

# Petrology JEO342E

## Lecture notes

### Lecture 1

Earth's internal structure

Compositional layering: Core, mantle, crust

Rheological layering: Lithosphere and asthenosphere

Continental crust and oceanic crust – composition, thickness, age

Plate tectonics

Mid-ocean ridges

Subduction zones

Transform fault

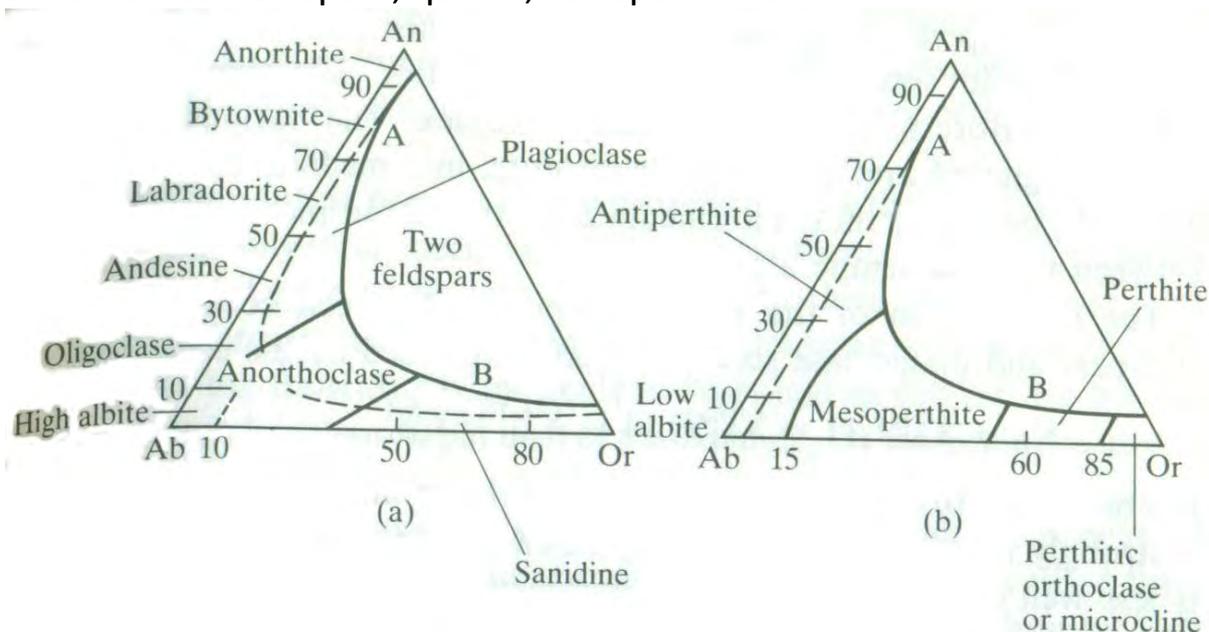
### Lecture 2 Structure and mineral chemistry of the rock-forming minerals

inosilicates: olivine, garnet, epidote, lawsonite, aluminium silicates

chain silicates: pyroxenes and amphiboles

sheet silicates: muscovite, biotite, chlorite, talc

framework silicates: feldspars, quartz, feldspathoids



**Fig. 125** Feldspar nomenclature: (a) for disordered ternary feldspars; (b) for ordered ternary feldspars in which phase separation is at or below the resolution of the optical microscope. Composition in mol per cent. Curve AB, limit of ternary solid solution.

## Feldspathoids

### Nepheline

$\text{NaAlSi}_3\text{O}_8$  -  $\text{Na}_3(\text{Na,K})\text{Al}_4\text{Si}_4\text{O}_{16}$

albite  $\text{NaAlSi}_3\text{O}_8$

compared to albite  $(\text{Na,K})\text{Al} = \text{Si}$

occurs in alkali igneous rocks

### Leucite

$\text{KAlSi}_2\text{O}_6$

occurs in potassium rich basic lavas

## Appendix 1

### Calculation of a Chemical Formula from a Mineral Analysis Hornblende Analysis

	(1) Wt per cent of oxides	(2) Molecular proportion of oxides	(3) Atomic proportion of oxygen from each molecule	(4) No. of anions on basis of 24(O,OH) i.e. col. (3) × 8.3735	(5) No. of ions in formula
SiO <sub>2</sub>	51.63	0.8594	1.7188	14.392	Si 7.196
Al <sub>2</sub> O <sub>3</sub>	7.39	0.0725	0.2175	1.821	Al 1.214
Fe <sub>2</sub> O <sub>3</sub>	2.50	0.0157	0.0471	0.394	Fe <sup>3+</sup> 0.263
FeO	5.30	0.0738	0.0738	0.618	Fe <sup>2+</sup> 0.618
MnO	0.17	0.0024	0.0024	0.020	Mn 0.020
MgO	18.09	0.4489	0.4489	3.759	Mg 3.759
CaO	12.32	0.2197	0.2197	1.840	Ca 1.840
Na <sub>2</sub> O	0.61	0.0098	0.0098	0.082	Na 0.164
H <sub>2</sub> O <sup>+</sup>	2.31	0.1282	0.1282	1.073	OH 2.146
Total	100.32		2.8662		
			$\frac{24}{2.8662} = 8.3735$		

atom proportions so that they total 24. This is done by multiplying all of them by 24/T and the results are given in *Column (4)*.

*Column (5)* gives the number of cations associated with the oxygens in *column (4)*. Thus for SiO<sub>2</sub> there is one silicon for two oxygens so the *column (4)* entry is divided by 2. For Al<sub>2</sub>O<sub>3</sub> there are two aluminiums for every three oxygens so the *column (4)* entry is multiplied by  $\frac{2}{3}$ . For divalent ions the *column (5)* value is the same as that of *column (4)*, and for monovalent ions (including hydrogen) the latter is doubled in *column (5)*.

The numbers of ions on the basis of 24 oxygens given in *column (5)* can be grouped as shown to conform to a structural formula. In the present example it is assumed that the tetrahedral sites which are not filled by Si are occupied by Al, and the remaining Al atoms are in octahedral coordination.

It should be noted that a chemical analysis in itself can give only the ratios of atoms in the formula, and that the actual numbers of atoms given depends on an assumption about the actual number of one of them or of a group of them. A check of the correctness of the formula can be made if the cell volume and specific gravity are accurately known, since a calculated specific gravity can then be compared with that measured.

A check of charge balance, made by adding positive and negative charges in the formula, is a check only on arithmetic and not on the quality of the analysis. This is because any analysis expressed in terms of neutral oxides must lead to numbers of cations and oxygens which balance electrically.

In many silicates, as in the example above, the only anion in the mineral is oxygen (or OH). Each element is expressed (and generally directly determined) as a weight percentage of oxide, even though the oxides do not exist as such in the mineral. The calculation procedure outlined is justifiable, since each element can be thought of as associated with its appropriate share of the oxygen atoms in the crystal structure.

When oxygen is not the only anion present the calculation is somewhat more complicated, and an example (a clinohumite) is shown overleaf.

The procedure for calculating a chemical formula is described by means of the above example, a hornblende.

*Column (1)* lists the composition of the mineral expressed in the usual manner as weight percentages of the constituent oxides.

*Column (2)* is derived by dividing each *column (1)* entry by the molecular weight of the oxide concerned. The figures so obtained therefore express the molecular proportions of the various oxides.

*Column (3)* is derived from *column (2)* by multiplying by the number of oxygen atoms in the oxide concerned. It thus gives a set of numbers proportional to the numbers of oxygen atoms associated with each of the elements concerned. At the foot of *column (3)* is its total (T).

