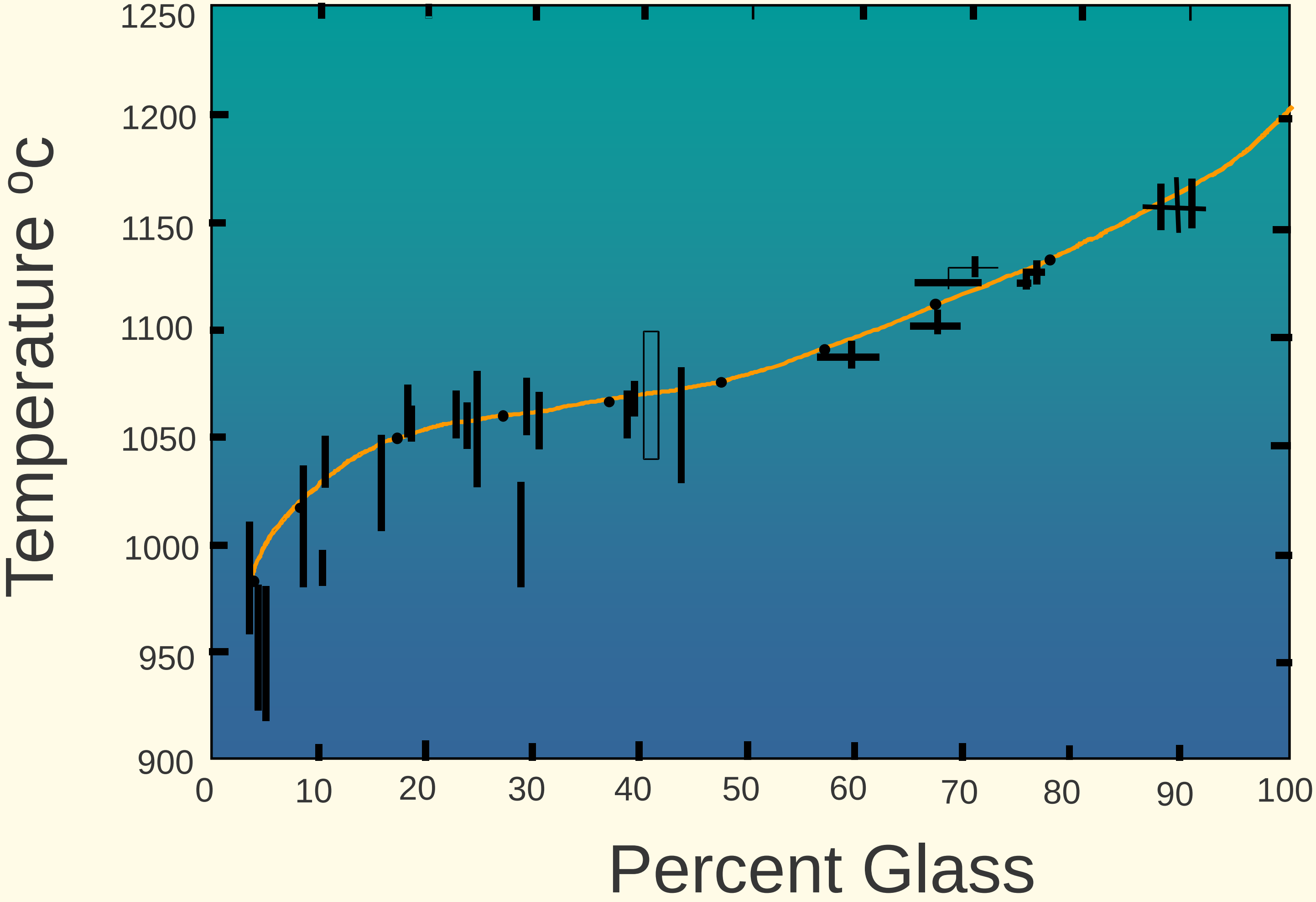


Fig. 6.1. From Wright and Okamura, (1977) *USGS Prof. Paper*, **1004**.

Makaopuhi Lava Lake

Minerals that form during crystallization

olivine
decreases
below
1175^{o}C

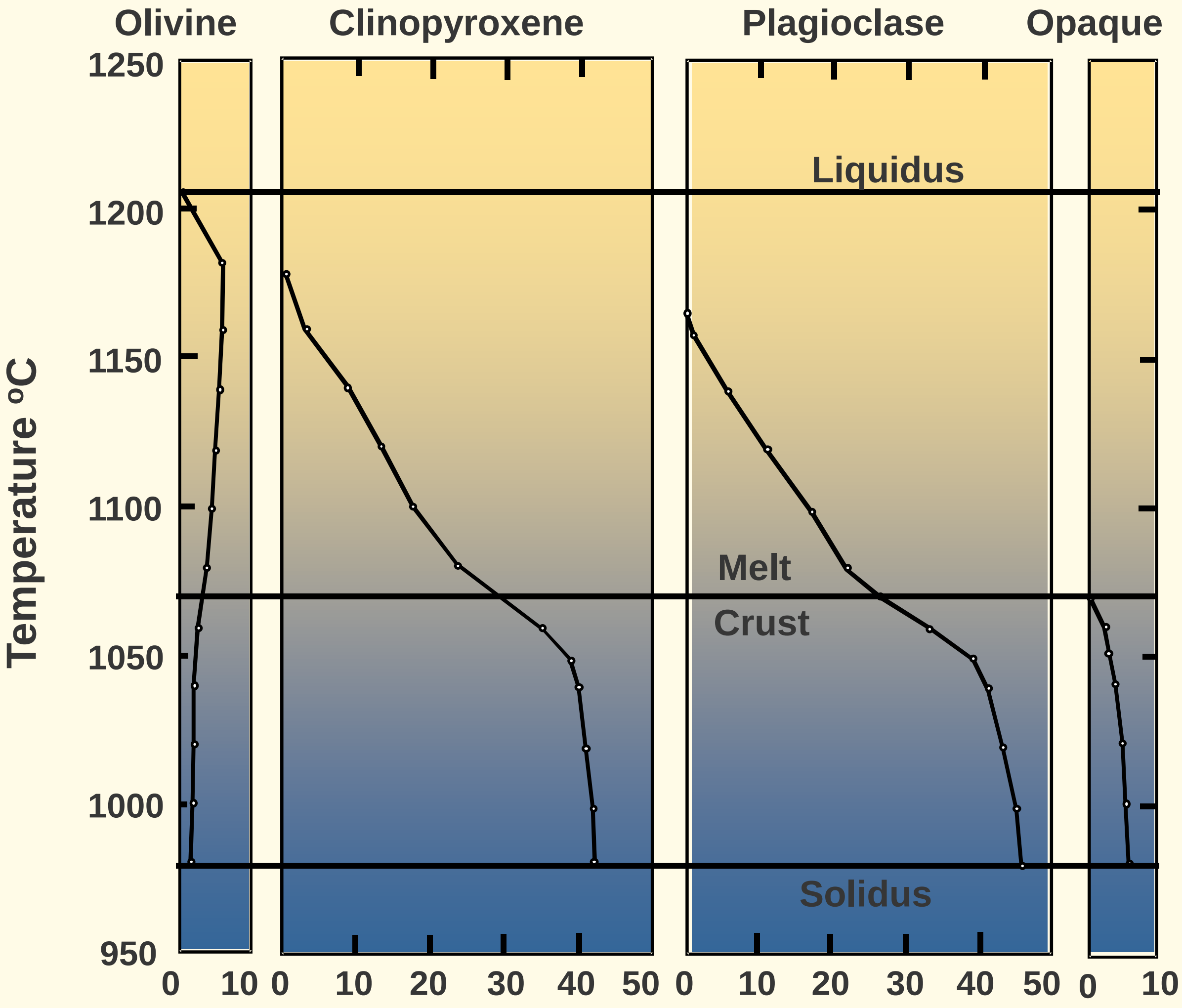


Fig. 6.2. From Wright and Okamura, (1977) *USGS Prof. Paper*, **1004**.

Makaopuhi Lava Lake

Mineral composition during crystallization

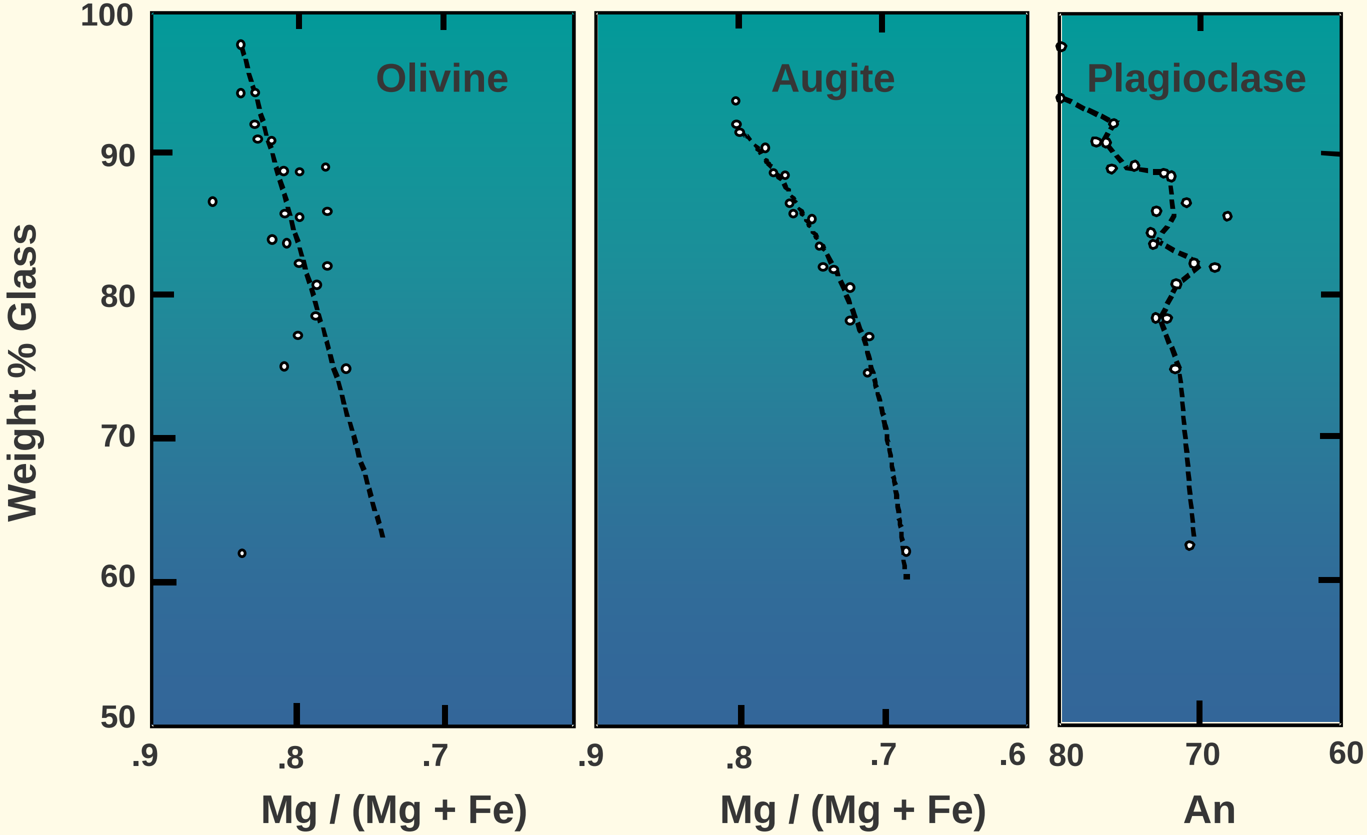


Fig. 6.3. From Wright and Okamura, (1977) *USGS Prof. Paper*, **1004**.

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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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

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 independently intensive parameters that must be specified in order to completely determine the system at *equilibrium conditions***

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

- **Examples: Pressure, Temperature, density, molar volume**

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C = minimum # 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

High Pressure Experimental Furnace

Cross section: sample in red

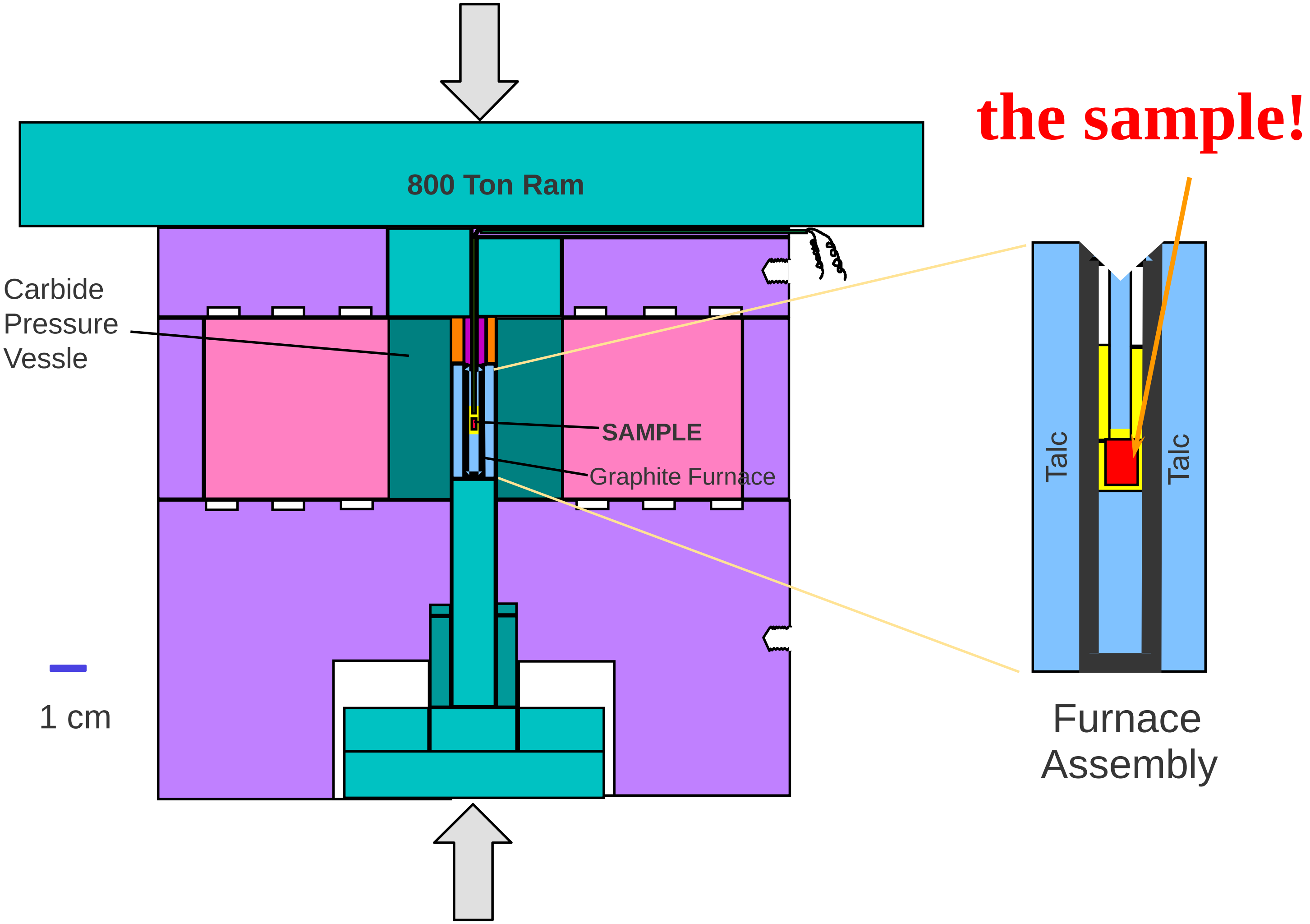


Fig. 6.5. After Boyd and England (1960), J. Geophys. Res., **65**, 741-748. AGU

1 - C Systems

1. The system SiO_2

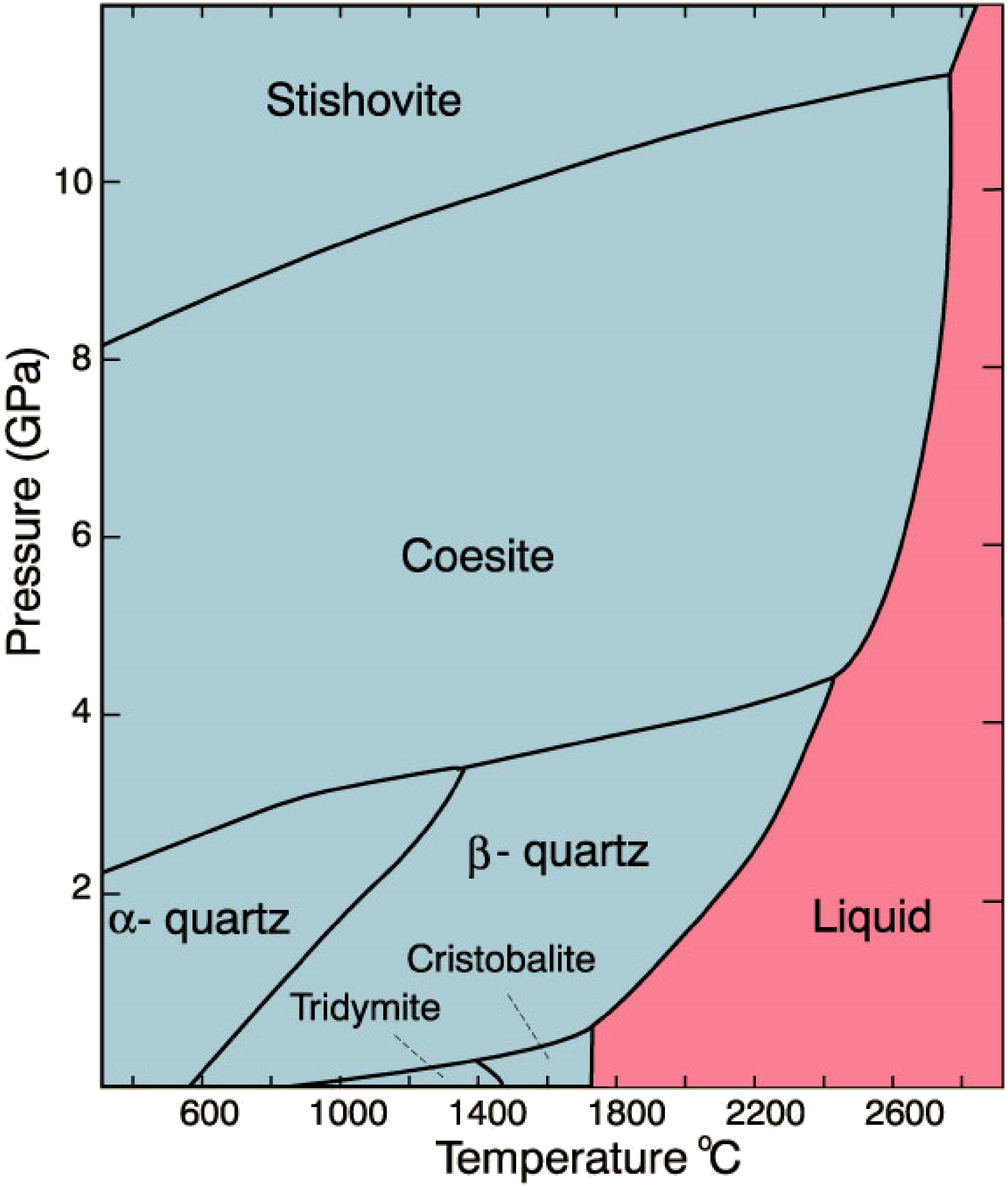


Fig. 6.6. After Swamy and Saxena (1994), J. Geophys. Res., 99, 11,787-11,794. AGU

1 - C Systems

2. The system H_2O

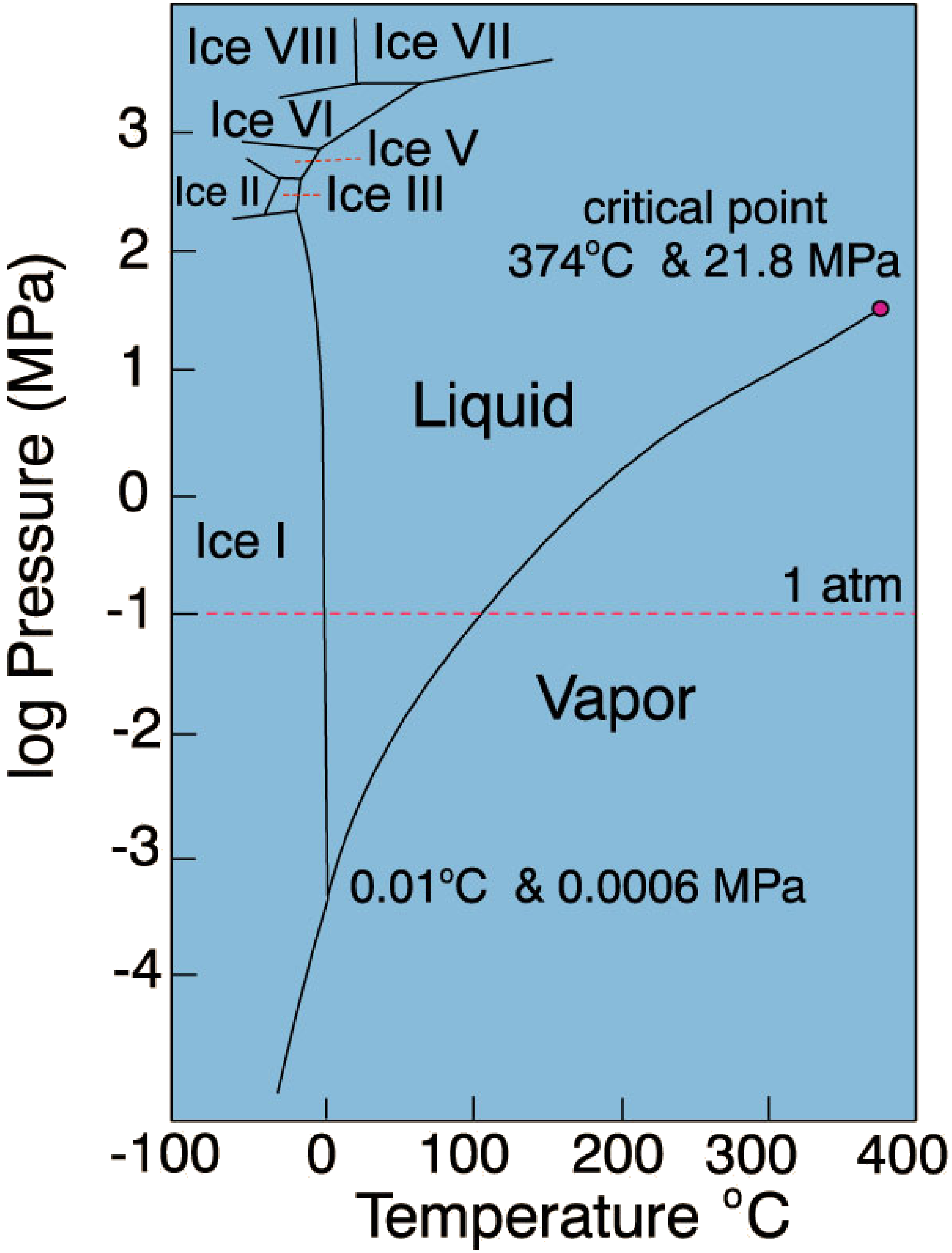


Fig. 6.7. After Bridgman (1911) Proc. Amer. Acad. Arts and Sci., 5, 441-513; (1936) J. Chem. Phys., 3, 597-605; (1937) J. Chem. Phys., 5, 964-966.