If we require the amphibole formula based upon 24 oxygen atoms (this represents half the content of the unit cell) we need to re-cast the oxygen

## Appendix 2

### Atomic and Molecular Weights for use in Calculations of Mineral Formulae from Chemical Analyses

Al <sub>2</sub> O <sub>3</sub>	101.96	H <sub>2</sub> O	18.015	S	32.06
B	10.81	HfO <sub>2</sub>	210.49	SO <sub>3</sub>	80.06
B <sub>2</sub> O <sub>3</sub>	69.62	K <sub>2</sub> O	94.20	Se <sub>2</sub> O <sub>3</sub>	137.91
BaO	153.33	La <sub>2</sub> O <sub>3</sub>	325.81	SiO <sub>2</sub>	60.08
BeO	25.01	Li <sub>2</sub> O	29.88	SnO	134.69
CO <sub>2</sub>	44.01	MgO	40.30	SrO	103.62
CaO	56.08	MnO	70.94	Ta <sub>2</sub> O <sub>5</sub>	441.89
CeO <sub>2</sub>	172.12	MnO <sub>2</sub>	86.94	ThO <sub>2</sub>	264.04
Ce <sub>2</sub> O <sub>3</sub>	328.24	Mn <sub>2</sub> O <sub>4</sub>	228.81	TiO <sub>2</sub>	79.88
Cl	35.45	Na <sub>2</sub> O	61.98	UO <sub>2</sub>	270.03
CoO	74.93	NiO	74.69	U <sub>3</sub> O <sub>8</sub>	842.08
Cr <sub>2</sub> O <sub>3</sub>	151.99	Nb <sub>2</sub> O <sub>5</sub>	265.81	V <sub>2</sub> O <sub>5</sub>	181.88
CuO	79.55	P <sub>2</sub> O <sub>5</sub>	141.94	Y <sub>2</sub> O <sub>3</sub>	225.81
F	19.00	PbO	223.20	ZnO	81.38
FeO	71.85	Rb <sub>2</sub> O	186.94	ZrO <sub>2</sub>	123.22
Fe <sub>2</sub> O <sub>3</sub>	159.69				

## End-Member Calculations

For some purposes it can be useful to express the formula of a mineral which can show a range of compositions between specified end-members, in terms of the percentages of these end members. There is no single procedure for the required calculation since different assumptions are needed for different minerals and different purposes. In general a relatively small number of 'major' constituent end members are specified. In the olivines, for example, Mg<sub>2</sub>SiO<sub>4</sub>(Fo) and Fe<sub>2</sub>SiO<sub>4</sub>(Fa) may suffice, but the Mn<sub>2</sub>SiO<sub>4</sub> (tephroite end member) could also be calculated. If Mn content is low it is usually included with Fe as part of the Fa component. For a minor constituent the decision needs to be taken as to whether to ignore it or include it as proxying for a major element, and if so, for which element.

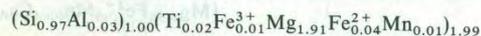
The examples given below help to indicate the kinds of procedures adopted.

### Olivine

Ideal formula (Mg,Fe)<sub>2</sub>SiO<sub>4</sub>.

End members: Mg<sub>2</sub>SiO<sub>4</sub>(Fo)–Fe<sub>2</sub>SiO<sub>4</sub>(Fa).

Example formula on basis of 4(O):



End-member percentages

$$\left. \begin{aligned} 100\text{Mg}/(\text{Mg} + \text{Fe}^*) &= 191/1.96 = 97.4\% \\ \text{(where Fe}^* &= \text{Fe}^{2+} + \text{Fe}^{3+}). \\ 100\text{Fe}^*/(\text{Mg} + \text{Fe}^*) &= 5/1.96 = 2.6\% \end{aligned} \right\} \text{Fo}_{97.4}\text{Fa}_{2.6}$$

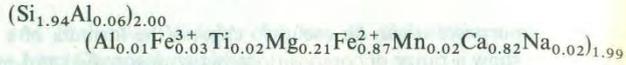
$$\text{If Fe}^* = \text{Fe}^{2+} + \text{Fe}^{3+} + \text{Mn. Fo} = 191/1.97 = 96.9\%. \quad \text{Fo}_{96.9}\text{Fa}_{3.1}$$

## Augite

Ideal formula  $(\text{Ca,Mg,Fe})_2(\text{Si,Al})_2\text{O}_6$ .

End members:  $\text{Mg}_2\text{Si}_2\text{O}_6(\text{En})$ – $\text{Fe}_2\text{Si}_2\text{O}_6(\text{Fs})$ – $\text{Ca}_2\text{Si}_2\text{O}_6(\text{Wo})$ .

Example formula on basis of 6(O):



End-member percentages

$$100\text{Mg}/(\text{Mg} + \text{Fe}^* + \text{Ca}) = 21/1.95 = 10.77\%$$

$$100\text{Fe}^*/(\text{Mg} + \text{Fe}^* + \text{Ca}) = 92/1.95 = 47.18\%$$

$$100\text{Ca}/(\text{Mg} + \text{Fe}^* + \text{Ca}) = 82/1.95 = 42.05\%$$

(where  $\text{Fe}^* = \text{Fe}^{2+} + \text{Fe}^{3+} + \text{Mn}$ ); i.e.  $\text{En}_{10.77}\text{Fs}_{47.18}\text{Wo}_{42.05}$

Alternative including end-member  $\text{NaFe}^{3+}\text{Si}_2\text{O}_6(\text{Ac})$

$$100\text{Na}/(\text{Mg} + \text{Fe}^* + \text{Ca} + \text{Na}) = 2/1.97 = 1.02\%$$

leaving 21/1.97(En), 92/1.97(Fs) and 82/1.97(Wo), i.e.  $\text{En}_{10.66}\text{Fs}_{46.70}\text{Wo}_{41.62}\text{Ac}_{1.02}$

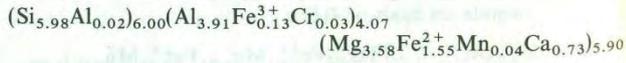
## Garnet

Ideal formula  $(\text{Mg,Fe}^{2+},\text{Mn,Ca})_3(\text{Al,Fe}^{3+},\text{Cr})_2(\text{Si,Al})_3\text{O}_{12}$ .

End members:  $\text{Mg}_3\text{Al}_2$  pyrope;  $\text{Fe}_3^{3+}\text{Al}_2$  almandine;  $\text{Mn}_3\text{Al}_2$  spessartine

$\text{Ca}_3\text{Al}_2$  grossular;  $\text{Ca}_3\text{Fe}_3^{2+}$  andradite;  $\text{Ca}_3\text{Cr}_2$  uvarovite

Example formula on basis of 24(O)



End-member percentages

$$\text{pyrope } 358/5.90 = 60.68\%, \text{ andradite } 13/4.07 = 3.19\%$$

$$\text{almandine } 155/5.90 = 26.27\%, \text{ uvarovite } 3/4.07 = 0.74\%$$

$$\text{spessartine } 4/5.90 = 0.67\%, \quad \Sigma(\text{and} + \text{uv}) = 3.93\%$$

$$\text{gro} + \text{and} + \text{uv} = 73/5.90 = 12.37\%$$

$$\text{gro} = 12.37 - \Sigma(\text{and} + \text{uv}) = 12.37 - 3.93 = 8.44\%$$

Result:  $\text{Py}_{60.7}\text{alm}_{26.3}\text{gro}_{8.4}\text{and}_{3.2}\text{uv}_{0.7}\text{sp}_{0.7}$

## Feldspar

Plagioclase feldspar: as for olivine but take

$$100\text{Ca}/(\text{Ca} + \text{Na}) = \text{An}$$

$$100\text{Na}/(\text{Ca} + \text{Na}) = \text{Ab}$$

Alkali feldspar: as for olivine but take

$$100\text{Na}/(\text{Na} + \text{K}) = \text{Ab}$$

$$100\text{K}/(\text{Na} + \text{K}) = \text{Or}$$

Ternary feldspar: as for augite but

$$100\text{Ca}/(\text{Ca} + \text{Na} + \text{K}) = \text{An}$$

$$100\text{Na}/(\text{Ca} + \text{Na} + \text{K}) = \text{Ab}$$

$$100\text{K}/(\text{Ca} + \text{Na} + \text{K}) = \text{Or}$$

## Lecture 3

### Classification and nomenclature of igneous rocks

#### Textural terms

phaneritic

aphanitic

pyroclastic

fine-grained – less than 1 mm

medium-grained 1-5 mm

coarse-grained 5-50 mm

equigranular

porphyritic – phenocrysts and groundmass

aphyric – no phenocrysts

euhedral

subhedral

anhedral

ophitic – large cpx enclosing plagioclase

cumulate textures

poikilitic texture

exsolution lamellae – feldspar perthite – albite lamellae in K-Feldspar

pseudomorphs

#### Compositional terms

felsic – composed mainly of felsic minerals

mafic – composed mainly of mafic minerals

ultramafic – more than 90% mafic minerals

color index (M') – percentage of mafic minerals

acidic –	more than 66 wt% SiO <sub>2</sub>
intermediate	52-66 wt % SiO <sub>2</sub>
basic	45-52 wt% SiO <sub>2</sub>
ultrabasic	less than 45 wt %