2 - C Systems

A. Systems with Complete Solid Solution

1. Plagioclase (Ab-An, $NaAlSi_3O_8$ - $CaAl_2Si_2O_8$)

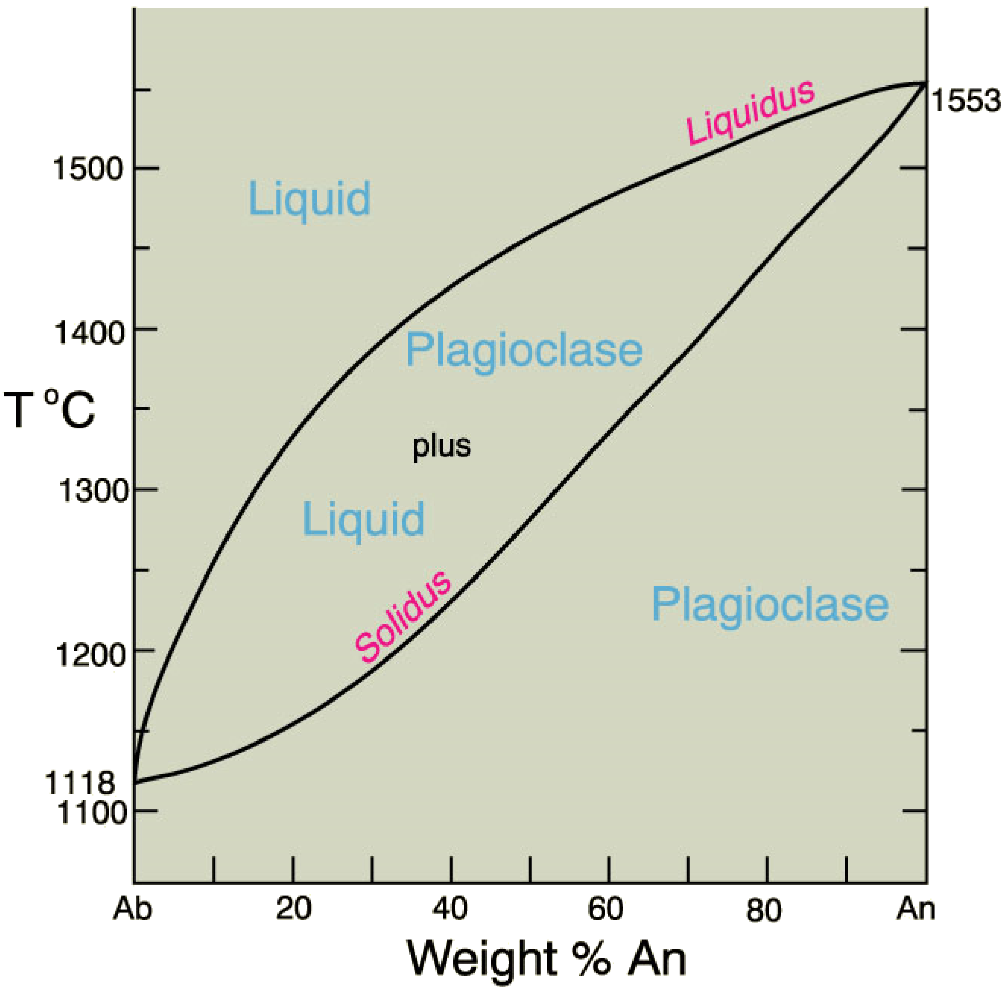
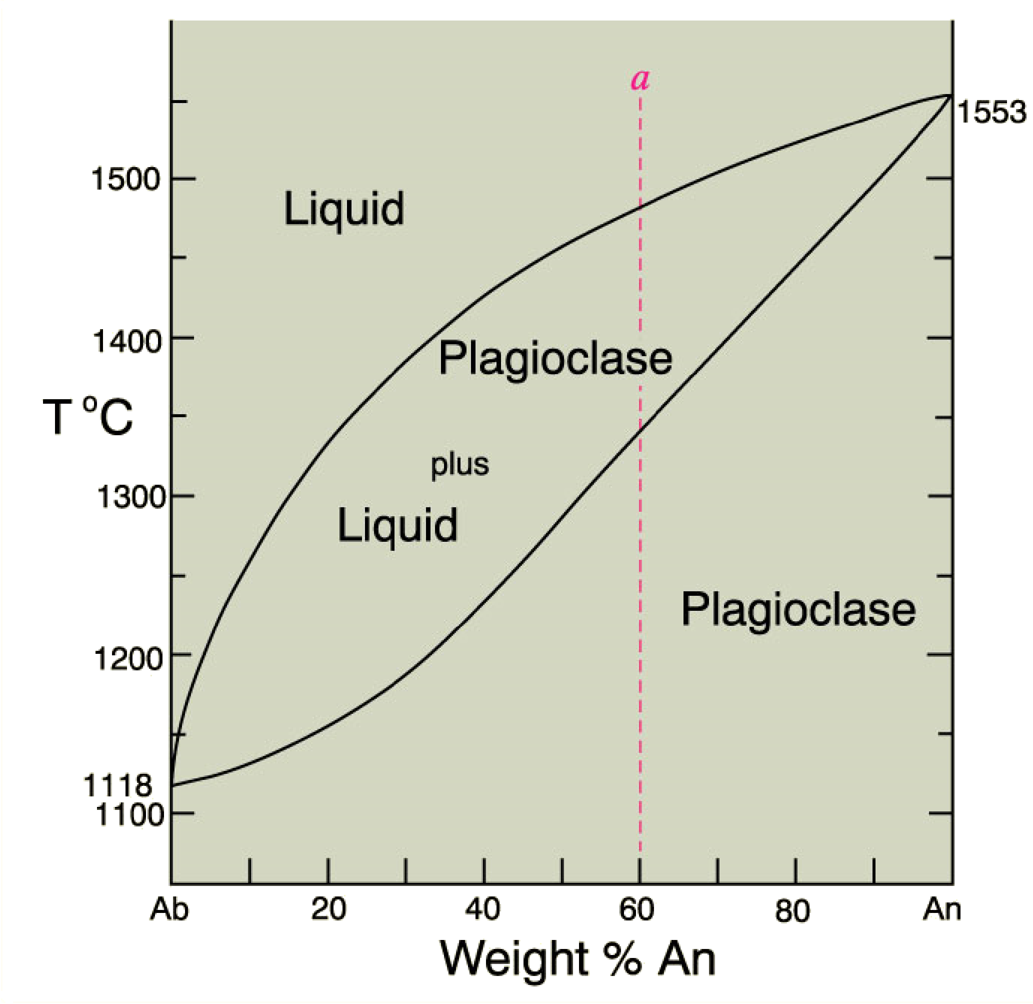


Fig. 6.8. Isobaric T-X phase diagram at atmospheric pressure. After Bowen (1913) Amer. J. Sci., 35, 577-599.

Bulk composition *a* = An_{60}

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

$X_{An} = 60/(60+40) = 0.60$



F = 2

1. Must specify 2 independent intensive variables in order to completely determine the system

   = a divariant situation

same as:

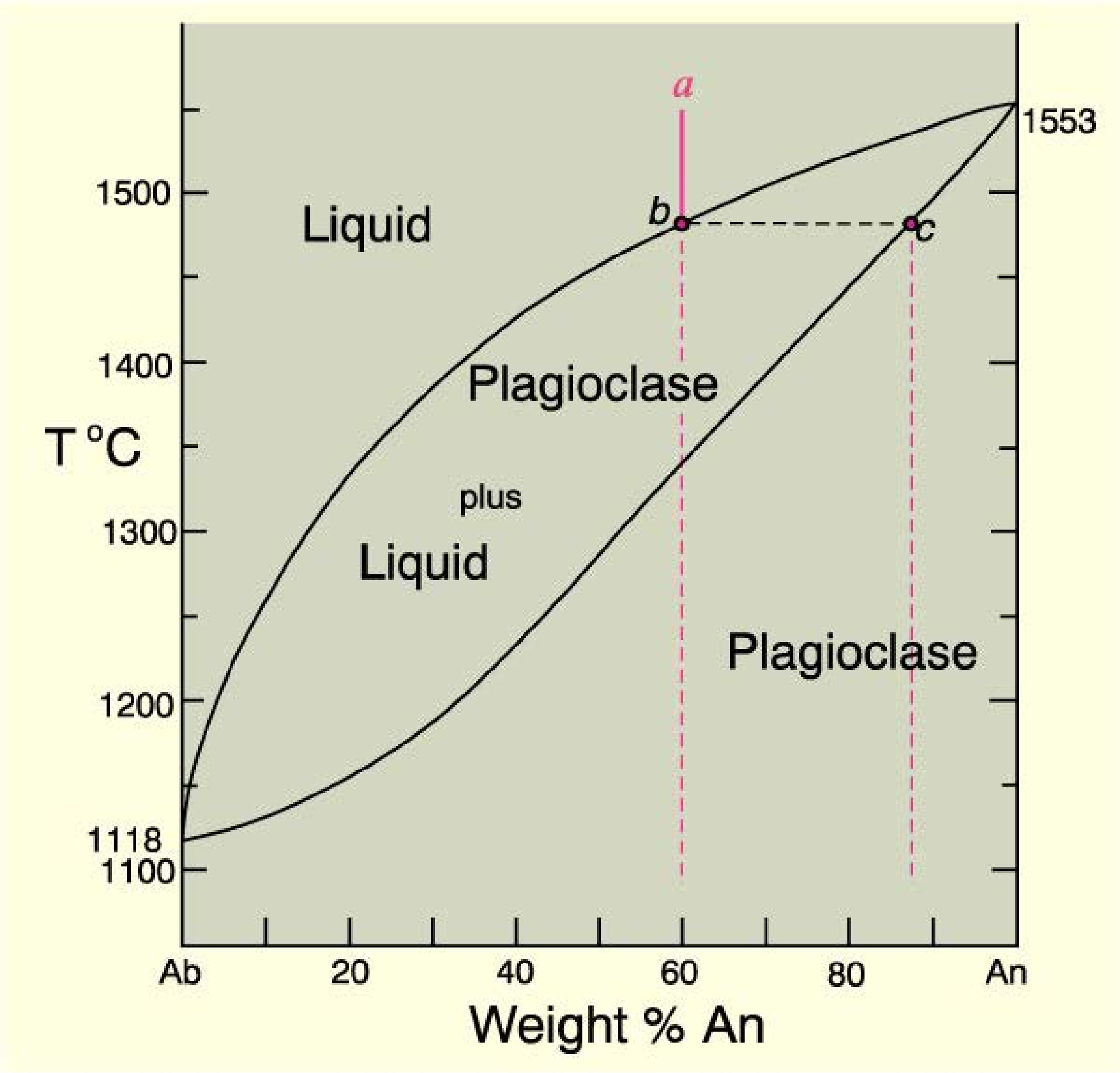
2. Can vary 2 intensive variables independently without changing ϕ, the number of phases

Get new phase joining liquid: first crystals of plagioclase: X_{An}^{plag} = 0.87 (point c)

Now cool to 1475°C (point b) What happens?

Must specify T and X_{An}^{liq} or can vary these without changing the number of phases

F = ?



$F = 2 - 2 + 1 = 1$ (“univariant”)

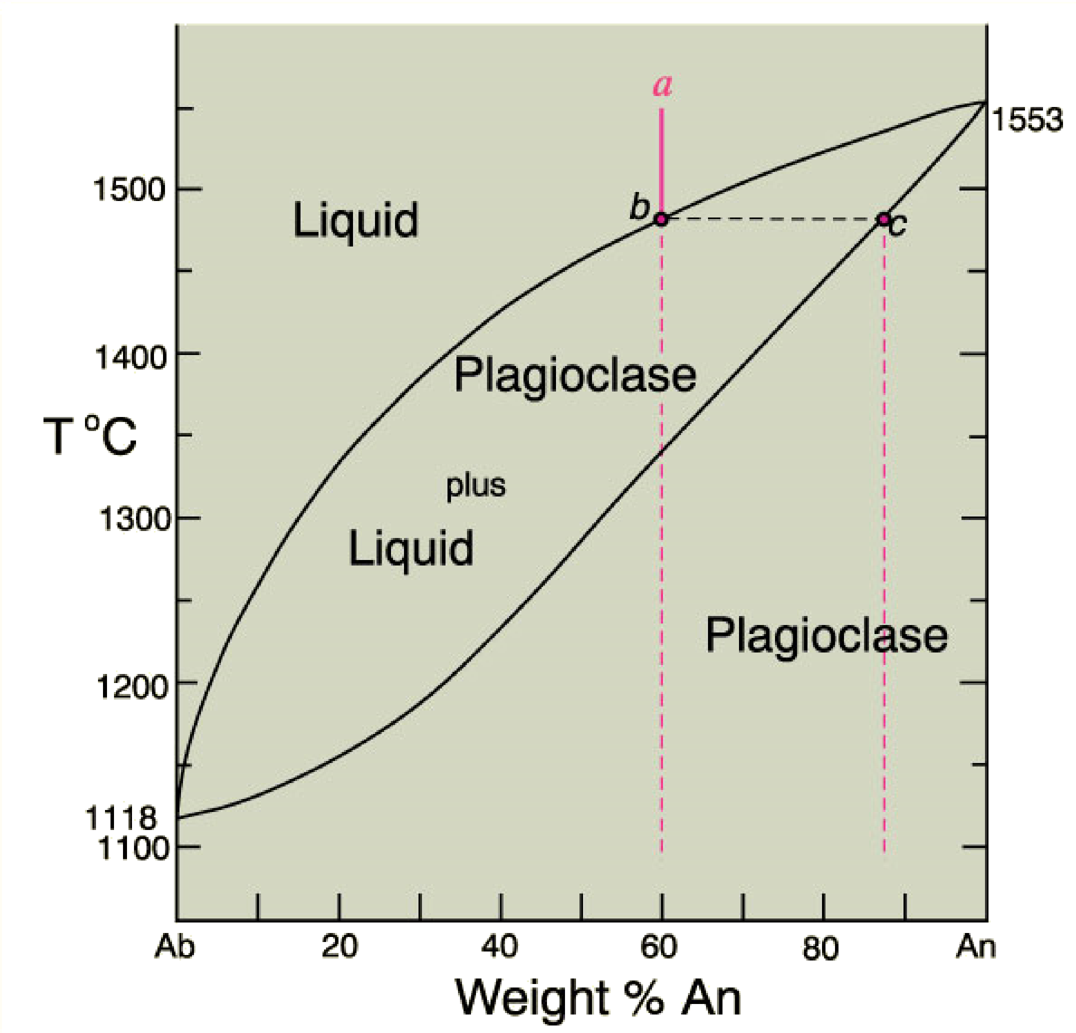
Must specify only one variable from among:

$T \quad X_{An}^{liq} \quad X_{Ab}^{liq} \quad X_{An}^{plag} \quad X_{Ab}^{plag}$ **(P constant)**

Considering an isobarically cooling magma,

X_{An}^{liq} and X_{An}^{plag} are dependent upon T

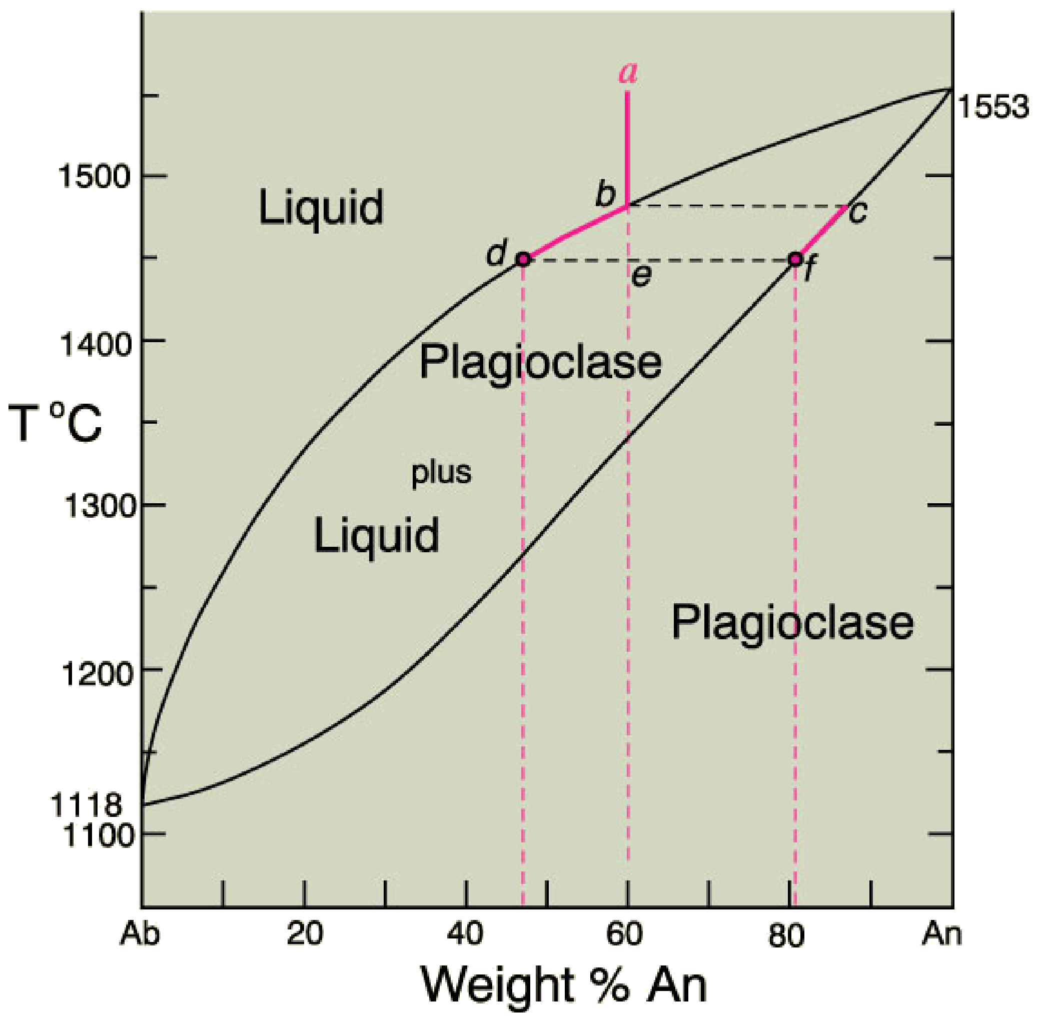
The **slope** of the solidus and liquidus are the expressions of this relationship