## **IUGS classification**

modifying terms

leuco

melano

## **aphanitic rocks**

classification by composition – principally SiO<sub>2</sub> versus Na<sub>2</sub>O + K<sub>2</sub>O

pyroclastic rocks

named after the type and size of pyroclasts

more than 64 mm – bombs (molten) or blocks

2-64 mm – lapilli

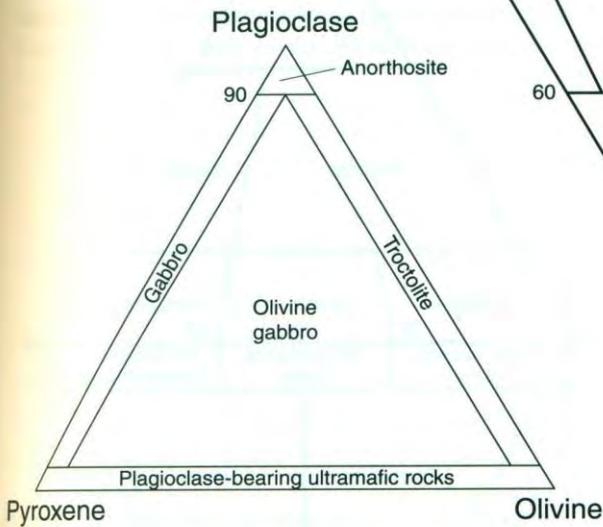
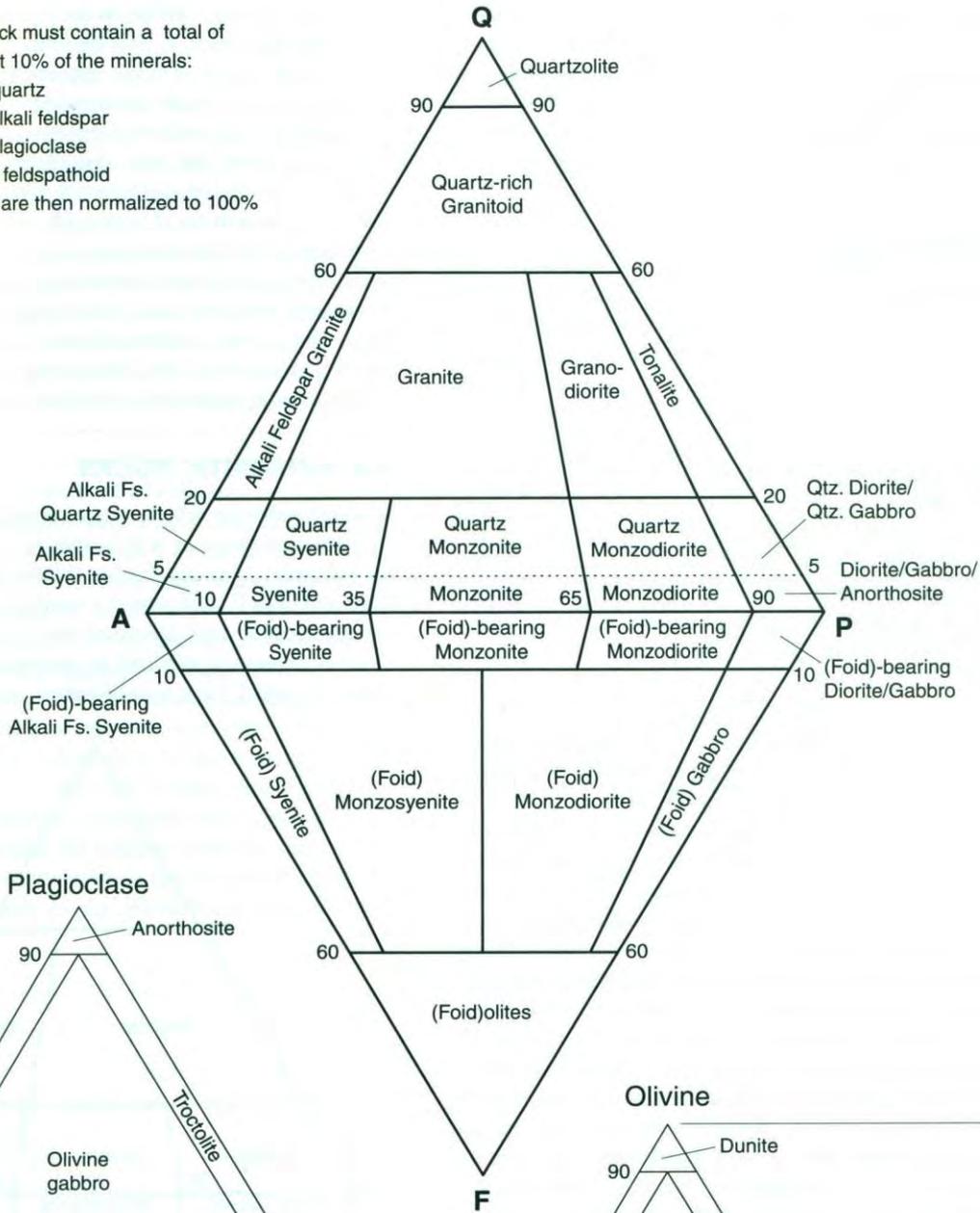
less than 2 mm – ash

pyroclasts could be crystal, glass or rock fragment

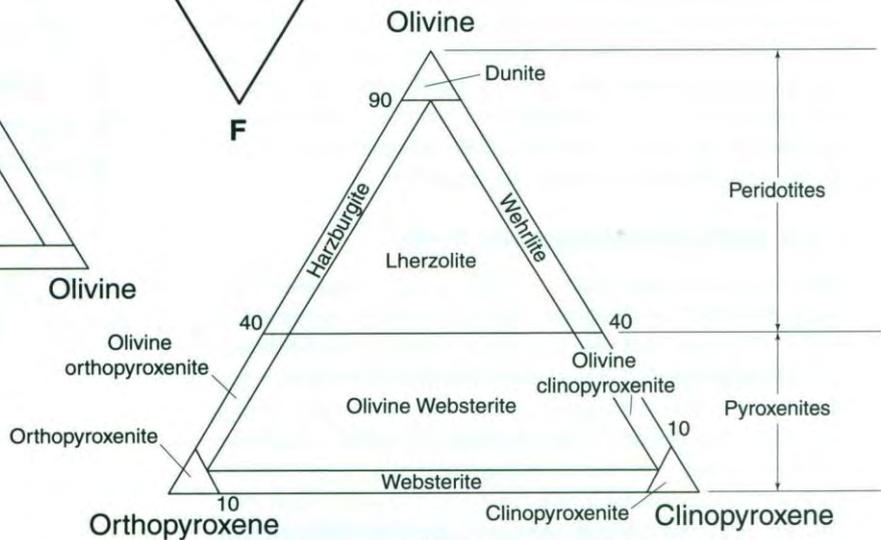
lithic tuff, crystal tuff, vitric tuff

epiclastic rocks

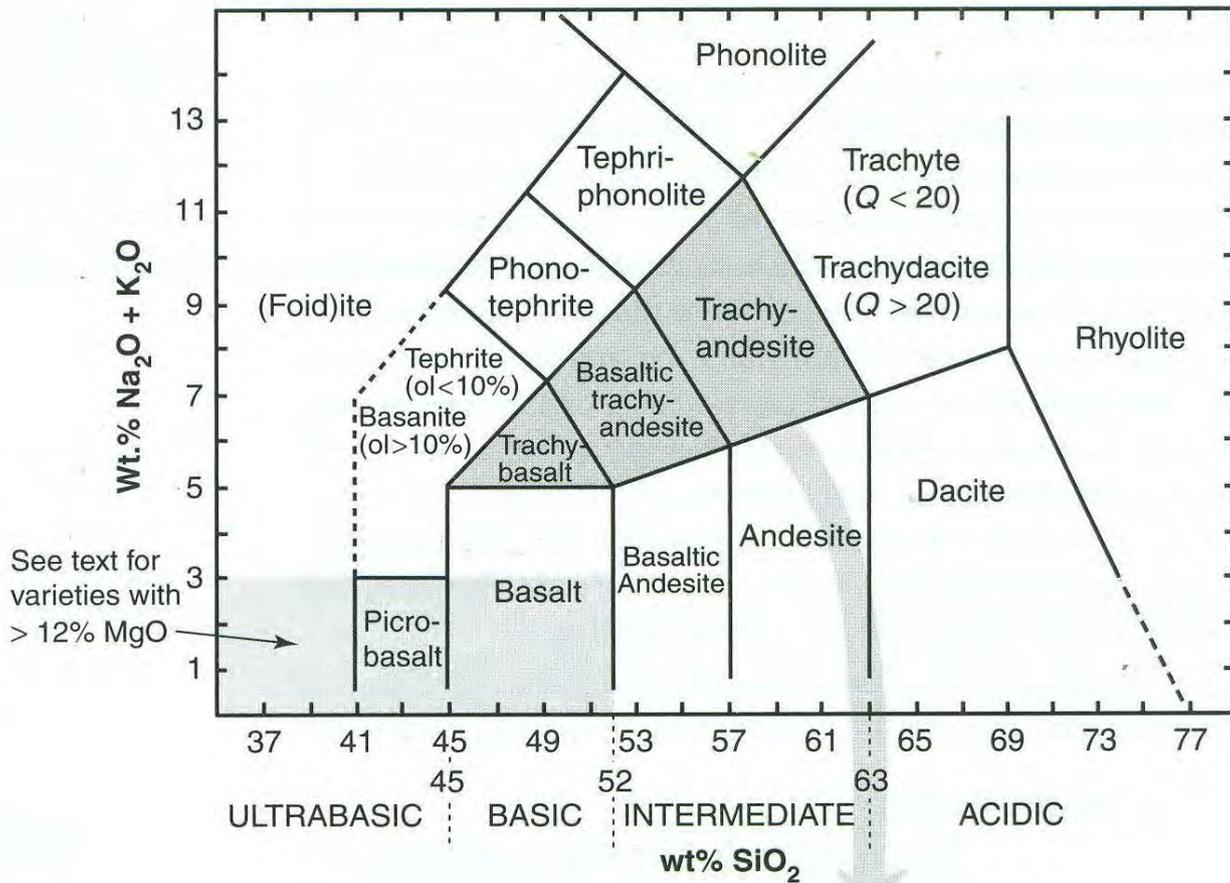
- (a) The rock must contain a total of at least 10% of the minerals:  
 Q - quartz  
 A - alkali feldspar  
 P - plagioclase  
 F - a feldspathoid  
 Which are then normalized to 100%



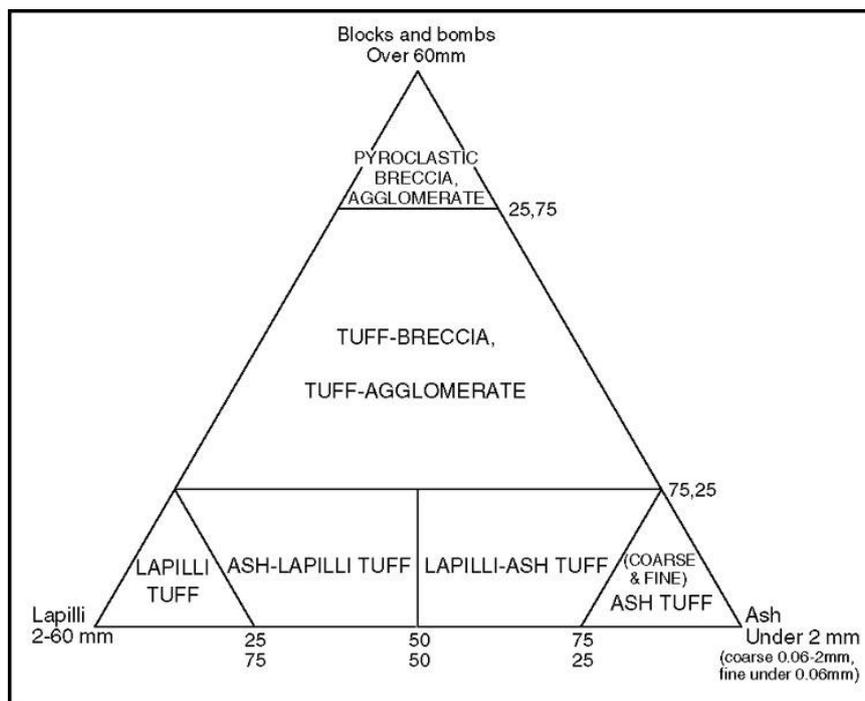
(b)



(c)



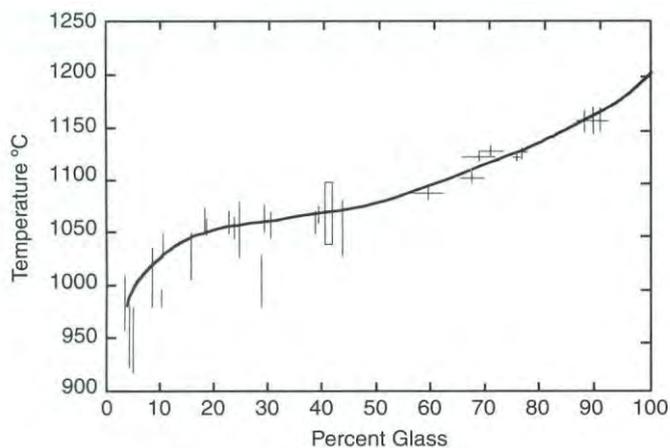
Further subdivisions of shaded fields	Trachybasalt	Basaltic Trachyandesite	Trachyandesite
$Na_2O - 2.0 \geq K_2O$	Hawaiite	Mugearite	Benmoreite
$Na_2O - 2.0 < K_2O$	Potassic Trachybasalt	Shoshonite	Latite



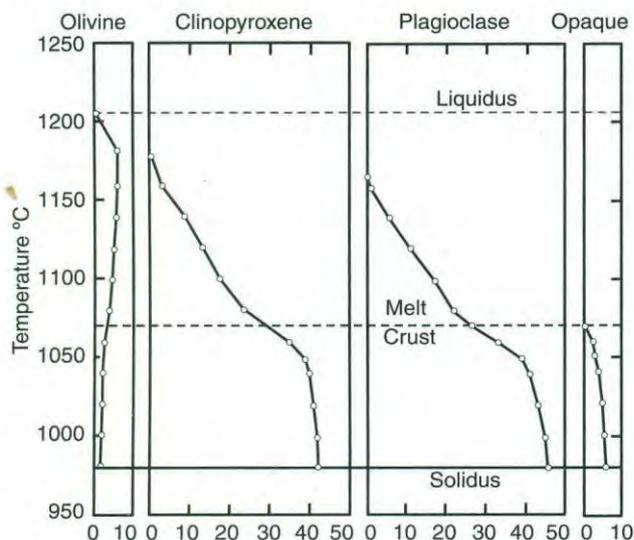
## Lecture 4

### Crystallization from the magma

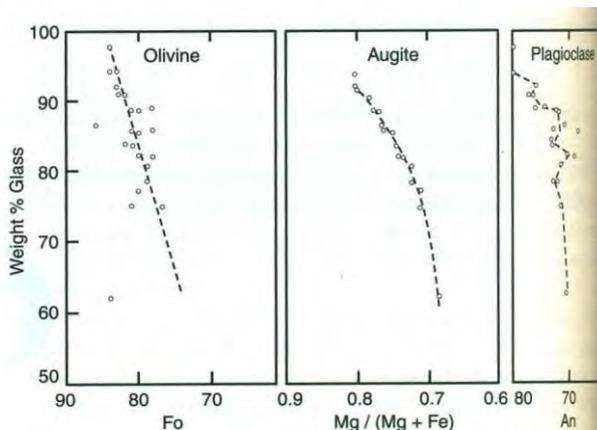
#### Results from the Makaopuhi lava lake



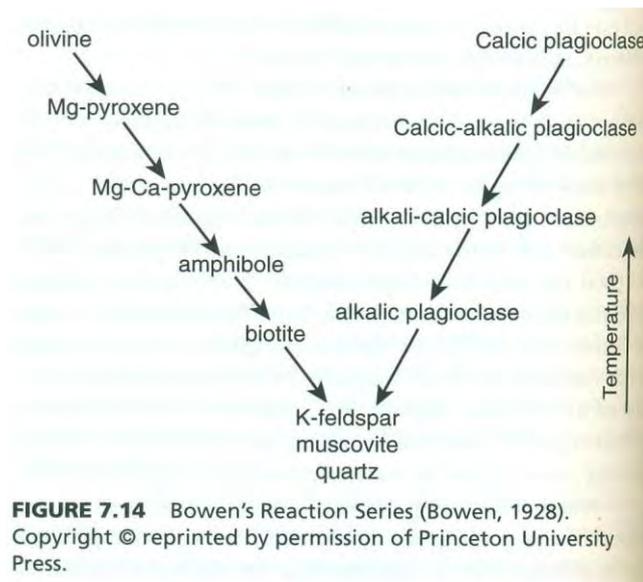
**FIGURE 6.1** Percent melt (glass) as a function of temperature in samples extracted from the cooling of basalt of the Makaopuhi lava lake, Hawaii. Lines represent ranges observed. After Wright and Okamura (1977).



**FIGURE 6.2** Weight percent minerals in Makaopuhi lava lake samples as a function of temperature. From Wright and Okamura (1977).