At 1450°C, liquid ***d*** and plagioclase ***f*** coexist at equilibrium

A continuous reaction of the type:

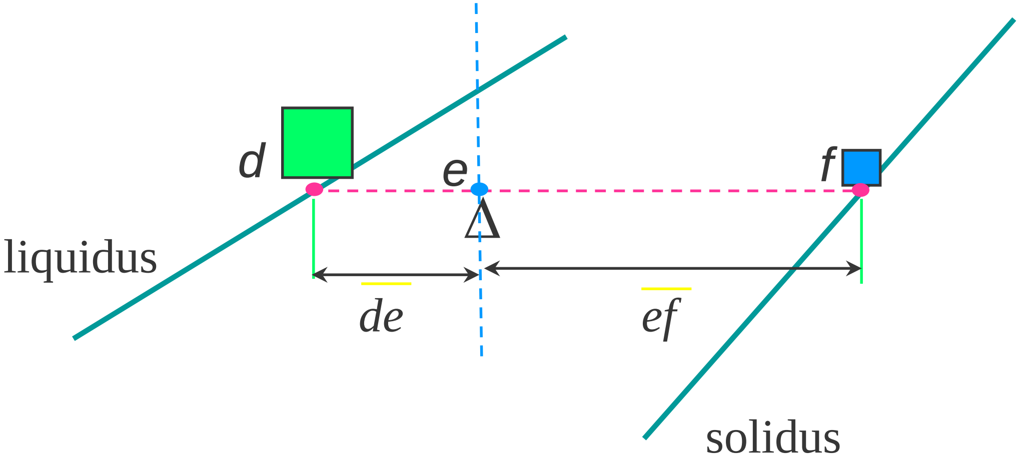
$\text{liquid}_B + \text{solid}_C =$
$\quad \text{liquid}_D + \text{solid}_F$



The lever principle:

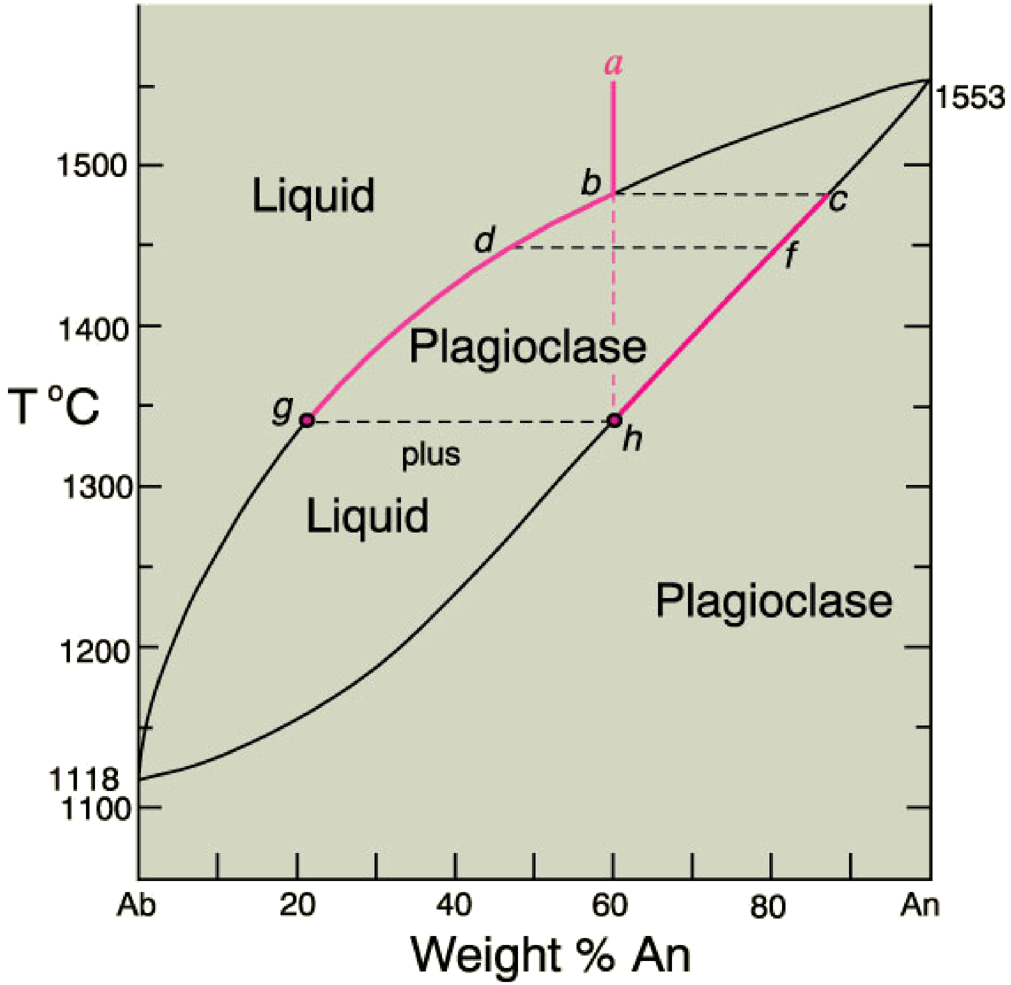
$$\frac{\text{🟩}}{\text{🟦}} \qquad \frac{\text{Amount of liquid}}{\text{Amount of solid}} = \frac{\overline{ef}}{\overline{de}}$$

where *d* = the liquid composition, *f* = the solid composition and *e* = the bulk composition



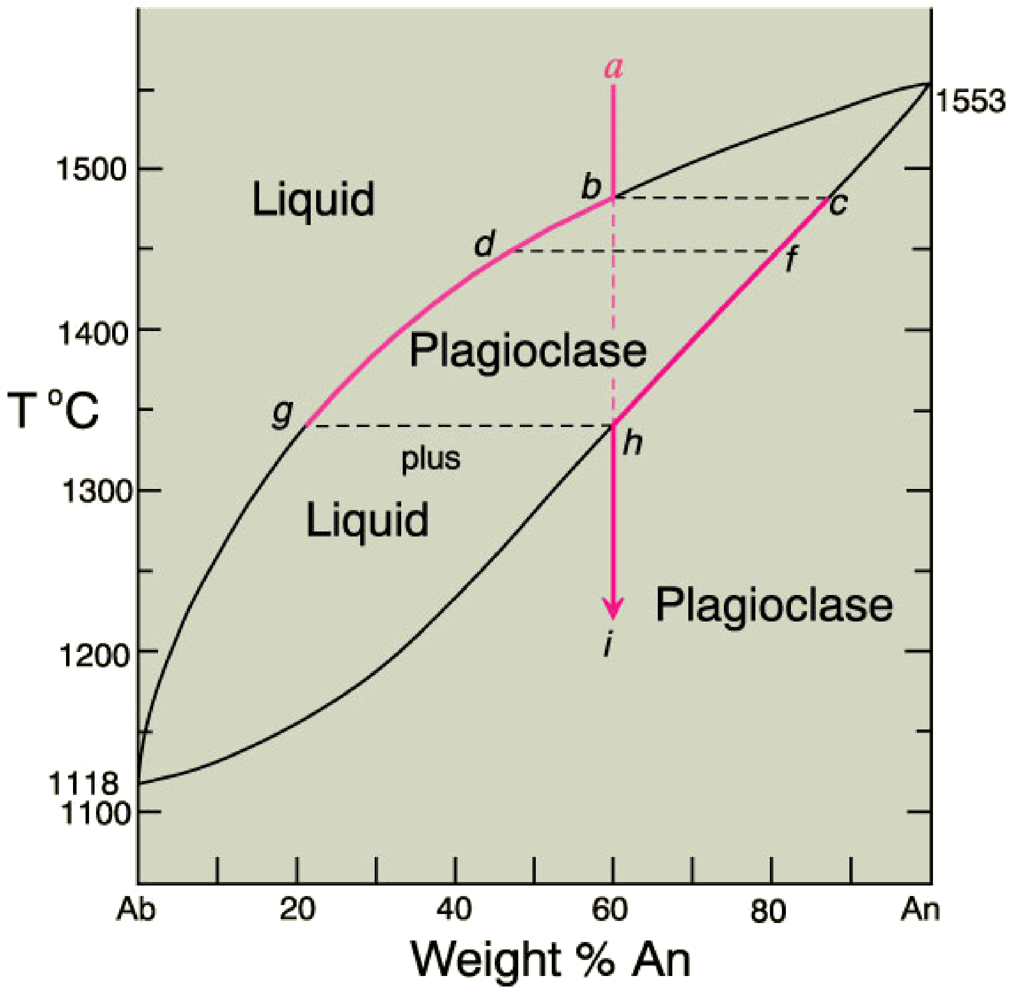
When $X_{plag} \rightarrow$ h, then $X_{plag} = X_{bulk}$ and, according to the lever principle, the amount of liquid → 0

Thus g is the composition of the last liquid to crystallize at 1340°C for bulk X = 0.60



Final plagioclase to form is i when $X_{An}^{plag} = 0.60$

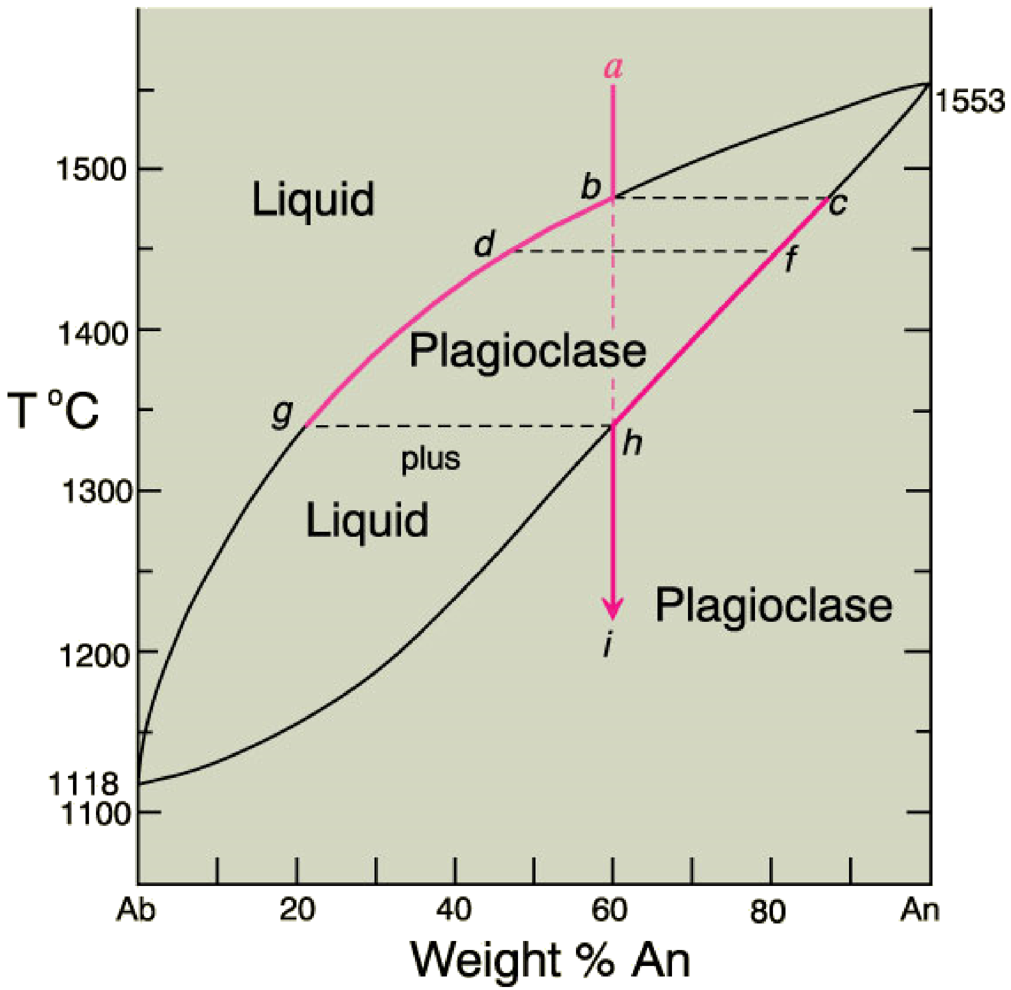
Now $\phi = 1$ so F = 2 - 1 + 1 = 2



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

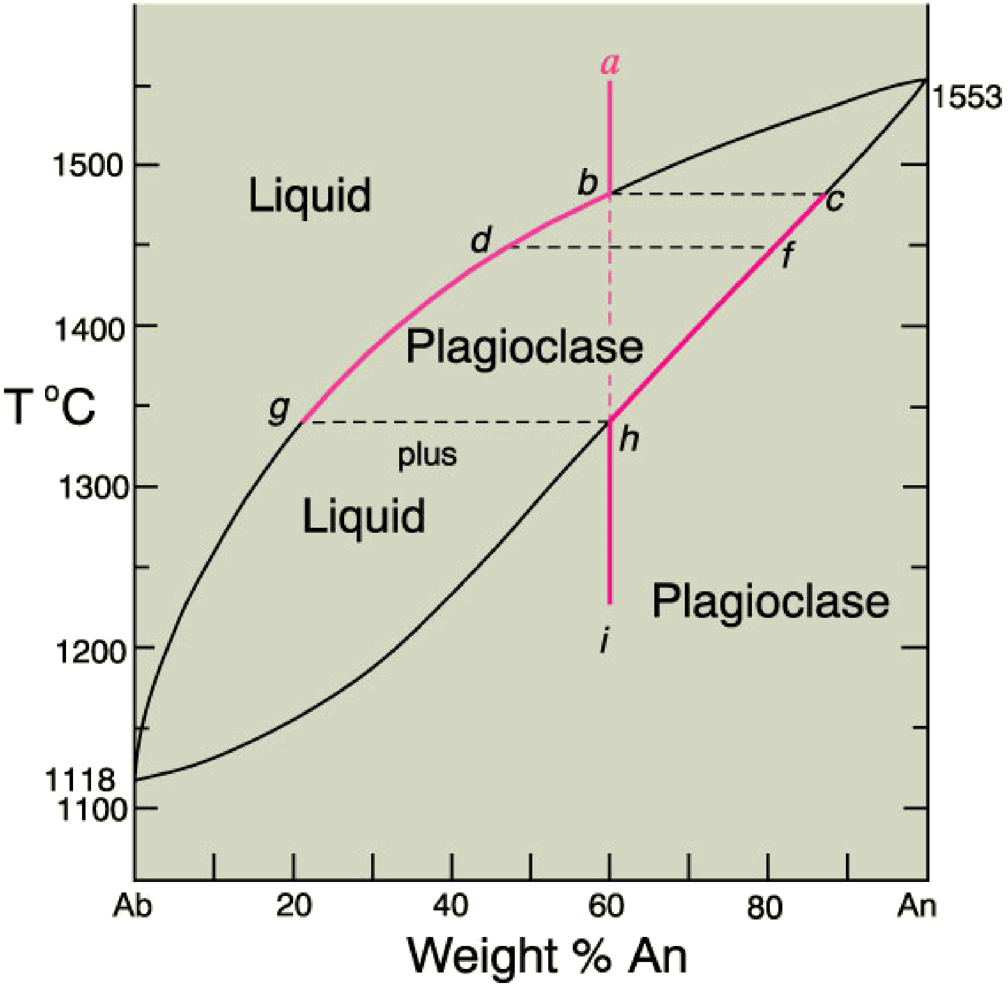
Numbers refer to the "behavior of melts" observations



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

Equilibrium melting is exactly the opposite

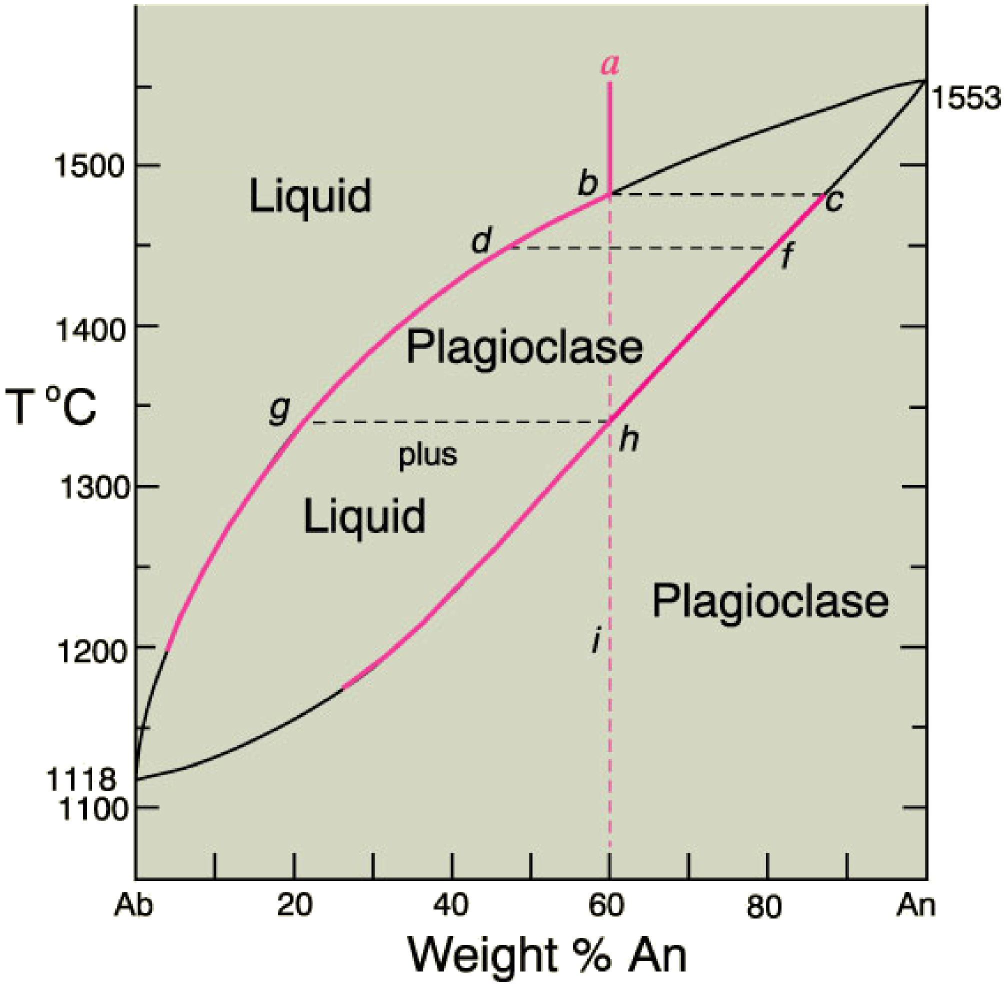
- Heat An_{60} and the first melt is g at An_{20} and 1340°C
- Continue heating: both melt and plagioclase change X
- Last plagioclase to melt is c (An_{87}) at 1475°C



Fractional crystallization:

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

At any T $X_{bulk} = X_{liq}$ due to the removal of the crystals

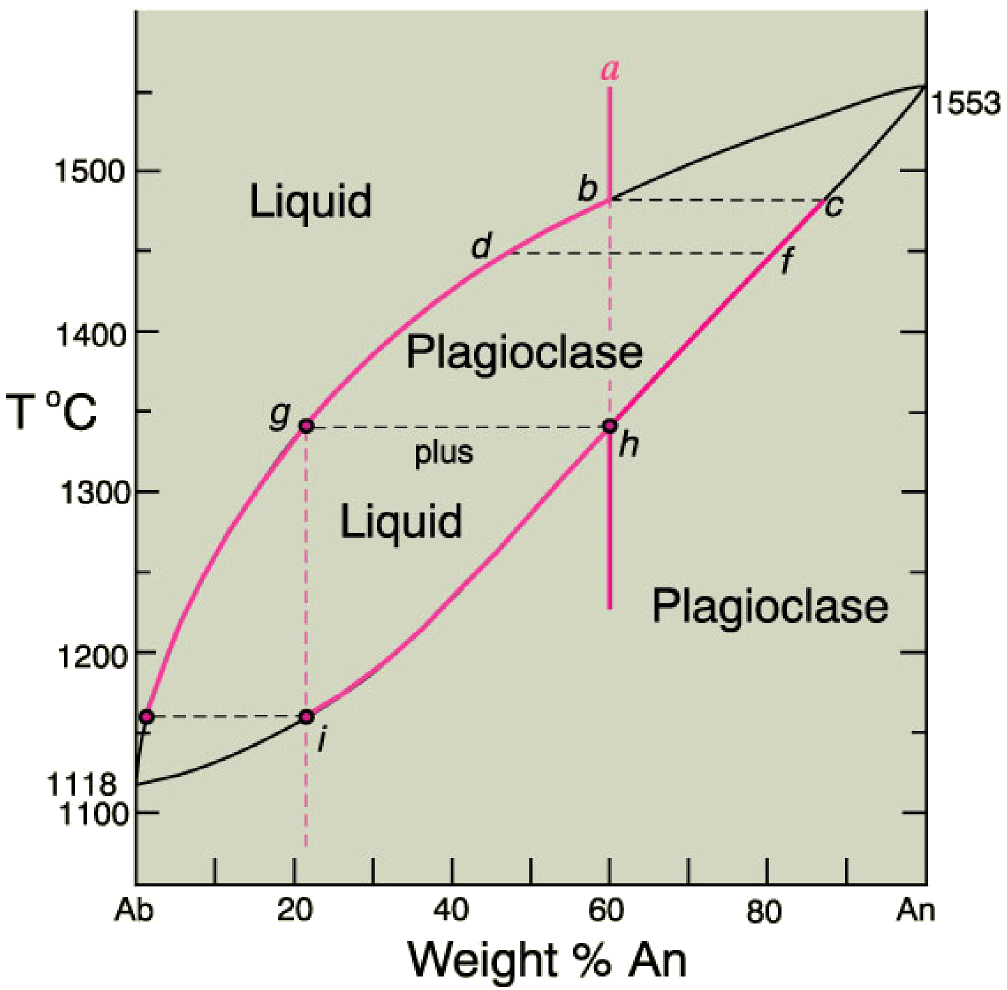


Partial Melting:

Remove first melt as forms

Melt X_{bulk} = 0.60 first liquid = ***g***

remove and cool bulk = g → final plagioclase = ***i***



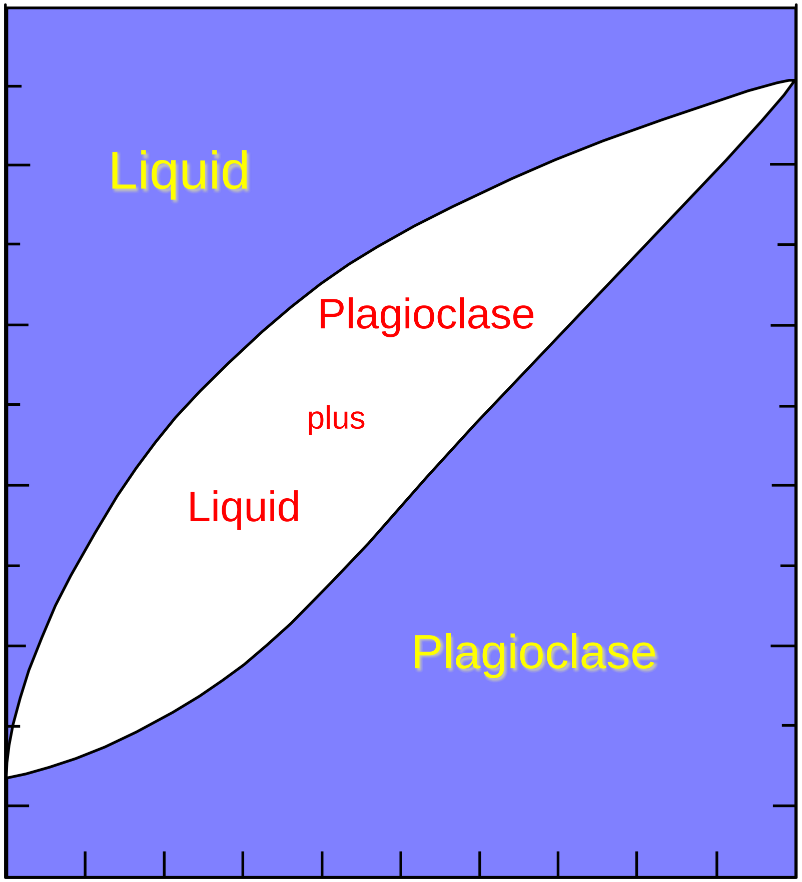
Note the difference between the two types of fields

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 (Mg_2SiO_4 - Fe_2SiO_4)

also a solid-solution series

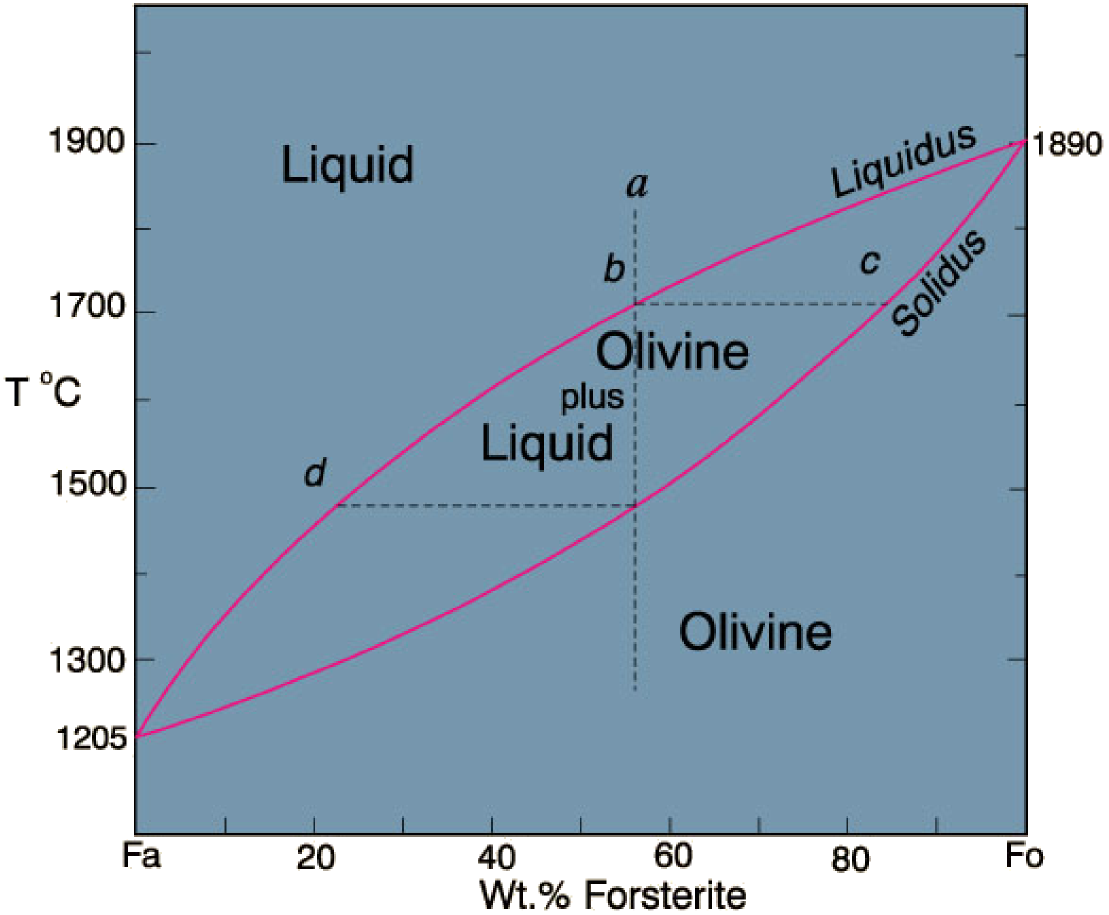


Fig. 6.10. Isobaric T-X phase diagram at atmospheric pressure After Bowen and Shairer (1932), Amer. J. Sci. 5th Ser., 24, 177-213.

2-C Eutectic Systems

Example: Diopside - Anorthite

No solid solution

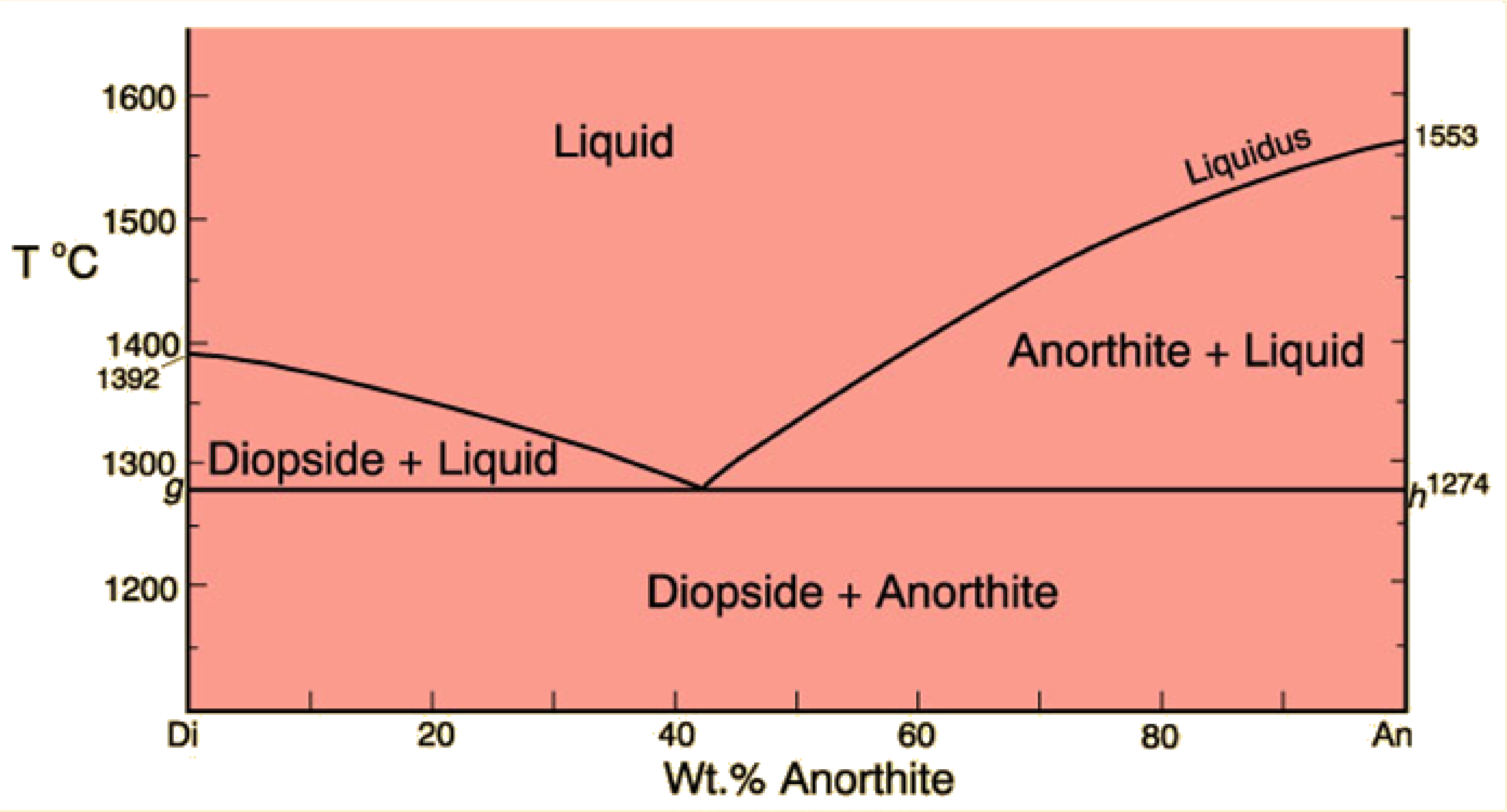
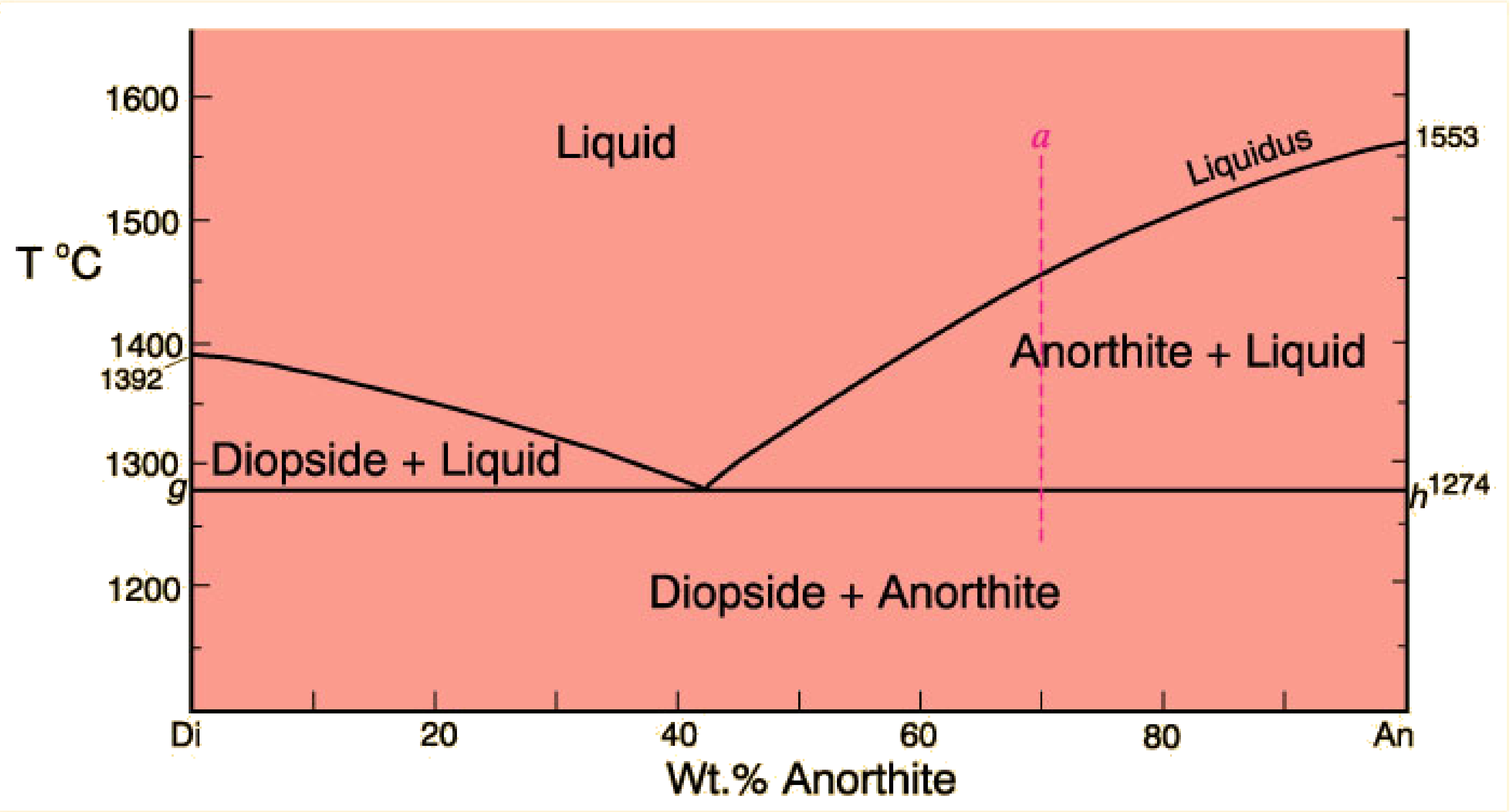


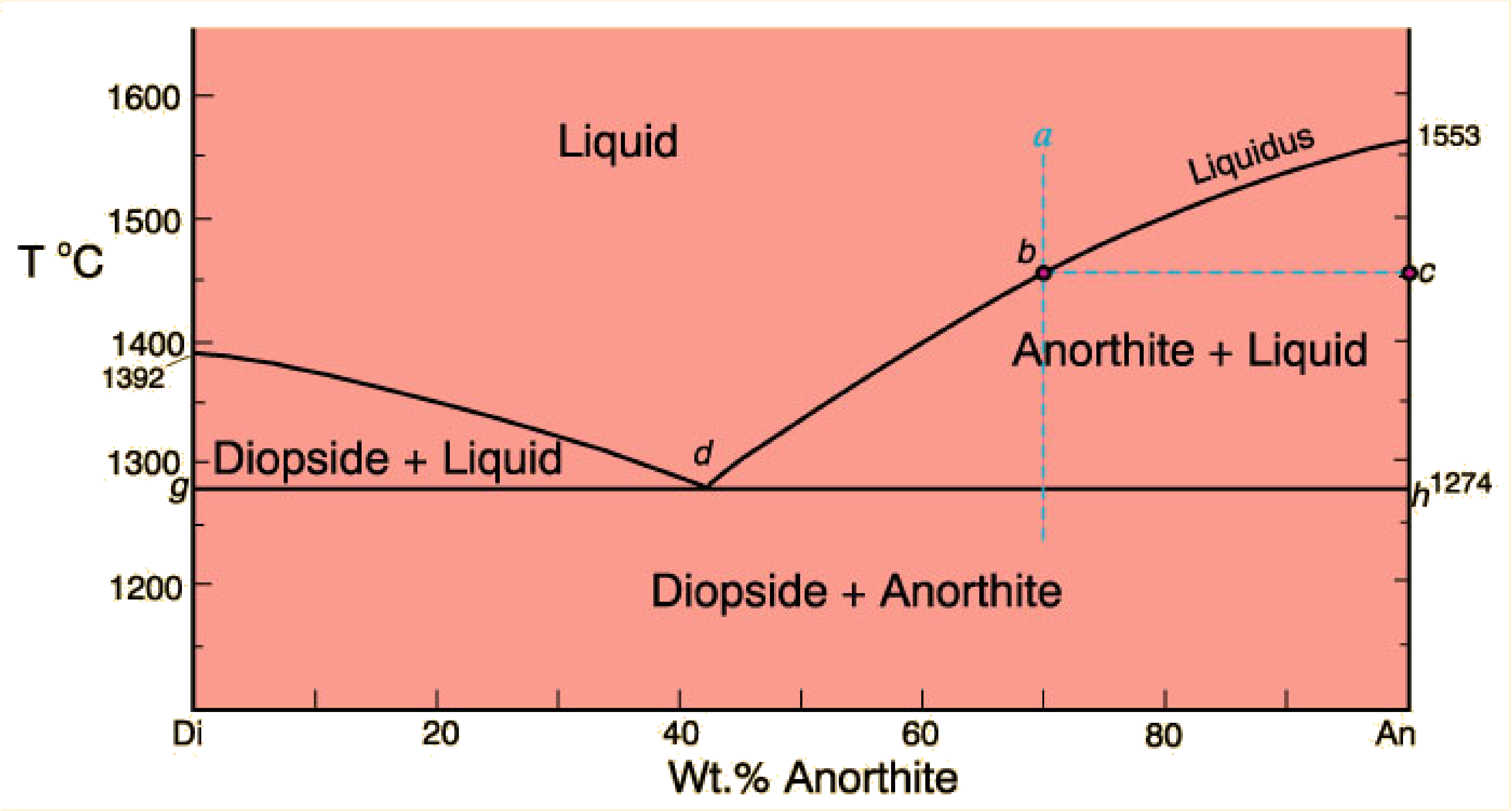
Fig. 6.11. Isobaric T-X phase diagram at atmospheric pressure. After Bowen (1915), Amer. J. Sci. 40, 161-185.