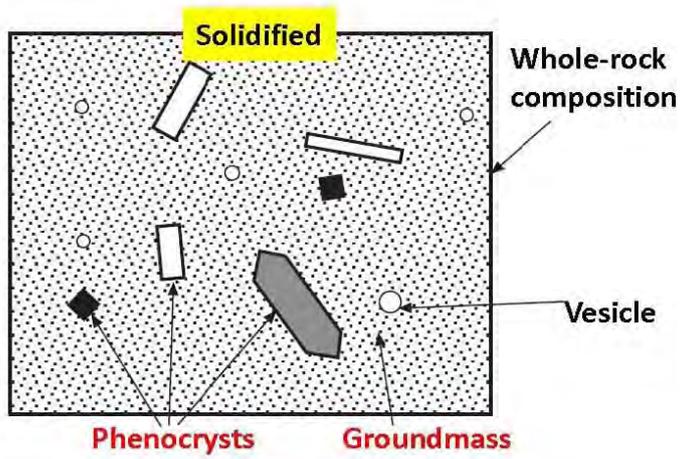
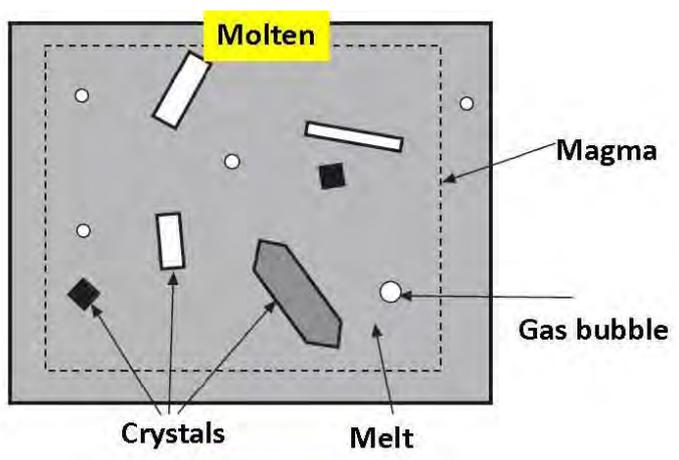


**FIGURE 6.3** Model composition of minerals in Makaopuhi lava lake samples. From Wright and Okamura (1977).



## Deductions

1. Melts crystallize over a span of time and temperature (in the case above 1200 to 970 C).
2. Several minerals crystallize at the same time; the number of minerals crystallized increases with decreasing temperature.
3. Minerals crystallize sequentially with considerable overlap.
4. Minerals change composition as cooling progresses.
5. The melt composition also changes during crystallization.
6. The minerals that crystallize and their composition depends on temperature and composition of the melt.
7. Apart from T, P and volatile components (H<sub>2</sub>O, CO<sub>2</sub>) can also affect the temperature range of crystallization and the sequence.



## Lecture 5

# PHASE DIAGRAMS

### Binary systems with complete solid solution at 1 bar (01. MPa)

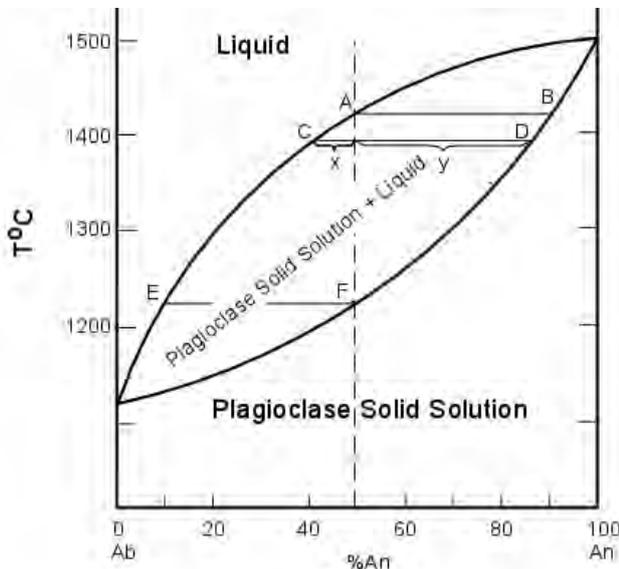


Figure 3

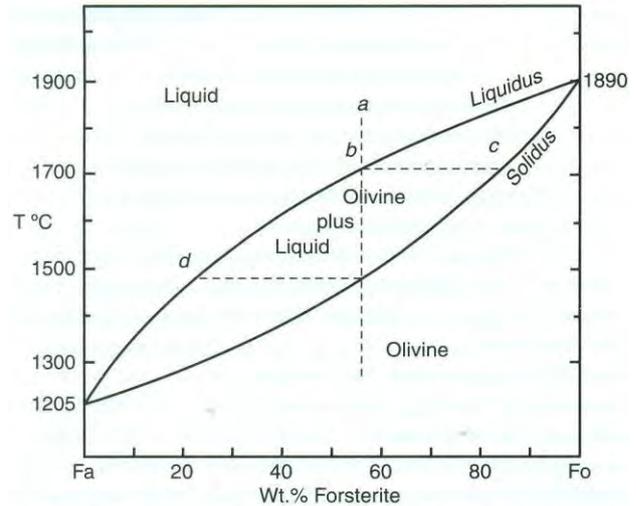


FIGURE 6.10 Isobaric T-X phase diagram of the olivine system at atmospheric pressure. After Bowen and Schairer (1932). Reprinted by permission of the *American Journal of Science*.

anorthite melting-crystallization 1553 C, albite 1118 C.

### solidus, liquidus

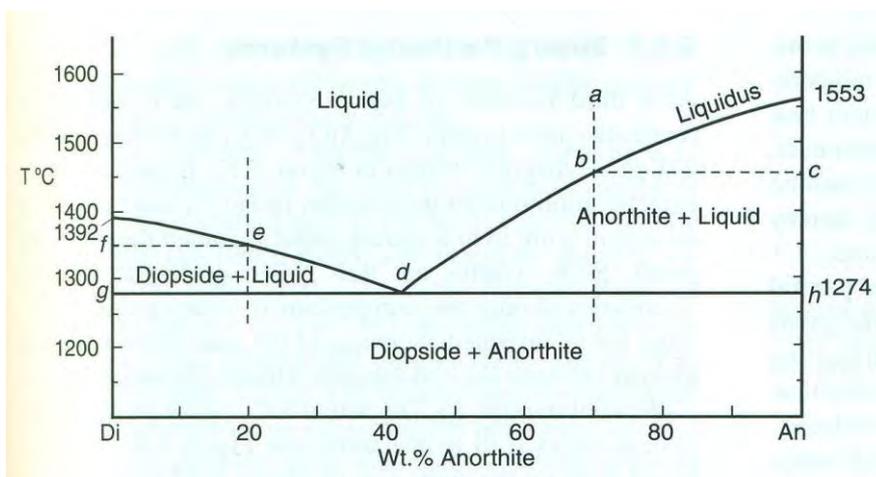
**Liquidus** - The line separating the field of all liquid from that of liquid plus crystals.

**Solidus** - The line separating the field of all solid from that of liquid plus crystals.

### Binary eutectic systems

system  $\text{CaMgSi}_2\text{O}_6$  (diopside) –  $\text{CaAl}_2\text{Si}_2\text{O}_8$  (anorthite)

basalt analog system – Bowen (1915)



**FIGURE 6.11** Isobaric (0.1 MPa) *T-X* phase diagram of the diopside–anorthite system. After Bowen (1915b). Reprinted by permission of the *American Journal of Science*.

No solidus because no solid solution

Crystallization of pure anorthite – no Na no solid solution

Eutectic point – 1274 C at 1bar - anorthite and diopside crystallize together.

**Eutectic point** - the point on a phase diagram where the maximum number of allowable phases are in equilibrium. When this point is reached, the temperature must remain constant until one of the phases disappears. A eutectic is an invariant point. It is the point with minimum melt temperature.

### **Equilibrium melting - Equilibrium crystallization**

The melt and the crystals remain in equilibrium during melting or during crystallization.

### **Fractional crystallization**

Physical separation of the crystal as soon as it forms

### **Fractional melting**

Extraction of melt increments as they are formed.

### **Partial melting**

A mixture of equilibrium and fractional melting; most natural magmas, once created, are extracted from the melted source rock at some point before melting is completed. Partial melting increases the concentration of low-melting-point component in the resulting melt system. Likewise it increases the concentration of high-melting component in the residual solids (basalt generation leaves behind refractory mantle)

A mixture of diopside and anorthite start to melt at 1274 C (pure anorthite melts at 1553 and pure diopside at 1392 C), and the melt produced has the composition of “d” (42% Anorthite – 58 % diopside).

Once the melting begins the system will stay at 1274 C until one of the two solids is consumed.

If  $X_{\text{bulk}}$  is between Di and d, anorthite is consumed and the liquid composition will follow the liquidus with increasing temperature towards diopside until the liquid composition reaches  $X_{\text{bulk}}$ .

Pure anorthite melts at 1553 C but adding a tiny amount of di reduces the melt temperature to 1274 C.

### **Partial melting**

If sufficient heat is available to initiate melting at eutectic temperature, consumption of one mineral could rise the melting point of the residual solid by several hundred degrees.

If partial melt separates from the solids during equilibrium melting and migrates to a shallower magma chamber, it will produce a rock of different diopside/anorthite ratio than the original bulk composition.

Partial melts do not have the same composition as their source area; they are enriched in low-temperature melting components – higher Fe/Mg and Na/Ca etc.