Cool composition a:

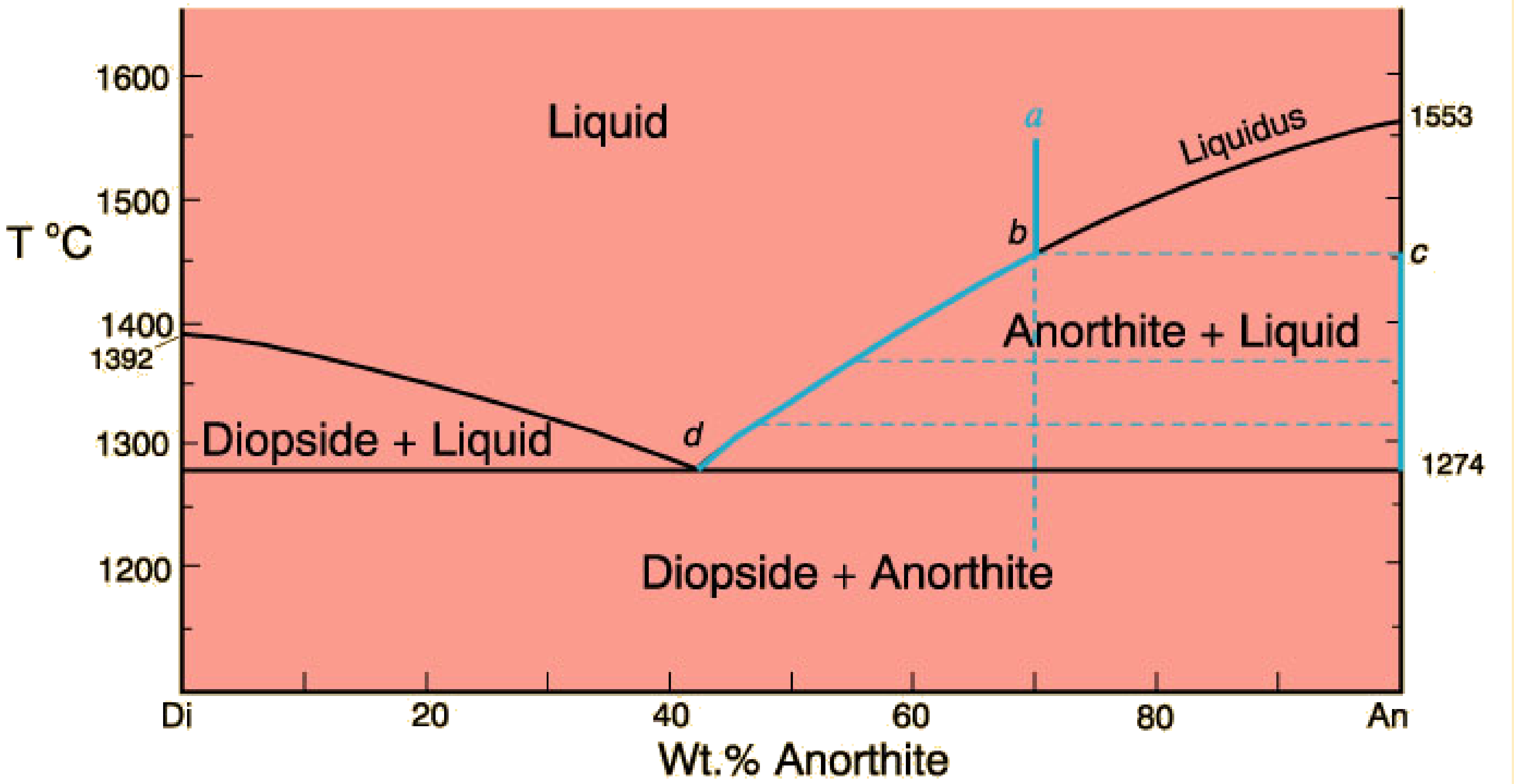
bulk composition = An_{70}



Cool to 1455°C (point b)

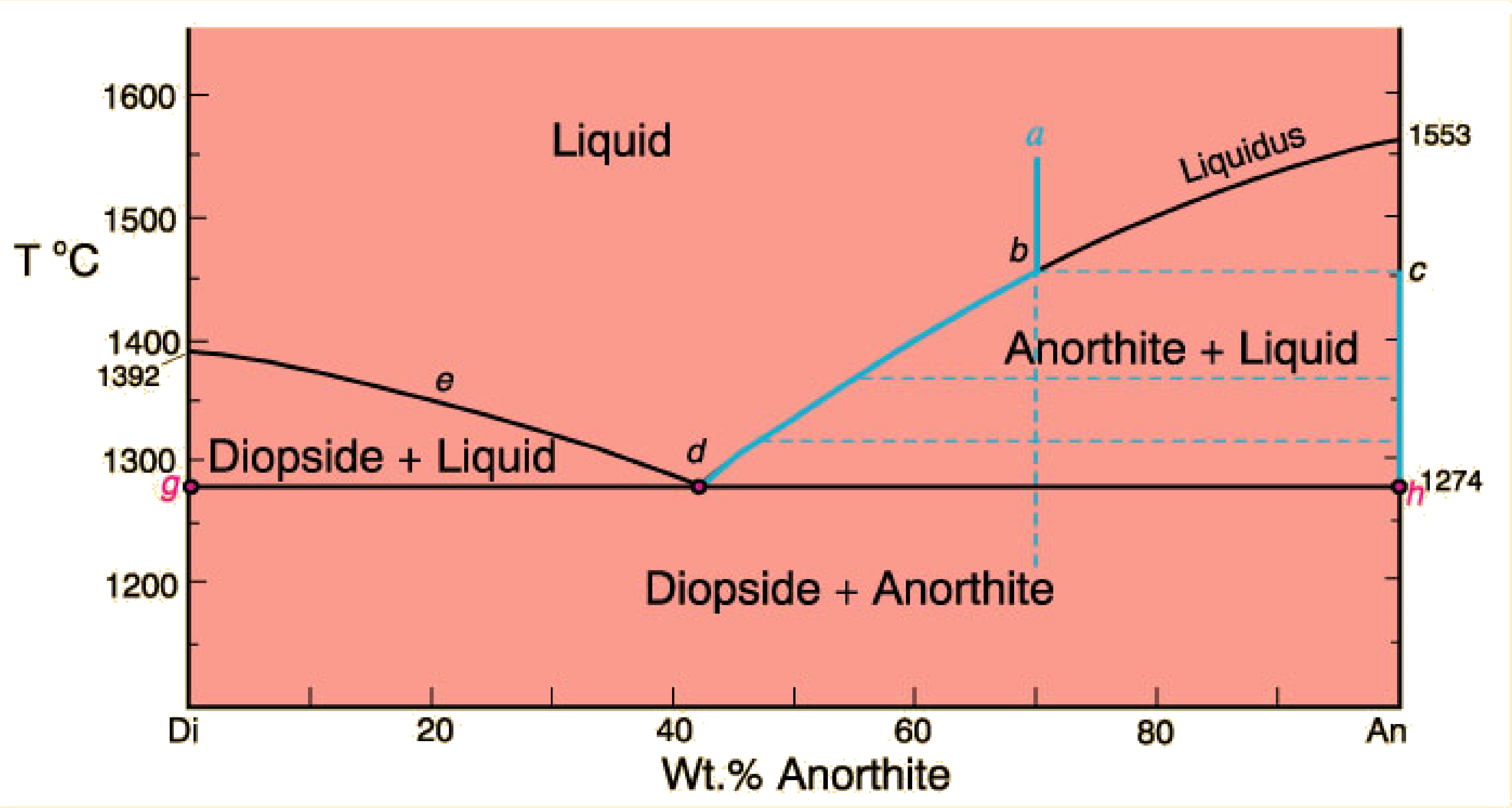


- Continue cooling as X_{liq} varies along the liquidus
- **Continuous reaction**: $liq_A \rightarrow$ anorthite + liq_B



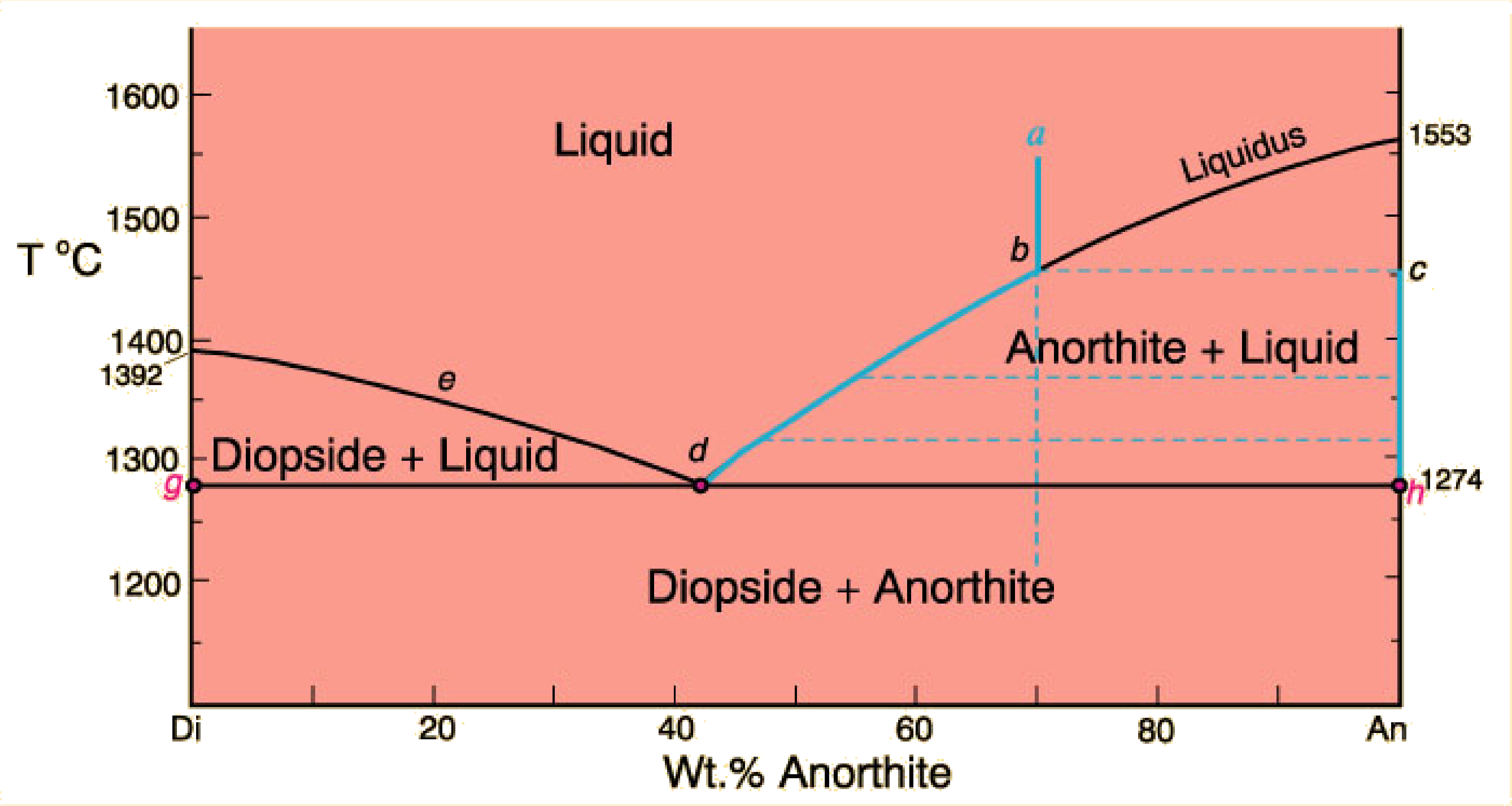
at 1274°C $\phi = 3$ so F = 2 - 3 + 1 = 0 invariant

- ☞ (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

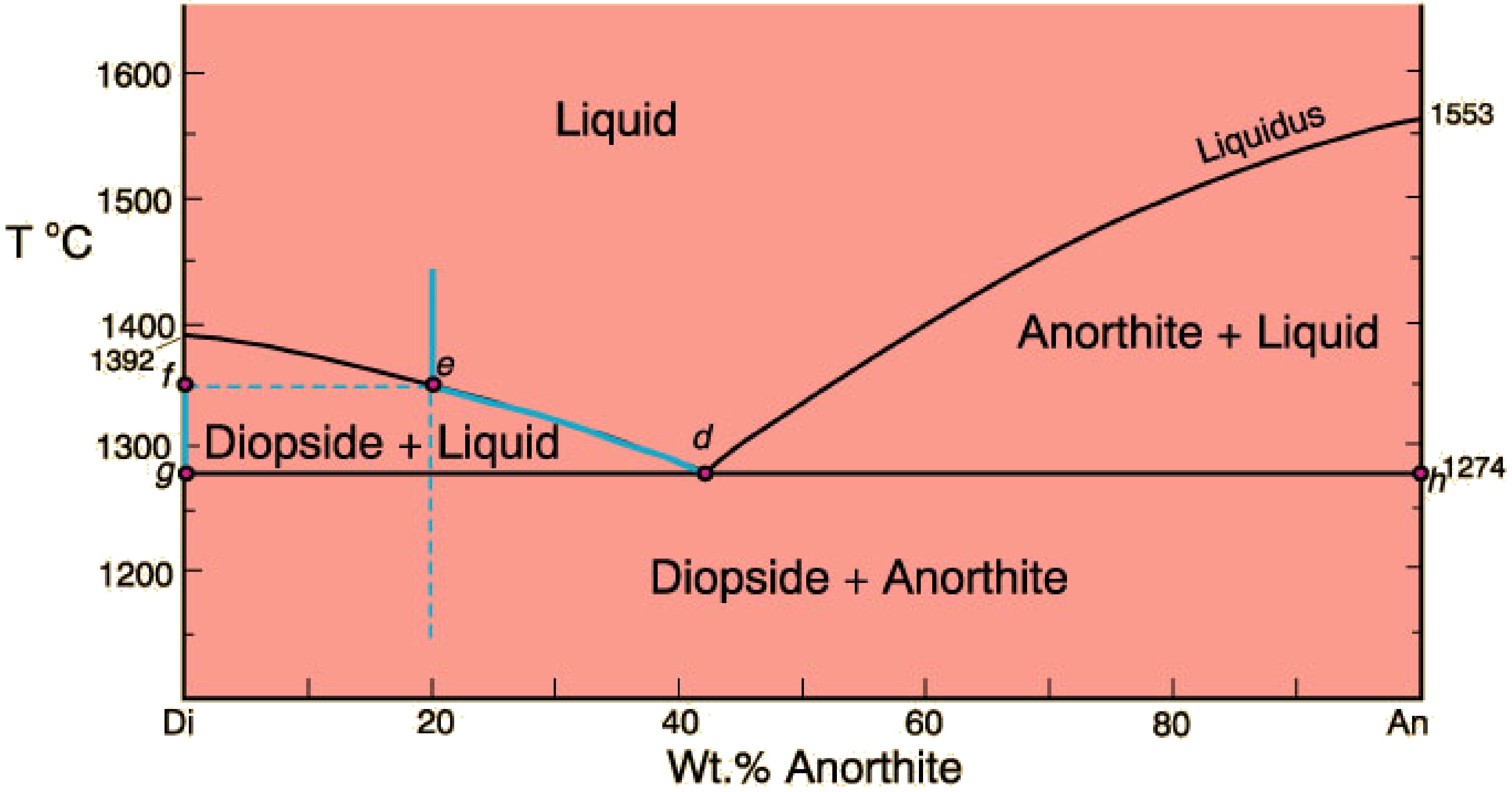


Discontinuous Reaction: all at a single T

- ☞ Use geometry to determine



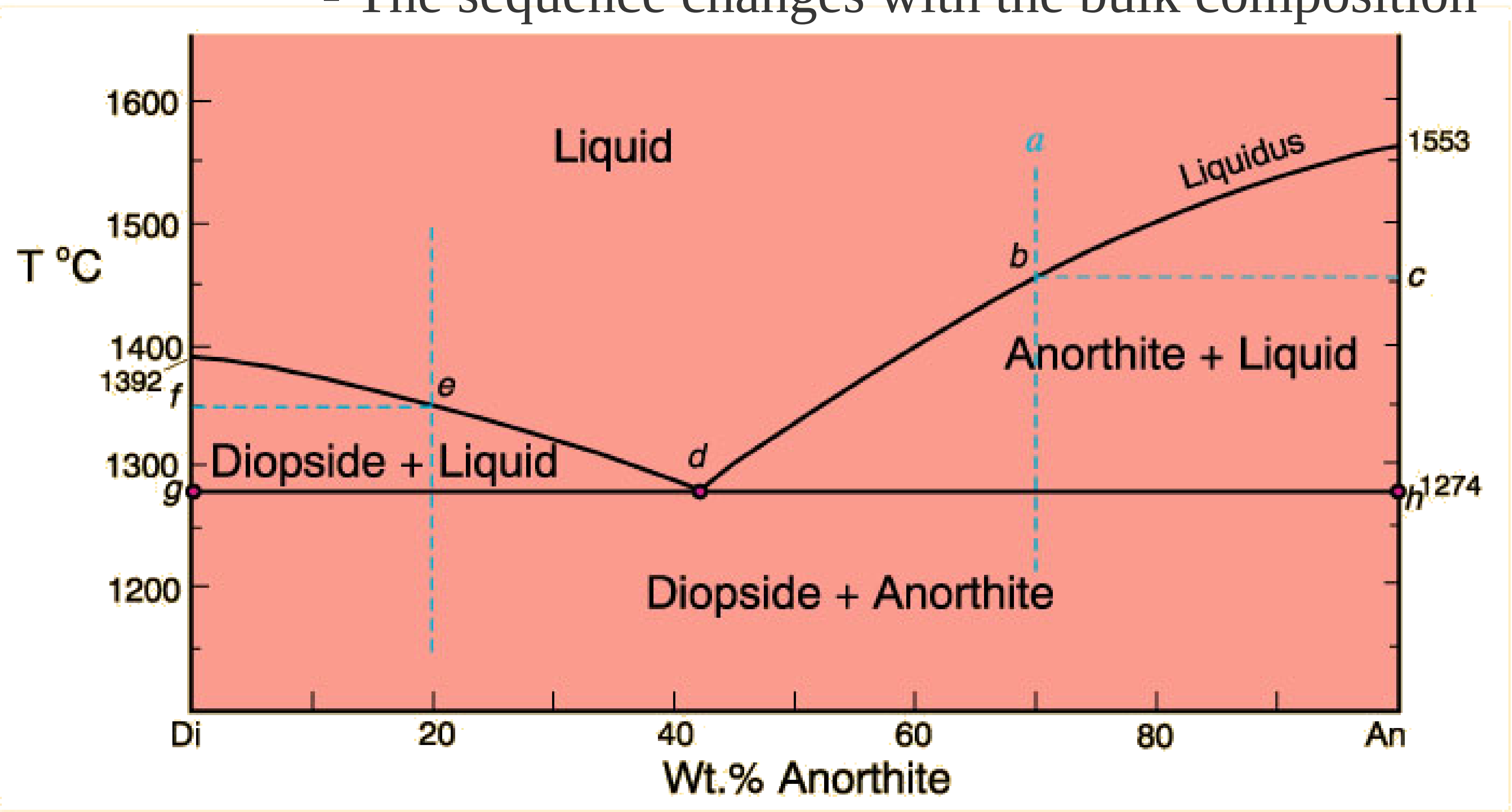
Left of the eutectic get a similar situation



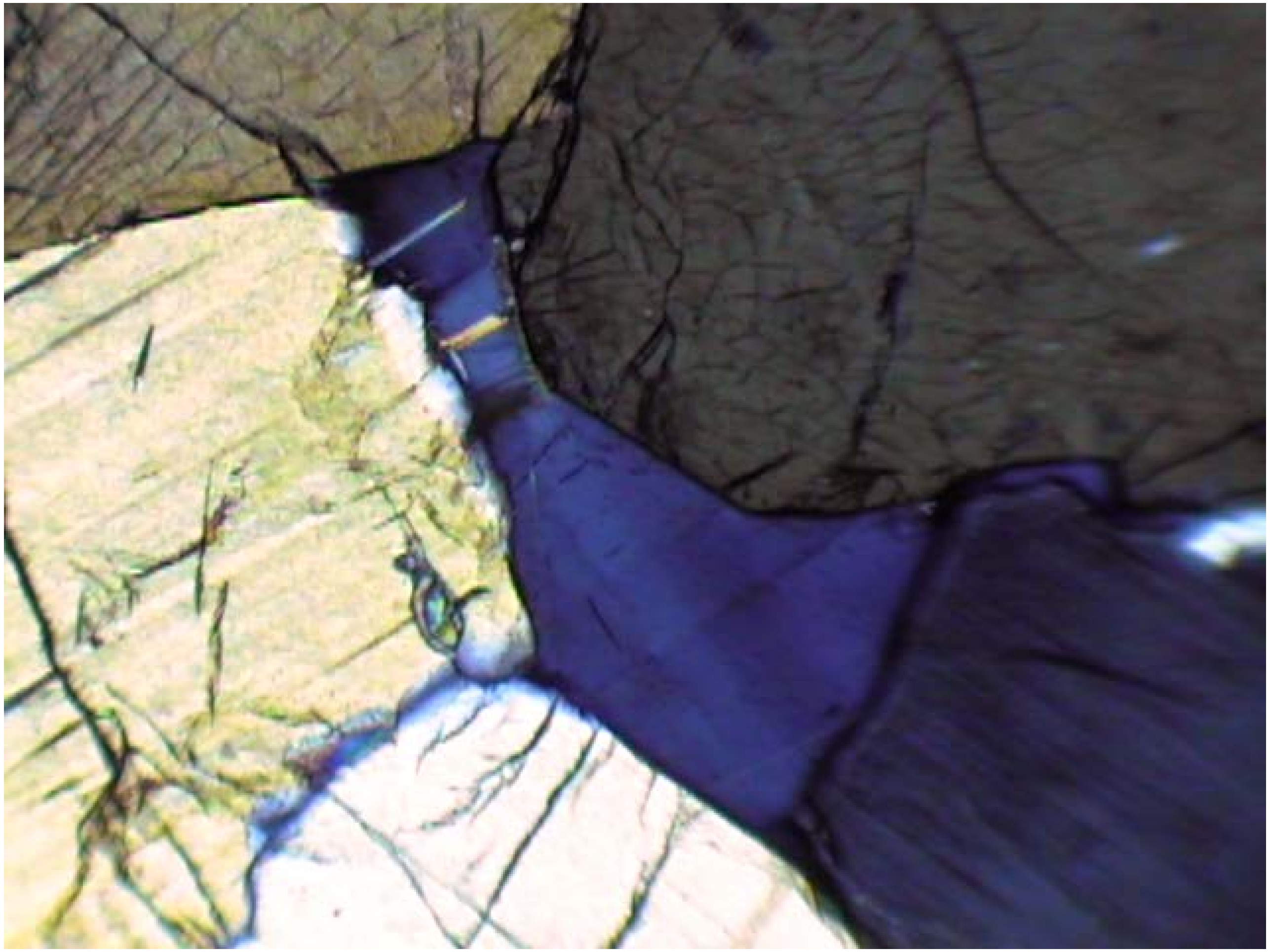
Note the following:

1. The melt crystallizes over a T range up to ~280^{o}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

#s are listed points in text



Augite forms before plagioclase



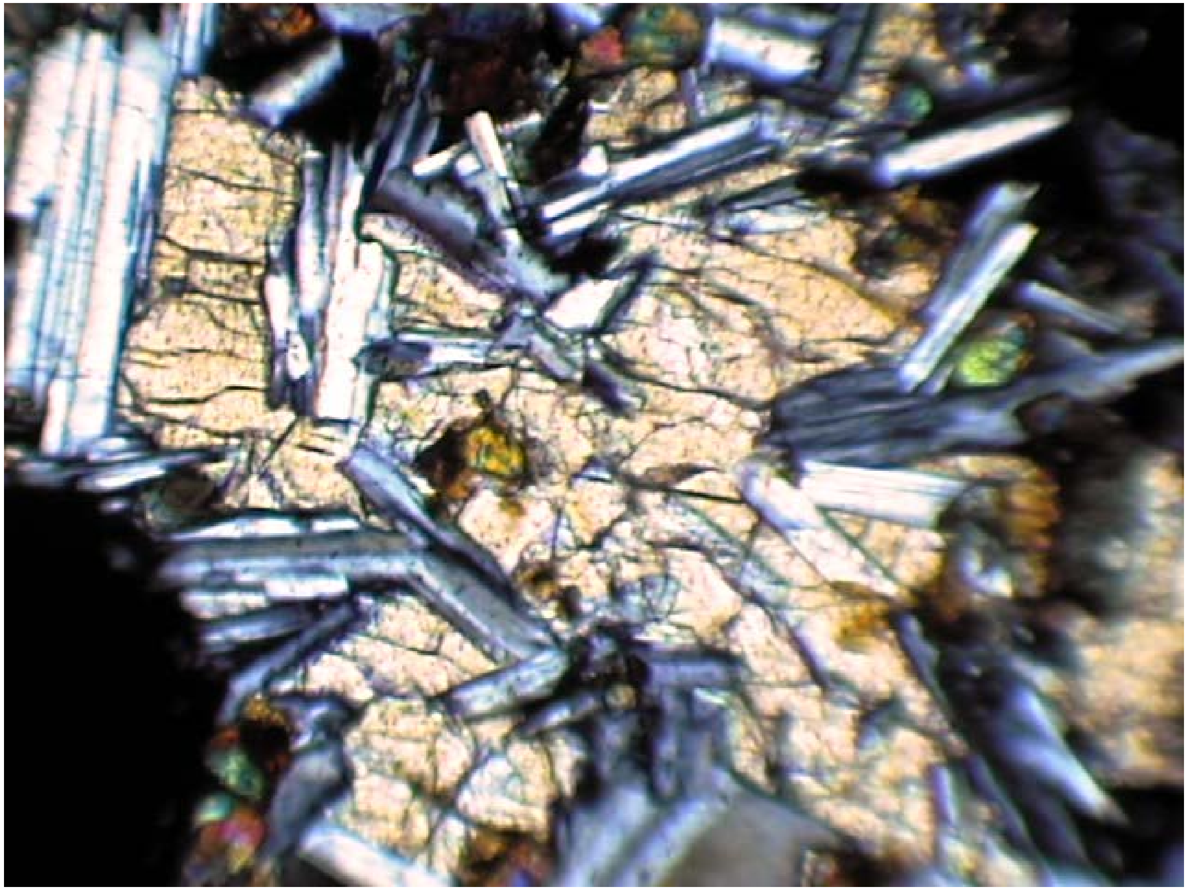
Gabbro of the Stillwater Complex, Montana

This forms on the left side of the eutectic

Plagioclase forms before augite

Ophitic texture

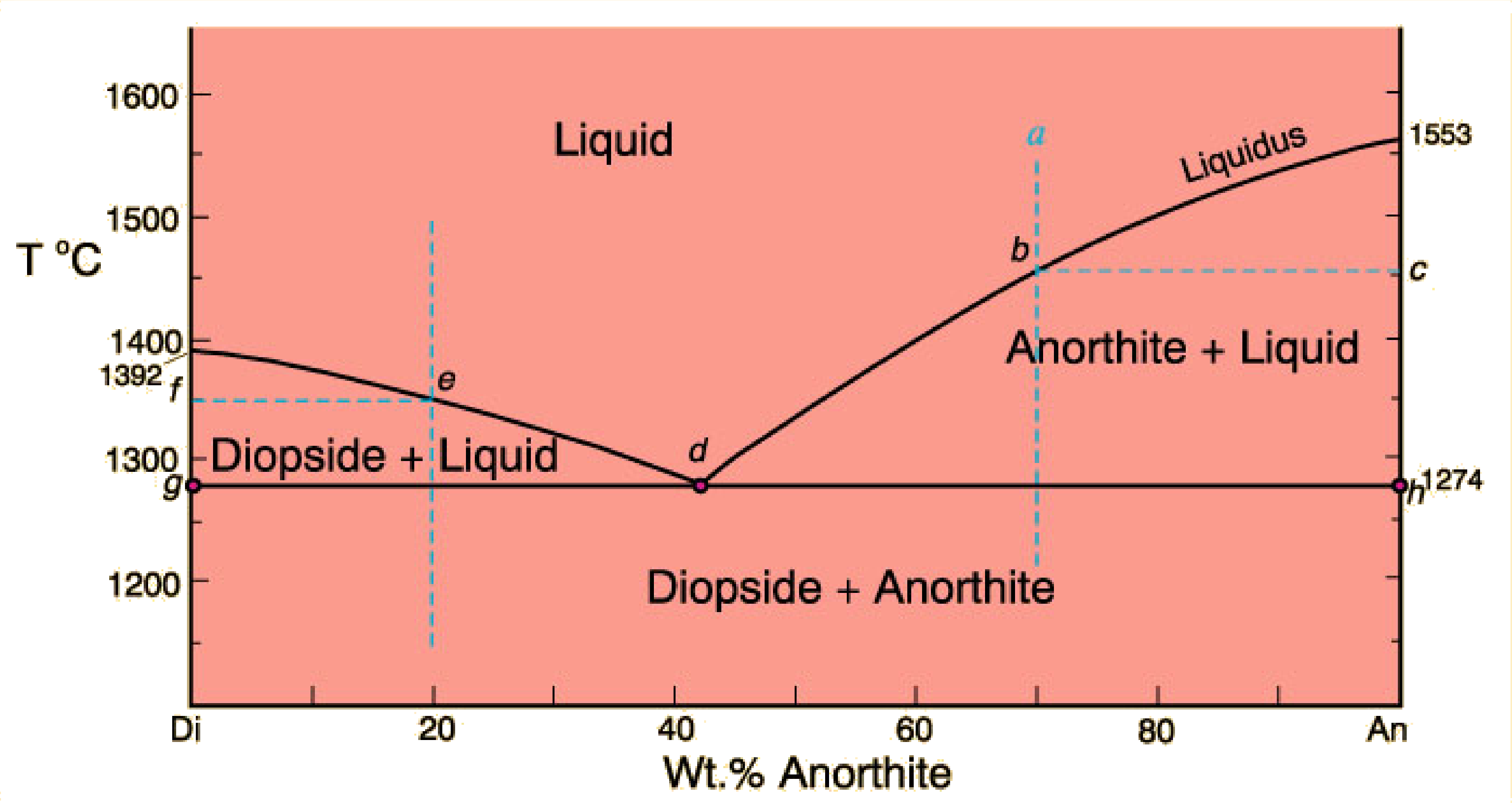
Diabase dike



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



Fractional crystallization:

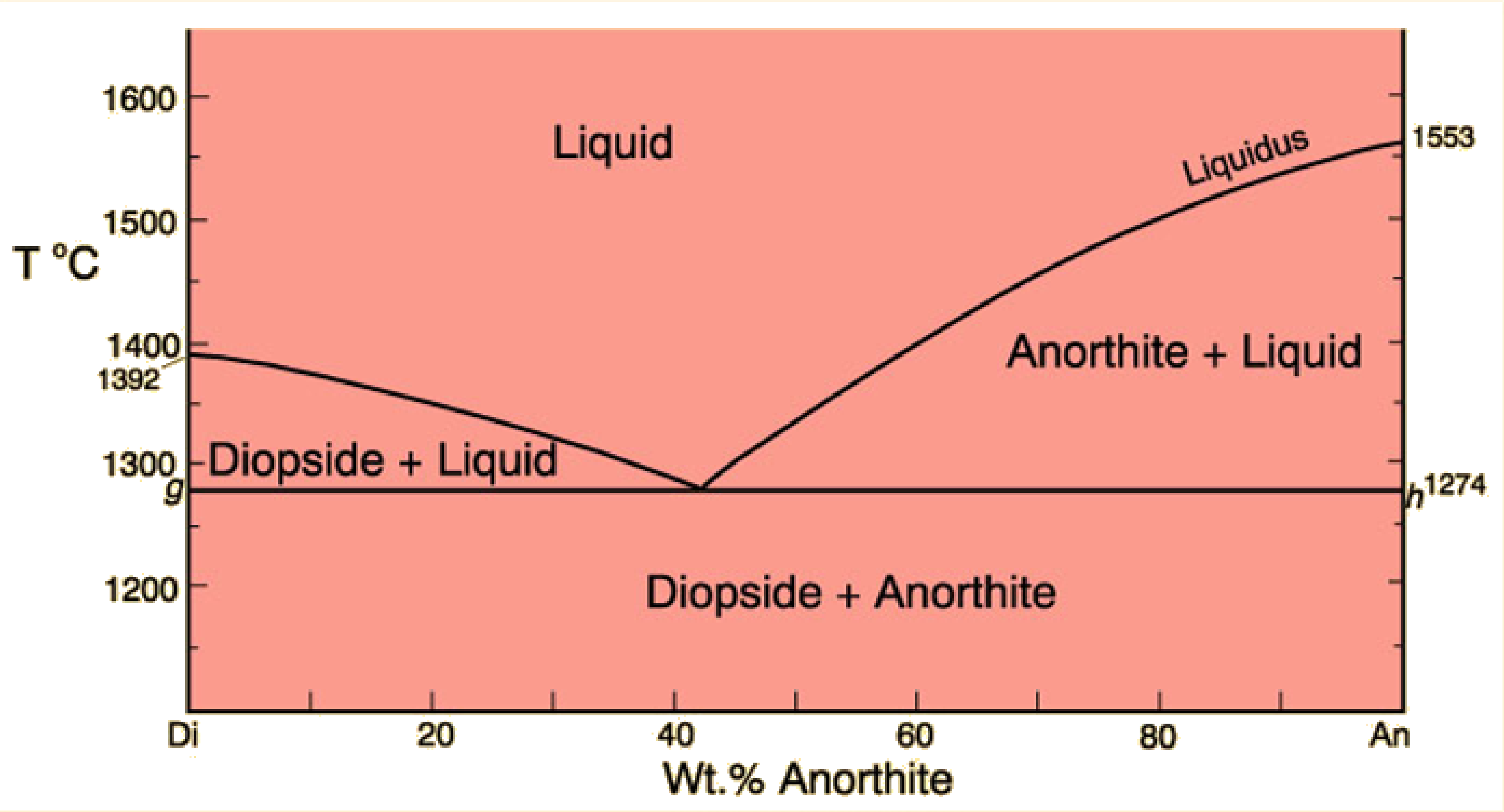
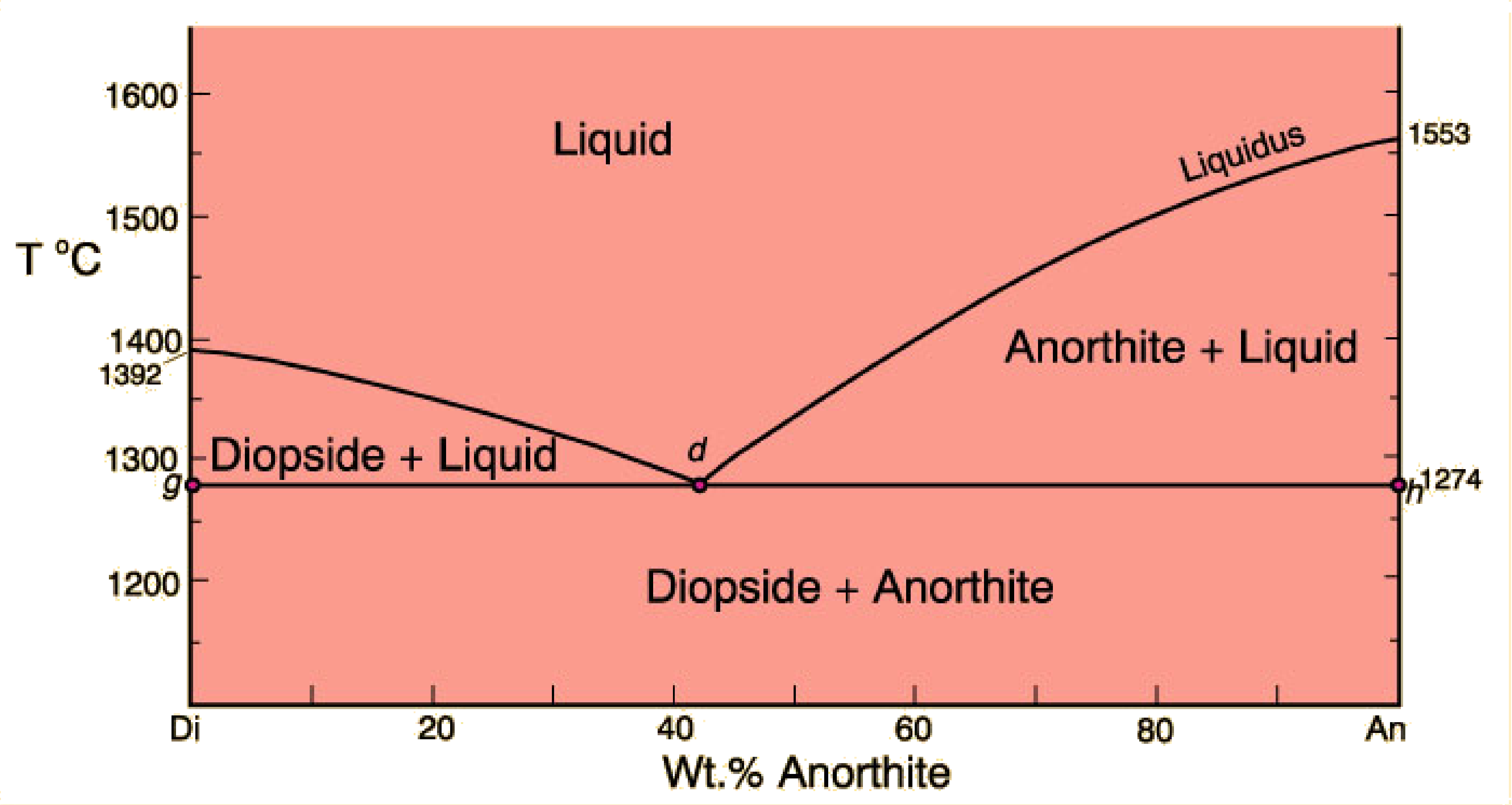


Fig. 6.11. **Isobaric T-X phase diagram at atmospheric pressure. After Bowen (1915), Amer. J. Sci. 40, 161-185.**

Partial Melting:



C. Binary Peritectic Systems

Three phases enstatite = forsterite + SiO_2

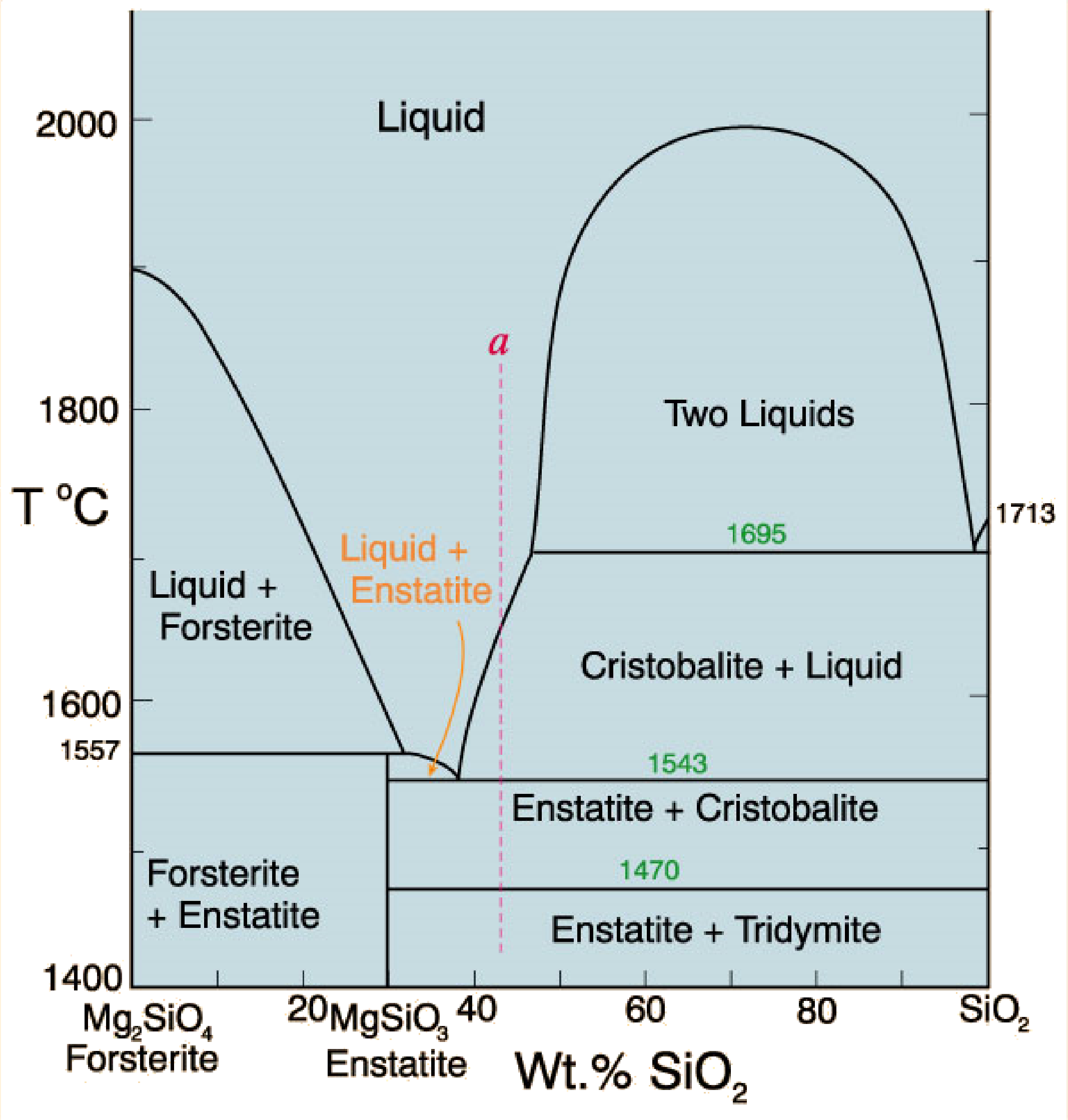
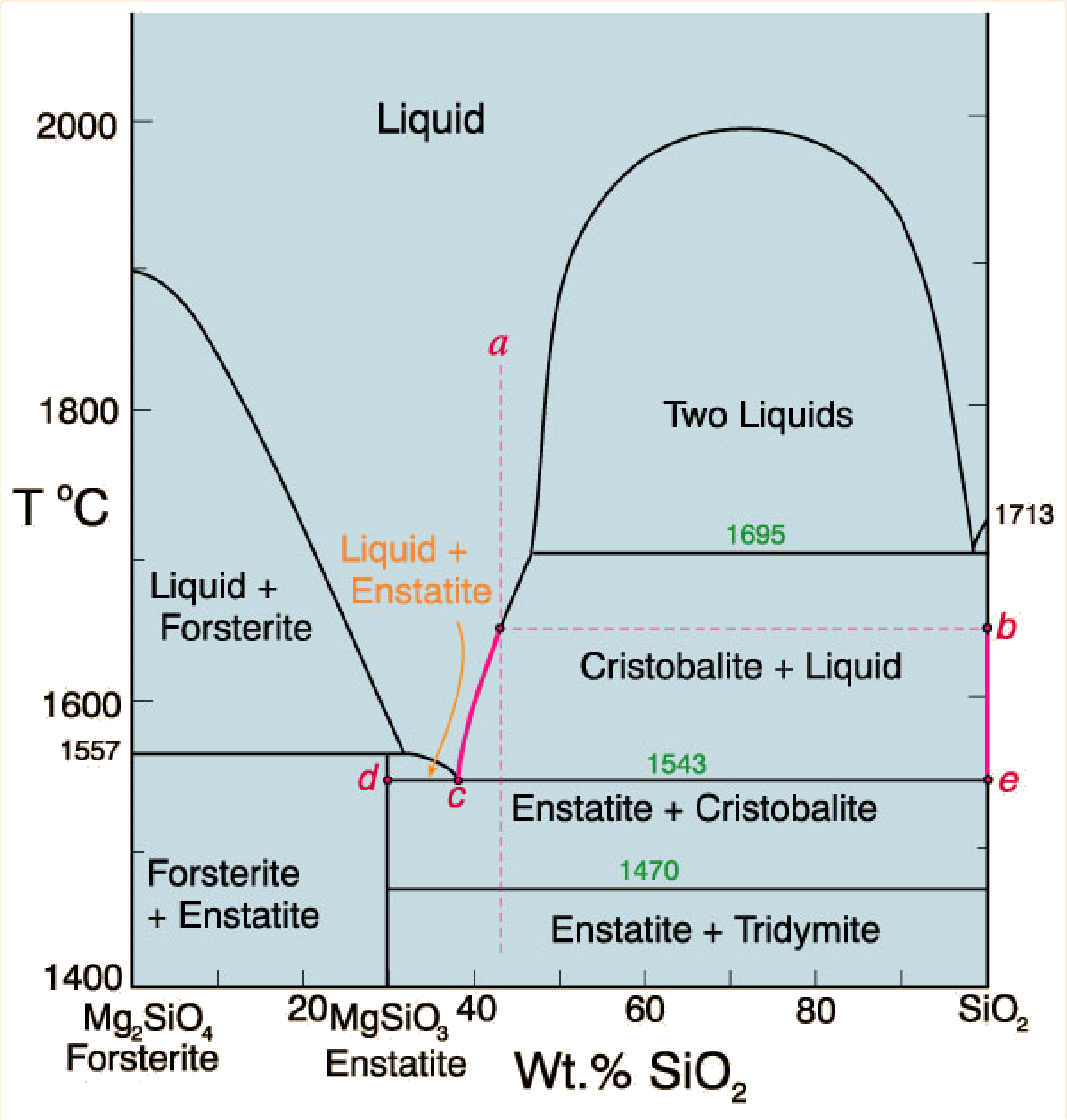


Figure 6.12. Isobaric T-X phase diagram of the system Fo-Silica at 0.1 MPa. After Bowen and Anderson (1914) and Grieg (1927). Amer. J. Sci.