Di-An system shows:

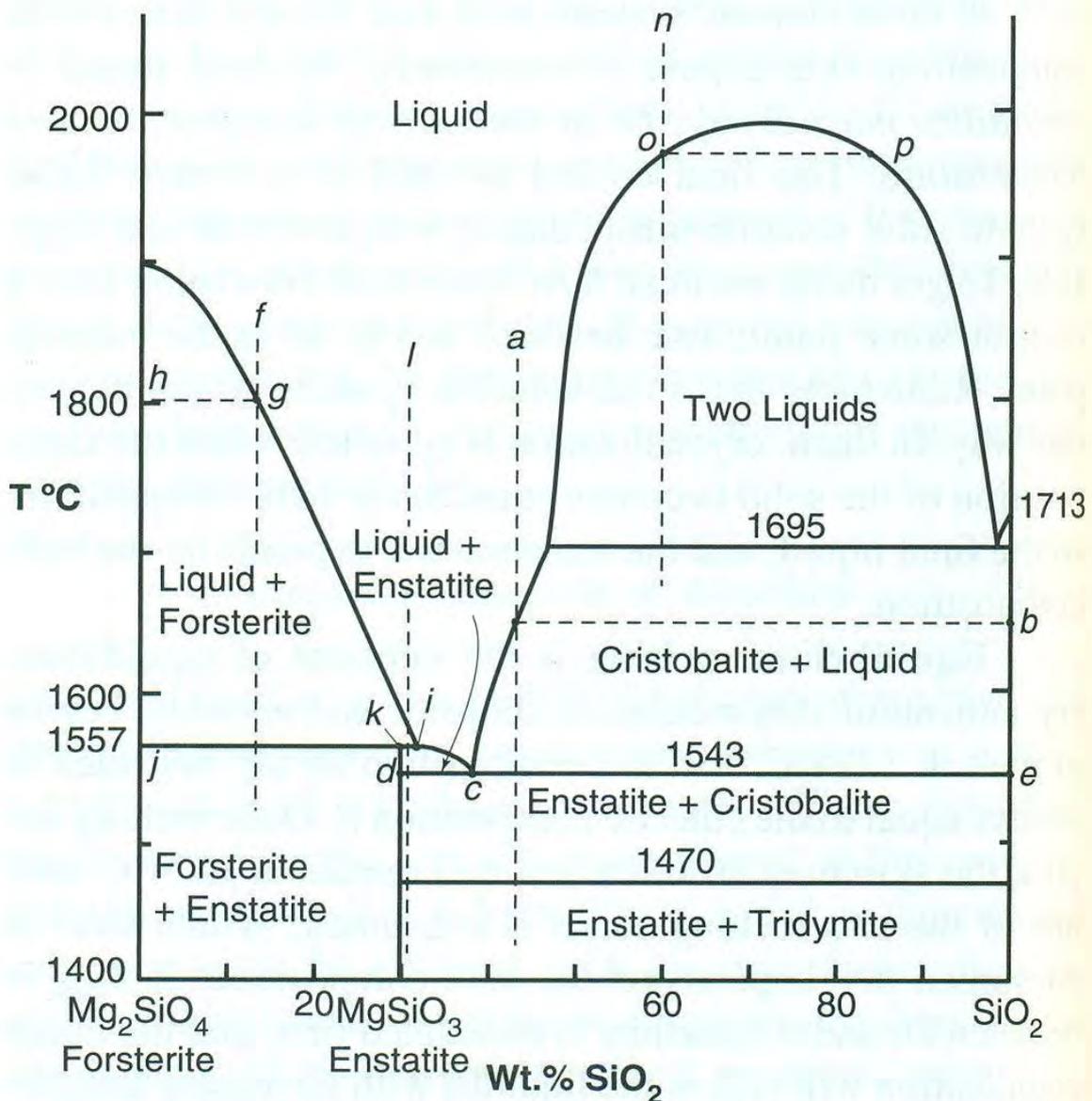
1. crystallization and melting occurs over a temperature range.
2. the sequence of mineral crystallization varies with melt composition.
3. Adding a component to the stem reduces the melting point.

## Binary peritectic systems

### forsterite-silica system ( $\text{Mg}_2\text{SiO}_4 - \text{SiO}_2$ )

In addition of eutectic point there is another inflection point called as the **peritectic point**

**Peritectic point** - The point on a phase diagram where a reaction takes place between a previously precipitated phase and the liquid to produce a new solid phase. When this point is reached, the temperature must remain constant until the reaction has run to completion. A peritectic is also an invariant point.



**FIGURE 6.12** Isobaric  $T$ - $X$  phase diagram of the system Forsterite-silica at 0.1 MPa. After Bowen and Anderson (1914) and Grieg (1927). Reprinted by permission of the *American Journal of*

Two components but there is an intermediate phase, enstatite, between forsterite and silica polymorph.



forsterite and quartz never coexists in rocks! No forsterite + quartz field in the phase diagram.

### **melt of composition f**

at 1800 C forsterite crystallizes

at 1557 forsterite + liquid = enstatite

resorption of olivine – enstatite mantling olivine

liquid finishes first and forsterite and enstatite remain stable

### **melt of composition i**

forsterite forms first but is completely resorbed at the peritectic point

the final rock will have enstatite and silica polymorphs

Fractional crystallization

If olivine separates from the system, the melt bulk composition shifts and the melt will reach the eutectic point.

### **Solvus**

liquid exsolution – separates in two immiscible liquids like oil and water.

### **Incongruent melting**

**Incongruent melting** - melting wherein a phase melts to a liquid with a composition different from the solid and produces a solid of different composition to the original solid.

If we melt pure enstatite, the product will be a liquid and forsterite – this is called incongruent melting.

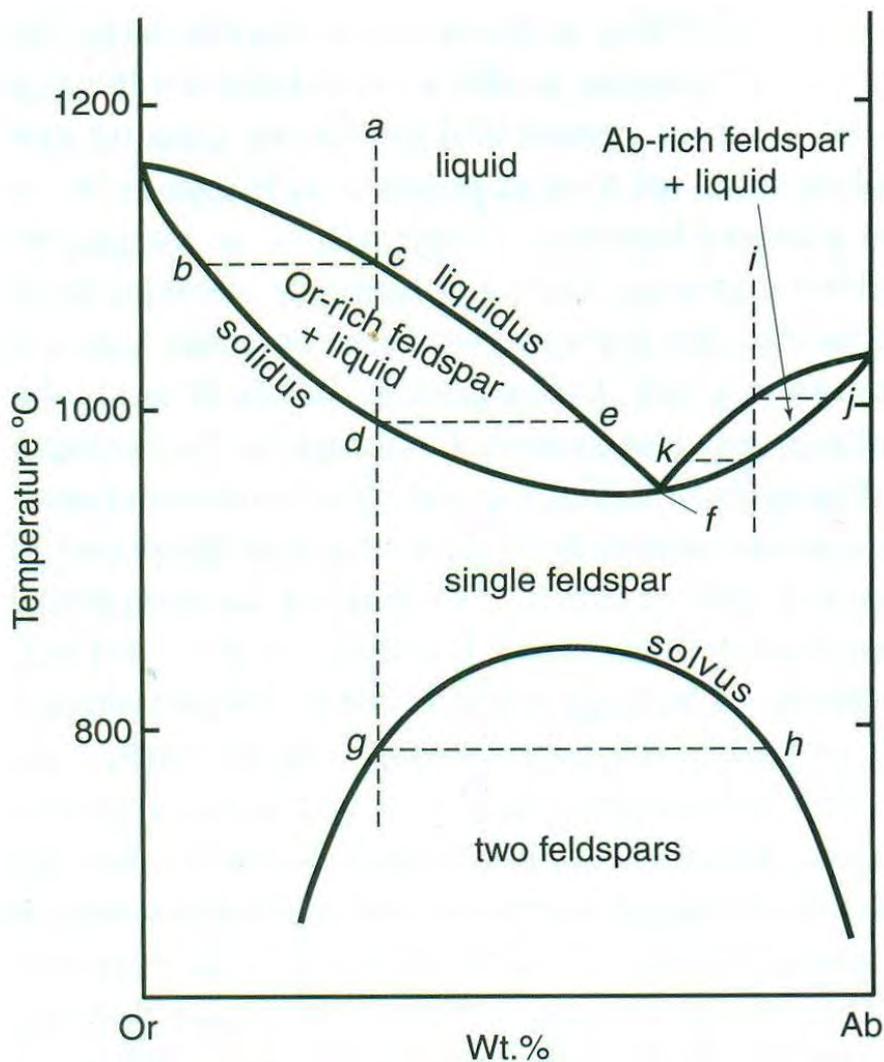
**Congruent melting** - melting wherein a phase melts to a liquid with the same composition as the solid.

## The Alkali feldspar system

NaAlSi<sub>3</sub>O<sub>8</sub>-KAlSi<sub>3</sub>O<sub>8</sub> system at 0.2 Gpa pressure

two loops meeting at a eutectic point

a liquid of composition a will not reach the eutectic because it will crystallize before



**FIGURE 6.16** *T-X* phase diagram of the system albite–orthoclase at 0.2 GPa H<sub>2</sub>O pressure. After Bowen and Tuttle (1950). Copyright © by the University of Chicago.

### solvus

separation of two solid phases from an homogeneous solid solution

caused by the difference of the ionic radius of K (1.59 Å) and Na (1.24 Å) atoms.

formation of exsolution lamella –  
 albite lamella in orthoclase – perthite  
 antiperthite

## geothermometry

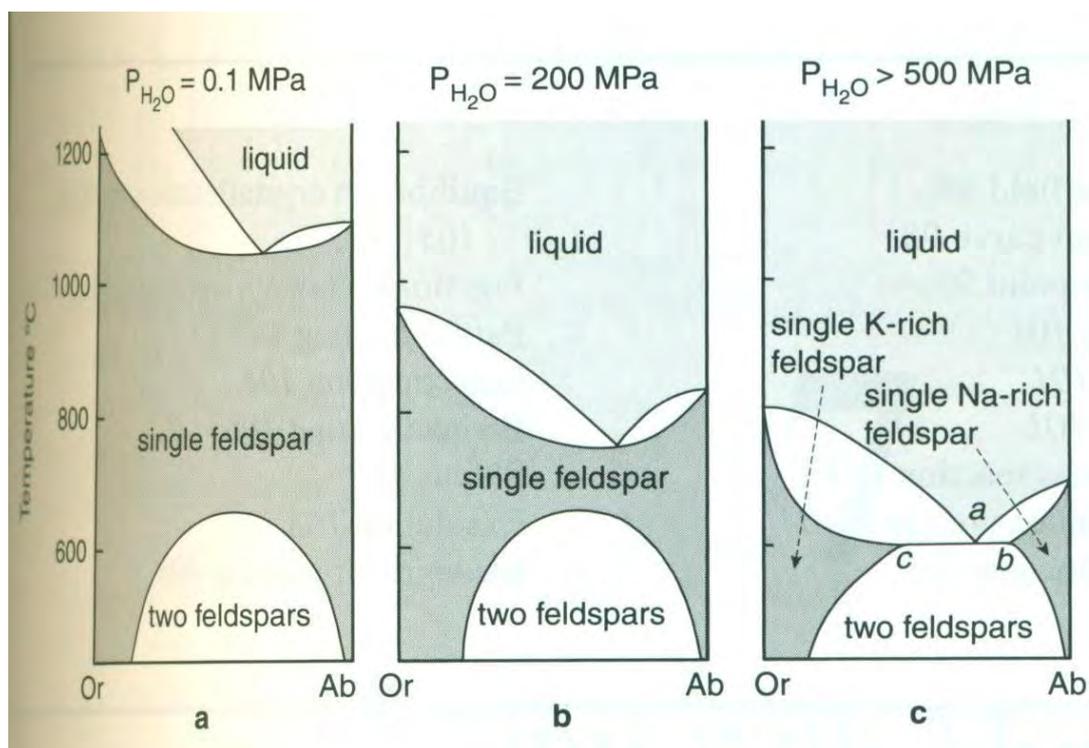
the composition of two coexisting feldspars are a function of temperature  
 effect of pressure on the system

Increasing  $P_{H_2O}$  will increase the stability field of the liquid (decrease the melting temperature) because  $H_2O$  will preferentially enter the liquid (it is more soluble in the melt than in the feldspar) – it will have little effect on the solvus.

With increasing  $P_{H_2O}$  the liquidus and solidus will move to lower temperatures and at about 500 MPa (5 kbar) the liquidus and solidus will intersect the solvus.

The area of a single feldspar is reduced with increasing  $P_{H_2O}$ .

Granitic rocks that have crystallized at shallow levels will have a single feldspar, while deep seated ones will have two feldspars.



**FIGURE 6.17** The albite–K–feldspar system at various H<sub>2</sub>O pressures. Shaded areas represent possible single-phase compositions. (a) and (b) after Bowen and Tuttle (1950), copyright © by the University of Chicago. (c) after Morse (1970). Reprinted by permission of Oxford University Press.

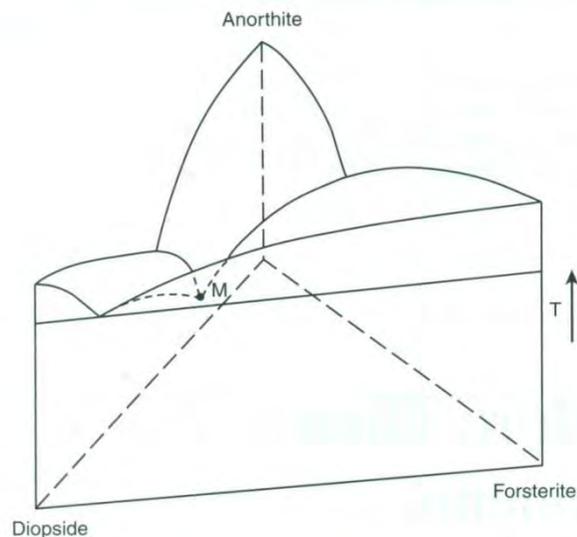
**1 bar equals 0.1 MPa**

**1 kbar equals 100 MPa or 0.1 GPa**

### Ternary eutectic systems

diopside (CaMgSi<sub>2</sub>O<sub>6</sub>) – forsterite (Mg<sub>2</sub>SiO<sub>4</sub>) – anorthite (CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>) **basalt** system

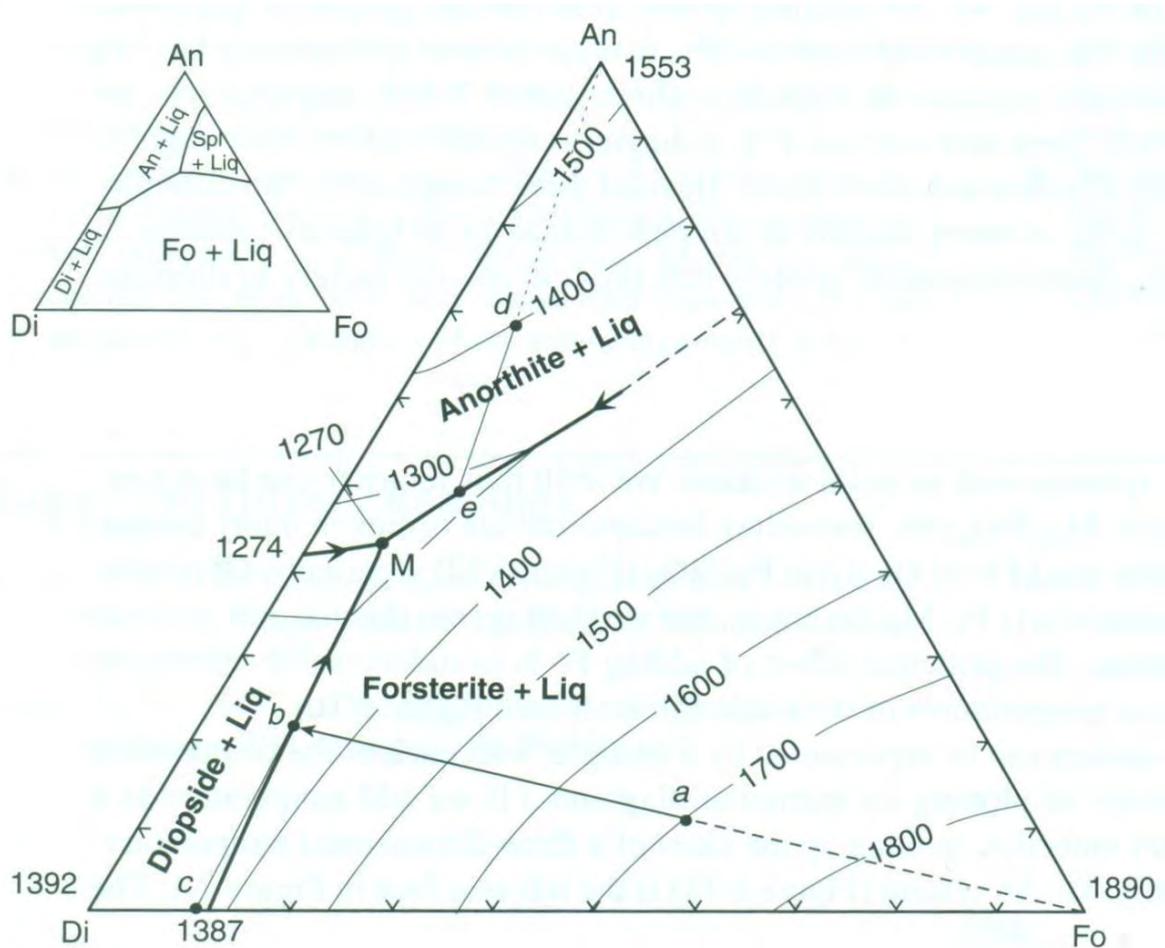
3 D temperature – composition triangular prism



**FIGURE 7.1** Three-dimensional representation of the diopside–forsterite–anorthite system versus temperature at atmospheric pressure. *M* is the ternary eutectic point. After Osborn and Tait (1952). Reprinted by permission of the *American Journal of Science*.