C. Binary Peritectic Systems



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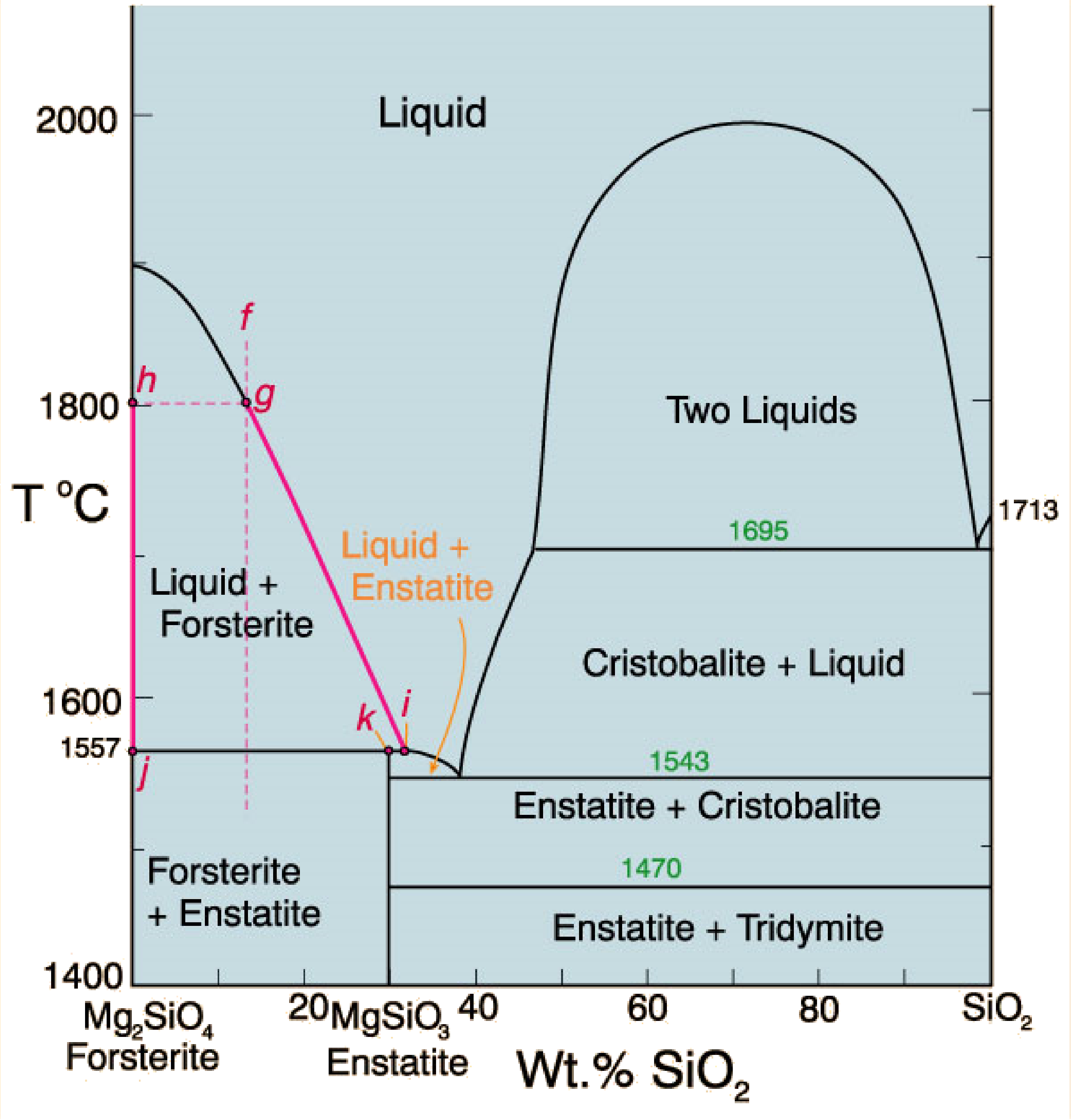


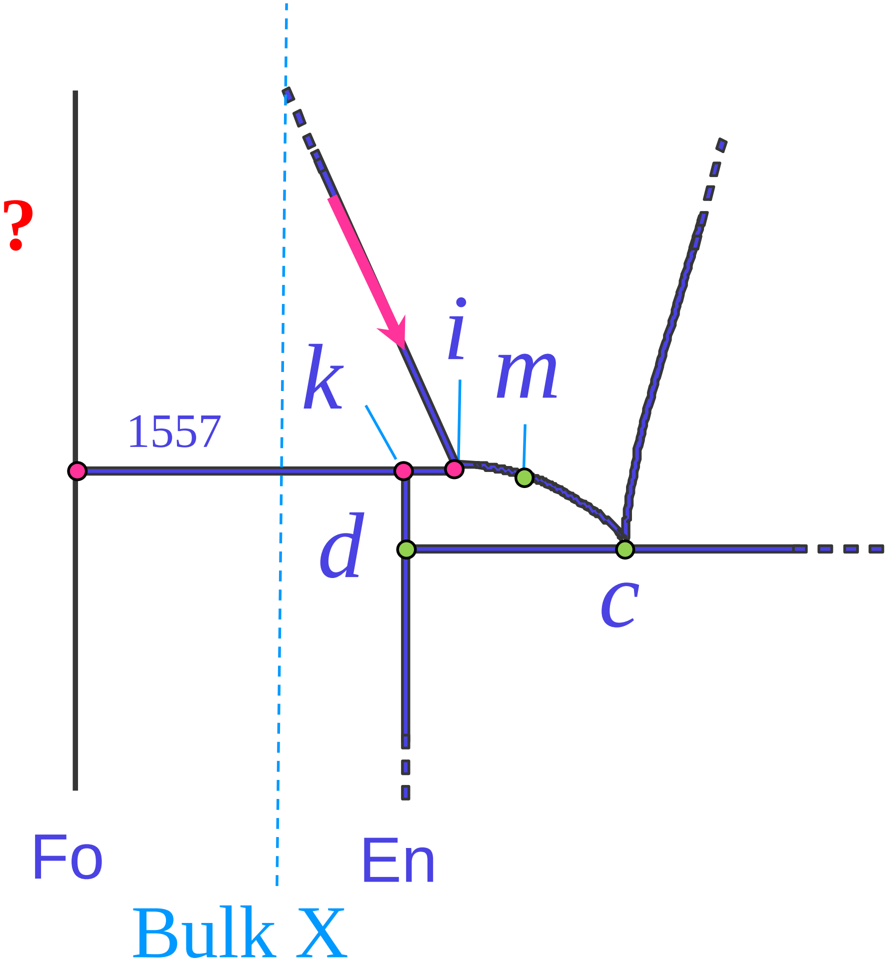
Figure 6.12. Isobaric T-X phase diagram of the system Fo-Silica at 0.1 MPa. After Bowen and Anderson (1914) and Grieg (1927). Amer. J. Sci.

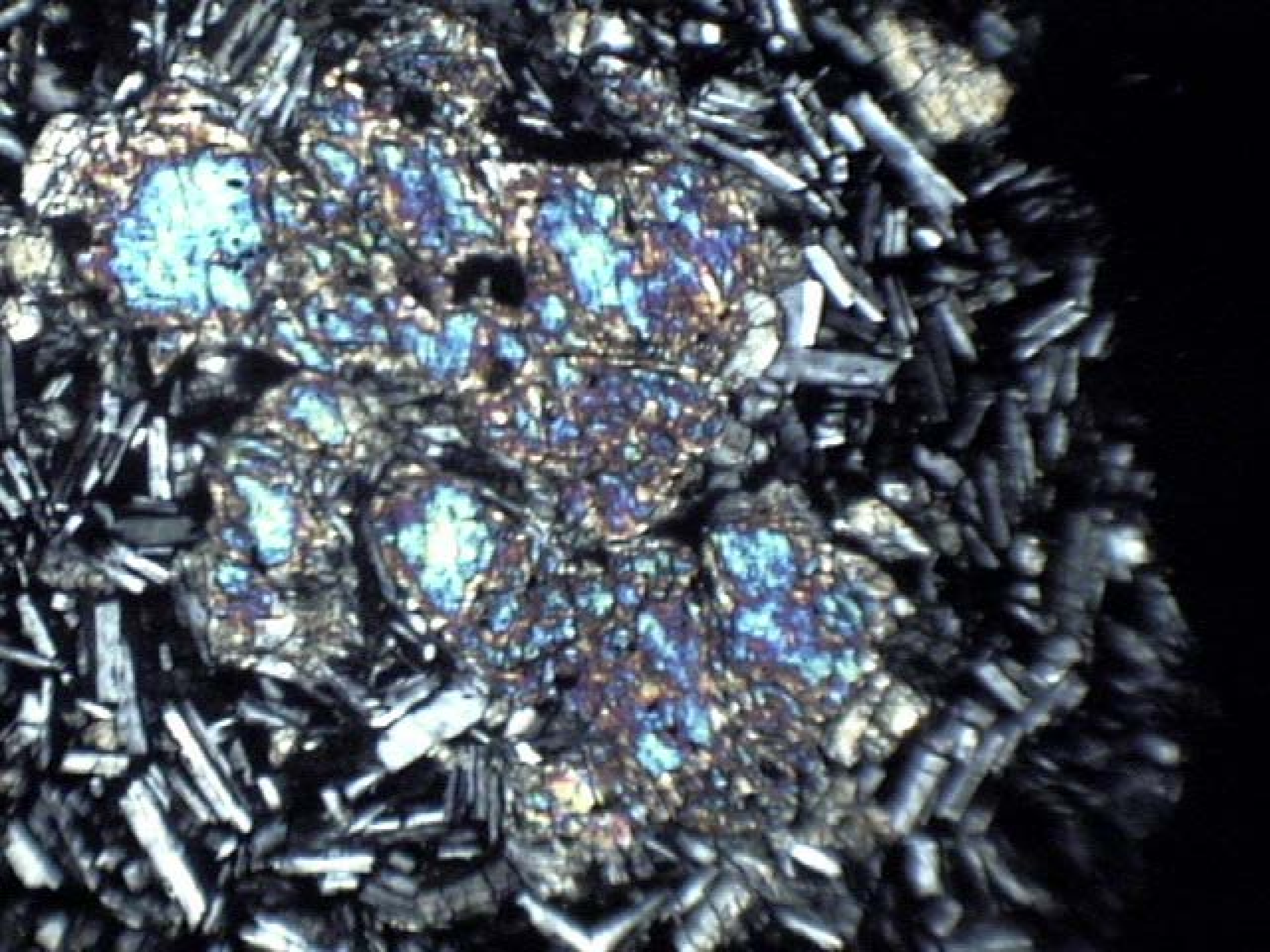
i = "peritectic" point

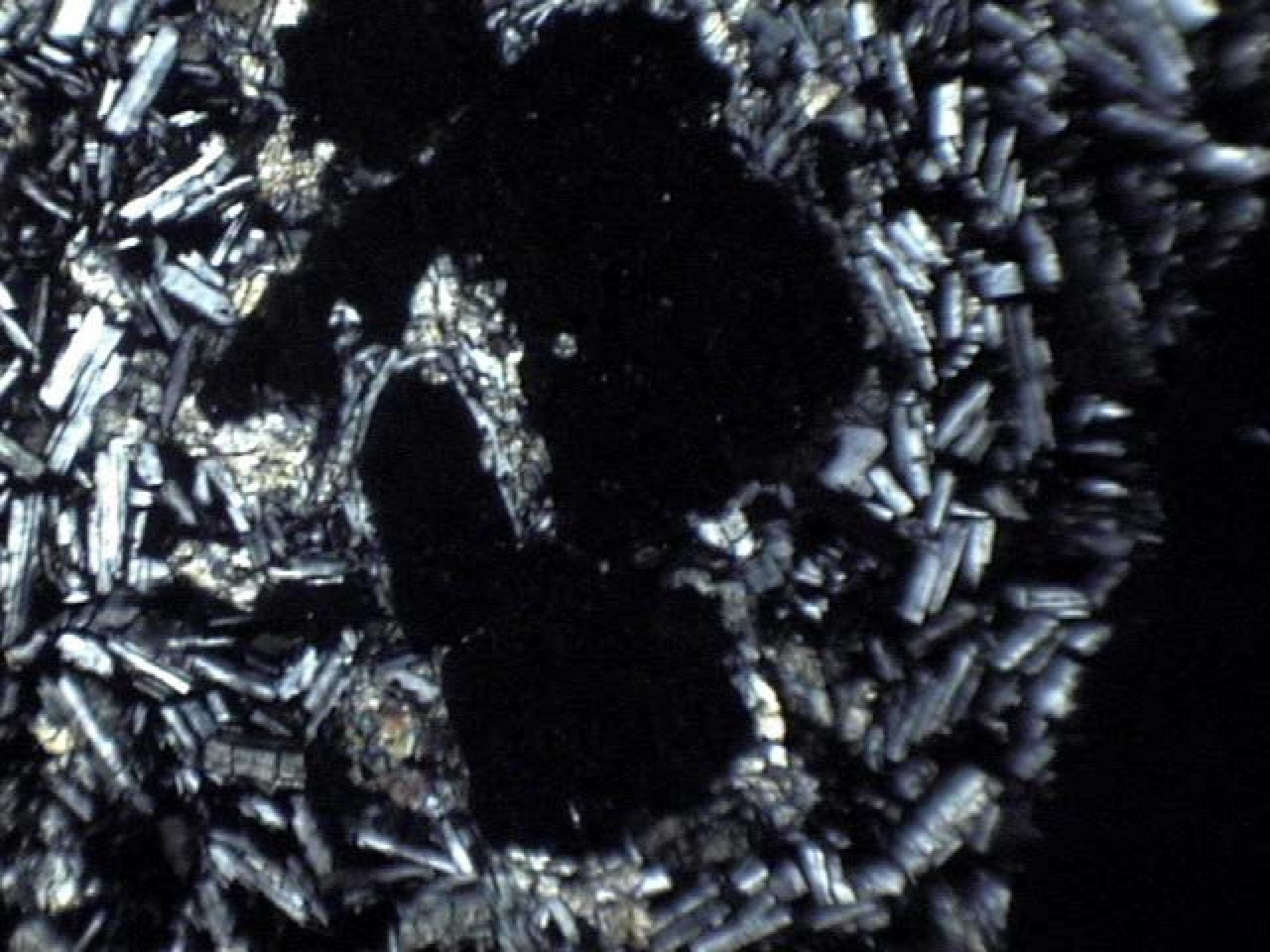
1557°C have colinear Fo-En-liq

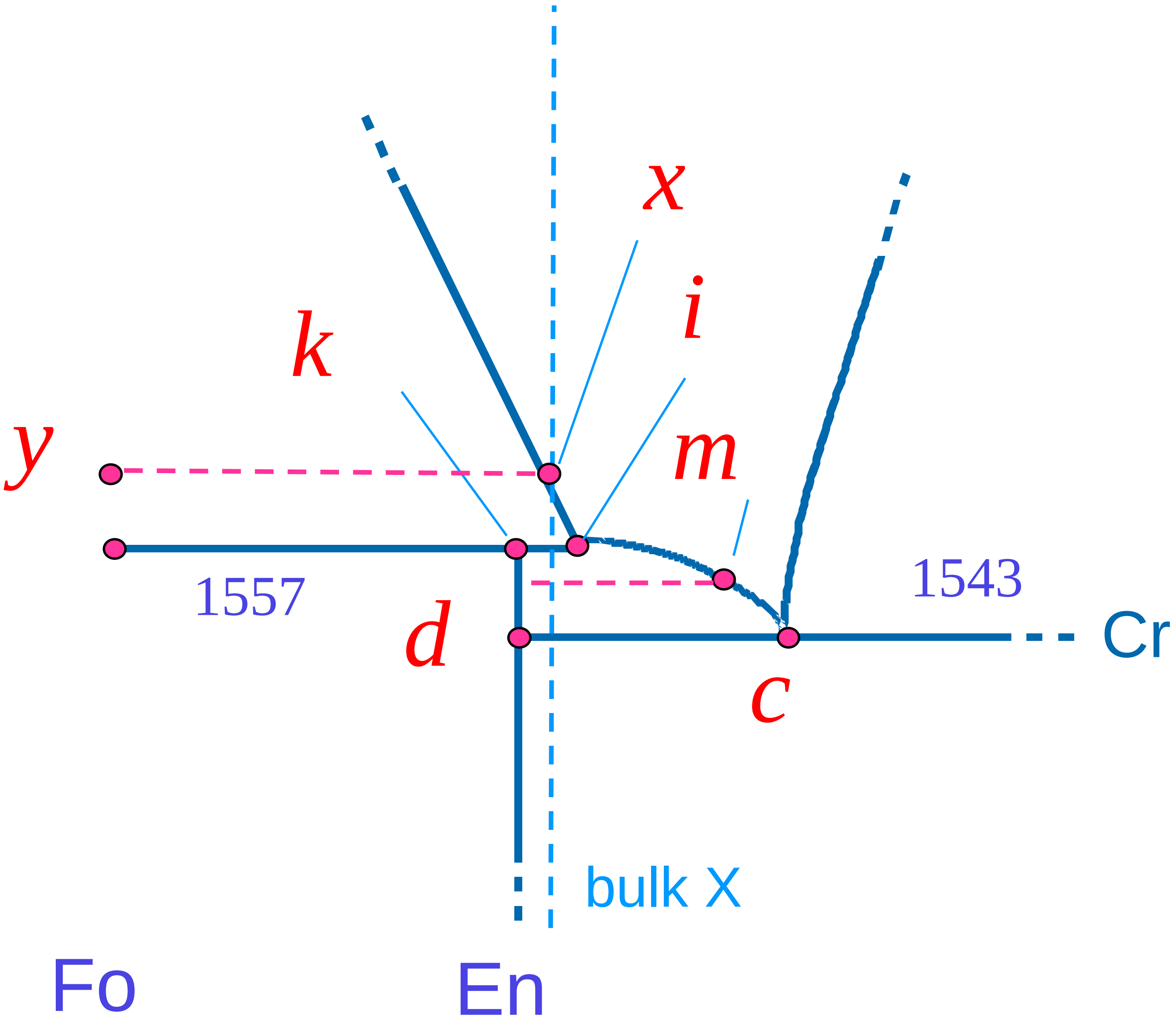
- ☞ geometry indicates a reaction: Fo + liq = En
- ☞ consumes olivine (and liquid) → resorbed textures

When is the reaction finished?







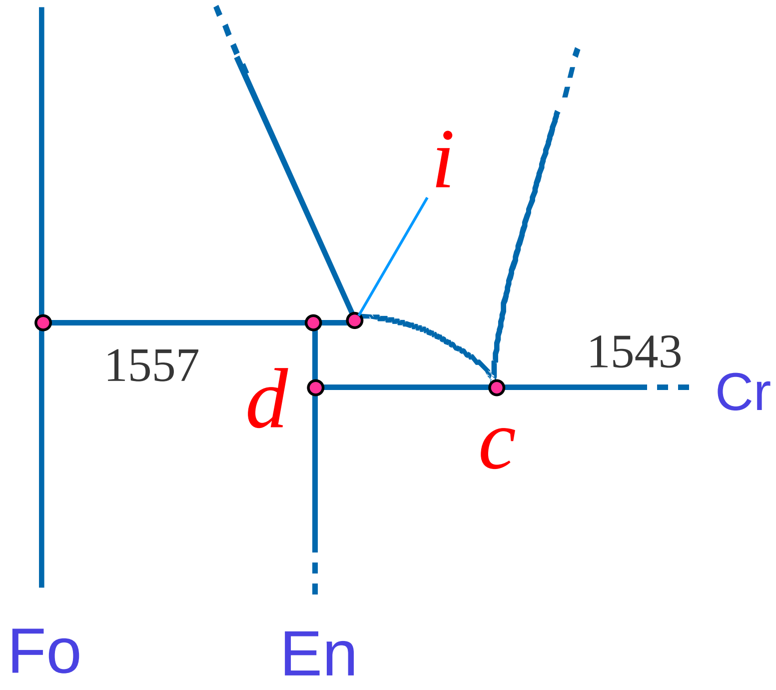

x
i
k
y
m
1557
1543
d
c
Cr
bulk X
Fo
En

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

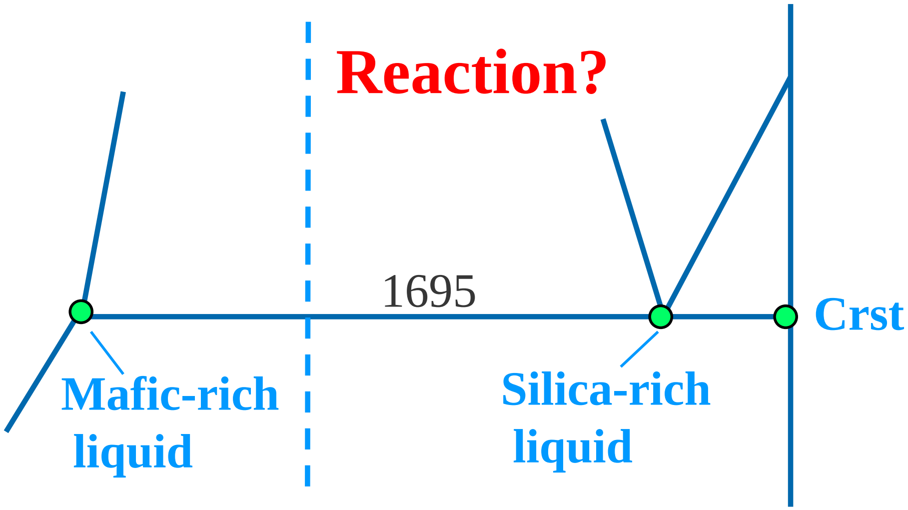
  exsolution

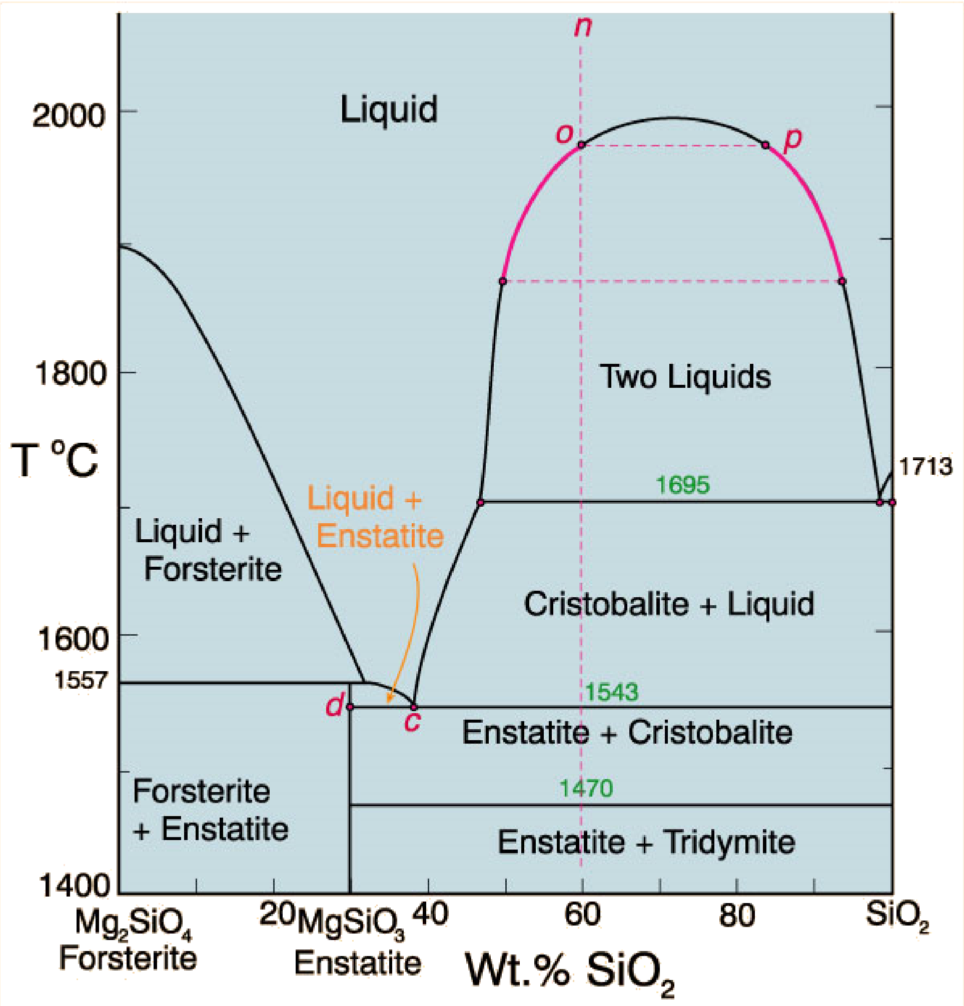
  → 2 liquids o and p

  $\phi = 2 \quad F = 1$

  both liquids follow solvus

At 1695°C get Crst also





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.)

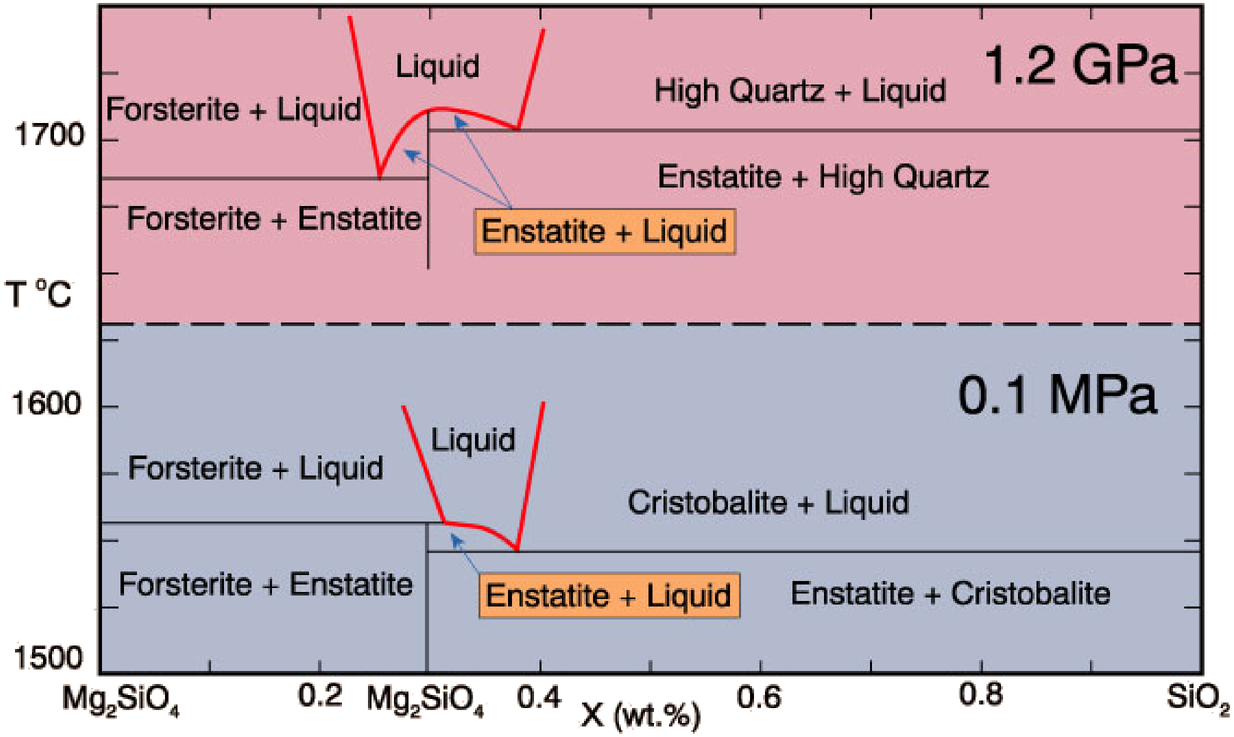


Figure 6.15. The system Fo-SiO_2 at atmospheric pressure and 1.2 GPa. After Bowen and Schairer (1935), Am. J. Sci., Chen and Presnall (1975) Am. Min.

D. Solid Solution with Eutectic: Ab-Or (the alkali feldspars)

Eutectic
liquidus
minimum

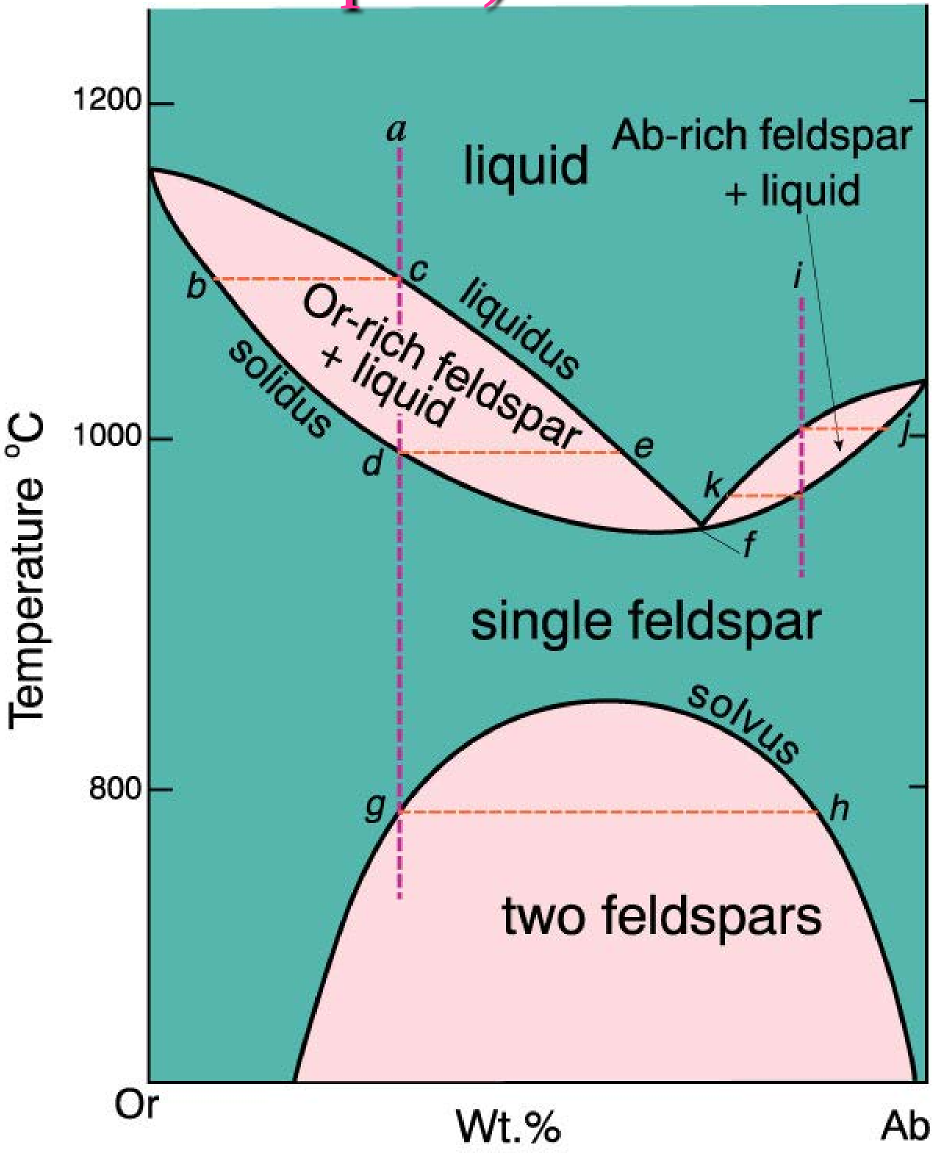
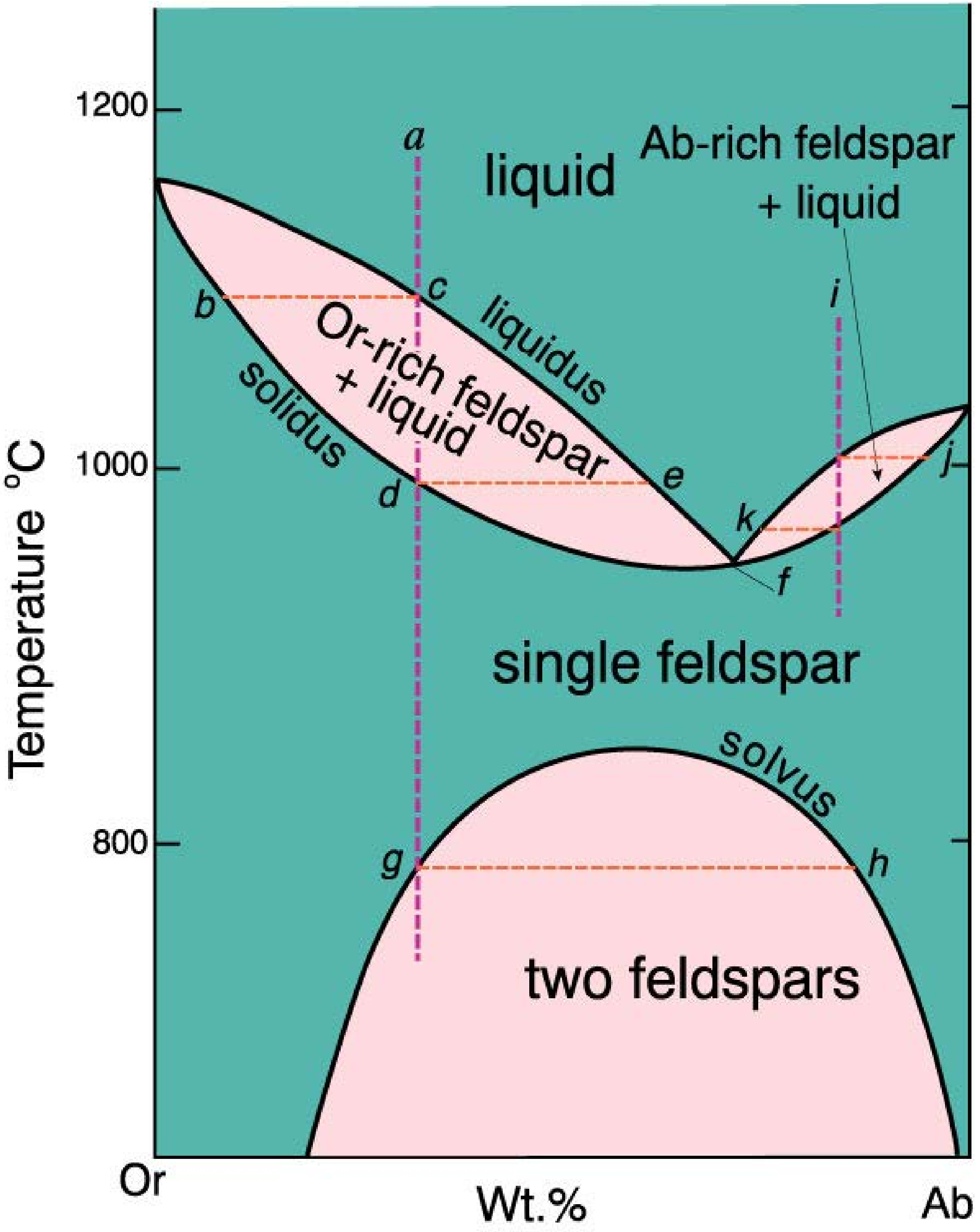


Figure 6.16. T-X phase diagram of the system albite-orthoclase at 0.2 GPa H_2O pressure. After Bowen and Tuttle (1950). J. Geology.


1200
1000
800
Temperature °C
Or
Wt.%
Ab
a
liquid
Ab-rich feldspar
+ liquid
b
c
liquidus
Or-rich feldspar
+ liquid
solidus
d
e
i
j
k
f
single feldspar
solvus
g
h
two feldspars

Effect of P_{H_2O} on Ab-Or

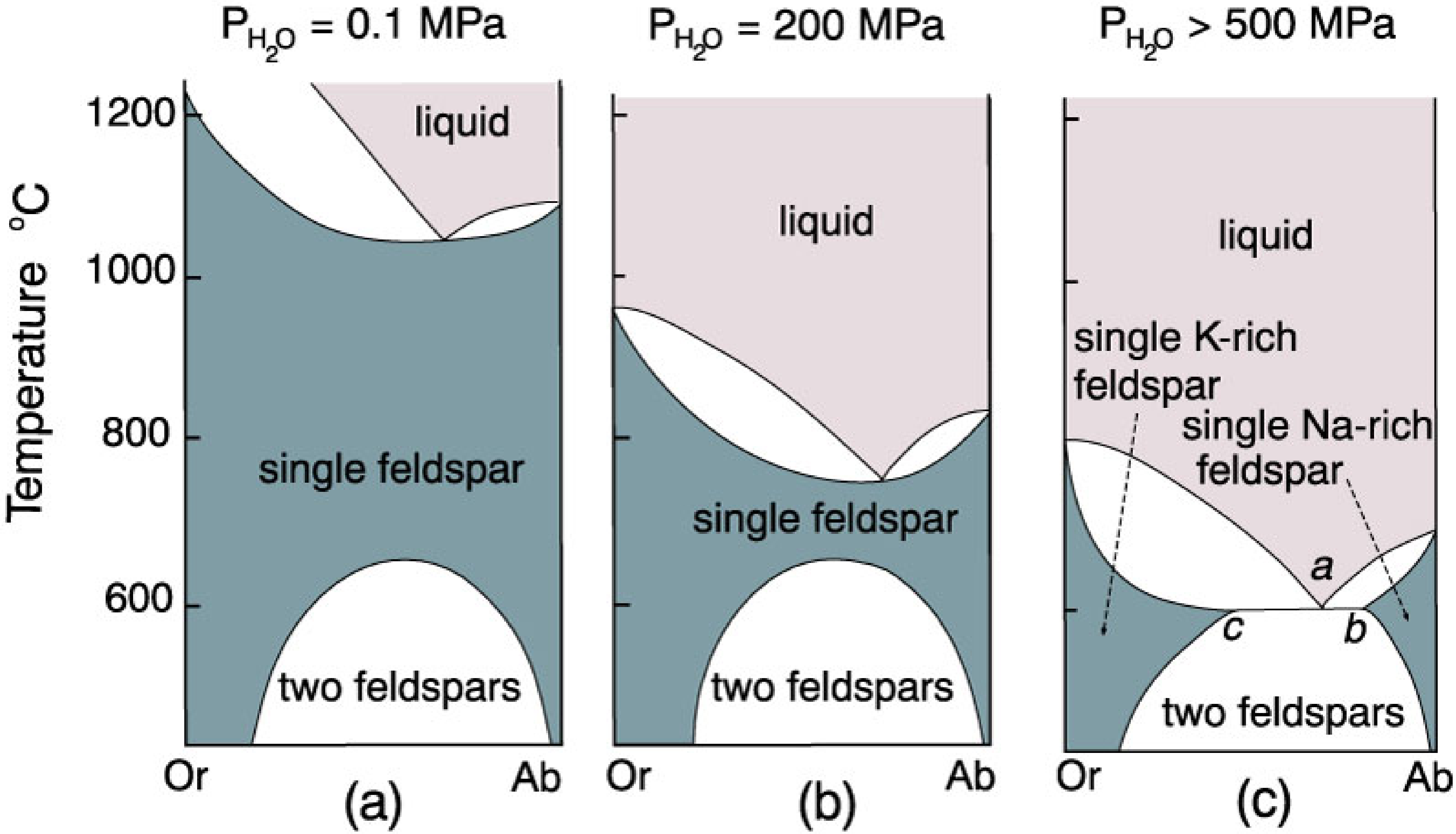


Figure 6.17. The Albite-K-feldspar system at various H_2O pressures. (a) and (b) after Bowen and Tuttle (1950), J. Geol, (c) after Morse (1970) J. Petrol.