**M** – ternary eutectic point

transform the 2D diagram to 2D by contouring the temperature



**FIGURE 7.2** Isobaric diagram illustrating the liquidus temperatures in the Di-An-Fo system at atmospheric pressure (0.1 MPa). The dashed part of the Fo-An cotectic is in a small spinel + liquid (insert) field that is ignored here. After Bowen

the diagram is plotted looking down the temperature axis

cotectic curves – extensions of binary eutectic points

liquid of composition a (Di<sub>36</sub>An<sub>10</sub>Fo<sub>54</sub>)

liquid a starts crystallizing forsterite at 1700 C by continuous reaction

liquid<sub>1</sub> = forsterite + liquid<sub>2</sub>

As the liquid cools to b diopside joins to forsterite and liquid in the system

liquid<sub>1</sub> = forsterite + diopside + liquid<sub>2</sub>

the ratio of diopside to forsterite that is crystallizing from the liquid at b can be calculated by drawing a tangent at point b to the forsterite-diopside join, which intersects at point c. The diopside/forsterite ratio is  $(Fo-c)/(Di-c)$ .

This instantaneous ratio is not to be confused with the cumulative ratio. Because forsterite has been crystallizing since 1700 C, its total amount is much greater than that of diopside.

At the ternary eutectic point M (Di<sub>50</sub>An<sub>43</sub>Fo<sub>7</sub>)

liquid = forsterite + diopside + anorthite

The curve a to b to M is called **liquid evolution curve** or **liquid line of descent**.

Removal of early phases by crystal fractionation (settling or floating) can affect the final composition of basalt.

the liquid at separation becomes the new bulk composition.

The final rock can then have any composition from a (Di<sub>36</sub>An<sub>10</sub>Fo<sub>54</sub>) to M (Di<sub>50</sub>An<sub>43</sub>Fo<sub>7</sub>)

### **Equilibrium melting**

any mixtures of di, an and fo produces a melt at composition M at 1270 C regardless of respective ratios.

The reaction proceeds until one of the phases disappear. If forsterite is consumed first, the liquid will follow the diopside-anorthite cotectic curve.

### **Partial melting**

The first melt is produced at eutectic point at 1270 C until one of the phases is consumed. If for example anorthite is consumed and the melt is removed we are left with diopside and forsterite. This mixture will not melt until a temperature of 1387 C is reached. If diopside is consumed at this T, the temperature has to rise to 1890 C for the forsterite to melt. Thus partial melting occurs at three distinct steps.

## Lecture 6

# Chemical Petrology

**major elements** > 1 wt% expressed as oxides

**minor element** 0.1 to 1.0 wt %

**trace elements** less than 0.1 wt % - expressed as elements

major elements control the mineralogy and crystallization-melting behavior, also control density, viscosity, diffusivity of magma and rock

minor elements substitute for major elements, e.g. Mn for Fe, Mg, however, if present sufficiently may form an accessory phase, e.g.,

zircon  $ZrSiO_4$ , apatite  $Ca_5(PO_4)_3(OH,F,Cl)$ , rutile  $TiO_2$ , sphene (titanite)  $CaTiSiO_4(O,OH,F)$ , ilmenite  $FeTiO_3$

trace elements are too dilute to form a separate phase (normally)

exception K is always a major element, P, Mn and Ti are regarded as minor elements.

## analytical results

major and minor elements are reported as wt% oxide, trace elements as ppm (parts per million in wt)

1 ppm = 1 gram in 1 million gram, e.g. 1 gram in 1 000 kg, 1 gr in one tonne

Gold's average concentration in the Earth's crust is 0.005 parts per million.

A lower grade gold ore would contain something like 5 grams per tonne (5 parts per million) – 1000 times concentration.

**1 wt% = 10 000 ppm**

**TABLE 8.1 Chemical Analysis of a Basalt  
(Mid-Atlantic Ridge)**

Oxide	Wt. %	Mol Wt.	Atom Prop.	Atom %
SiO <sub>2</sub>	49.2	60.09	0.82	17.21
TiO <sub>2</sub>	2.03	79.88	0.03	0.53
Al <sub>2</sub> O <sub>3</sub>	16.1	101.96	0.32	6.64
Fe <sub>2</sub> O <sub>3</sub>	2.72	159.70	0.03	0.72
FeO	7.77	71.85	0.11	2.27
MnO	0.18	70.94	0.00	0.05
MgO	6.44	40.31	0.16	3.36
CaO	10.5	56.08	0.19	3.93
Na <sub>2</sub> O	3.01	61.98	0.10	2.04
K <sub>2</sub> O	0.14	94.20	0.00	0.06
P <sub>2</sub> O <sub>5</sub>	0.23	141.94	0.00	0.07
H <sub>2</sub> O <sup>+</sup>	0.70	18.02	0.08	1.63
H <sub>2</sub> O <sup>-</sup>	0.95	18.02	0.11	2.22
(O)			2.82	59.27
Total	99.92		4.76	100.00

	ppm		ppm
Ba	5	137.33	0.8
Co	32	58.93	11.4
Cr	220	52	88.9
Ni	87	58.7	31.1
Pb	1.29	207.2	0.1
Rb	1.14	85.47	0.3
Sr	190	87.62	45.6
Th	0.15	232.04	0.0
U	0.16	238.03	0.0
V	280	50.94	115.5
Zr	160	91.22	36.9

Data from Carmichael et al. (1974), p. 376, col. 1.

Table above shows typical analysis

errors are 1 to 5 relative per cent, e.g. an error of 3 % in MgO would indicate  $6.44 \pm 0.19$  wt %, whereas for SiO<sub>2</sub> the same error is 1.47 wt%,  $49.2 \pm 1.5$  wt %

No need for mistaken accuracy, the lecture starts at 8.30

**precision (reproducibility) versus accuracy (closeness to real number)**

H<sub>2</sub>O is the most common volatile constituent in rocks

H<sub>2</sub>O<sup>+</sup> - structural water – amphiboles and micas

H<sub>2</sub>O<sup>-</sup> - absorbed or trapped in grain boundaries

H<sub>2</sub>O<sup>-</sup> can be determined by heating the sample to 100 C and determining the weight loss –

**LOI – loss on ignition** – weight loss when the sample is heated to 800 C at which all H<sub>2</sub>O will be released.

Heating is done in two steps.

Analysis is good if total falls between 99.8 and 100.2 wt%

exception limestone analysis will indicate CaO 56%

**trace elements are not included in total**

### Major and minor elements in the crust

**TABLE 8.2** Estimated Relative Abundances of the Major Elements in the Continental Crust

Element	Wt. % Oxide	Atomic %
O		60.8
Si	59.3	21.2
Al	15.3	6.4
Fe	7.5	2.2
Ca	6.9	2.6
Mg	4.5	2.4
Na	2.8	1.9
K	2.2	1.0
Total	98.5	98.5

After Poldervaart (1955) and Ronov and Yaroshevsky (1976).

Eight elements (seven oxides) constitute 99% of the crust

Fe is the only element, which occurs in two valence states in the crust. Ferric/ferrous ration increases with increasing oxygen fugacity.

Ferric is concentrated in opaque phases (hematite Fe<sub>2</sub>O<sub>3</sub>, magnetite Fe<sub>3</sub>O<sub>4</sub>), so when the rock is oxidized, the mafic silicate content of the rock decreases.

Fe<sub>2</sub>O<sub>3</sub>, FeO, FeO<sup>\*</sup>

$\text{Fe}_2\text{O}_3$ , can be converted to FeO by multiplying with 0.8998, and vice versa by 1.1113.

**TABLE 8.3** Chemical Analyses of Some Representative Igneous Rocks

Oxide	Peridotite	Basalt	Andesite	Rhyolite	Phonolite
$\text{SiO}_2$	44.8	49.2	57.9	72.8	56.2
$\text{TiO}_2$	0.19	1.84	0.87	0.28	0.62
$\text{Al}_2\text{O}_3$	4.16	15.7	17.0	13.3	19.0
$\text{Fe}_2\text{O}_3$	1.36	3.79	3.27	1.48	2.79
FeO	6.85	7.13	4.04	1.11	2.03
MnO	0.11	0.20	0.14	0.06	0.17
MgO	39.2	6.73	3.33	0.39	1.07
CaO	2.42	9.47	6.79	1.14	2.72
$\text{Na}_2\text{O}$	0.22	2.91	3.48	3.55	7.79
$\text{K}_2\text{O}$	0.05	1.10	1.62	4.30	5.24
$\text{H}_2\text{O}^+$	0.0	0.95	0.83	1.10	1.57
Total	99.36	99.02	99.27	99.51	99.20

Peridotite: average for Lizard (Green, 1964); other averages from LeMaitre (1976a).

## Variation diagrams

to show systematic variation of igneous rocks in a **petrogenetic province**

### Bivariate plots

#### Harker diagram

$\text{SiO}_2$  against other oxides

example from Cascades recent volcanic rocks

shows certain smooth trends as well as scatter – natural variation, analytical error

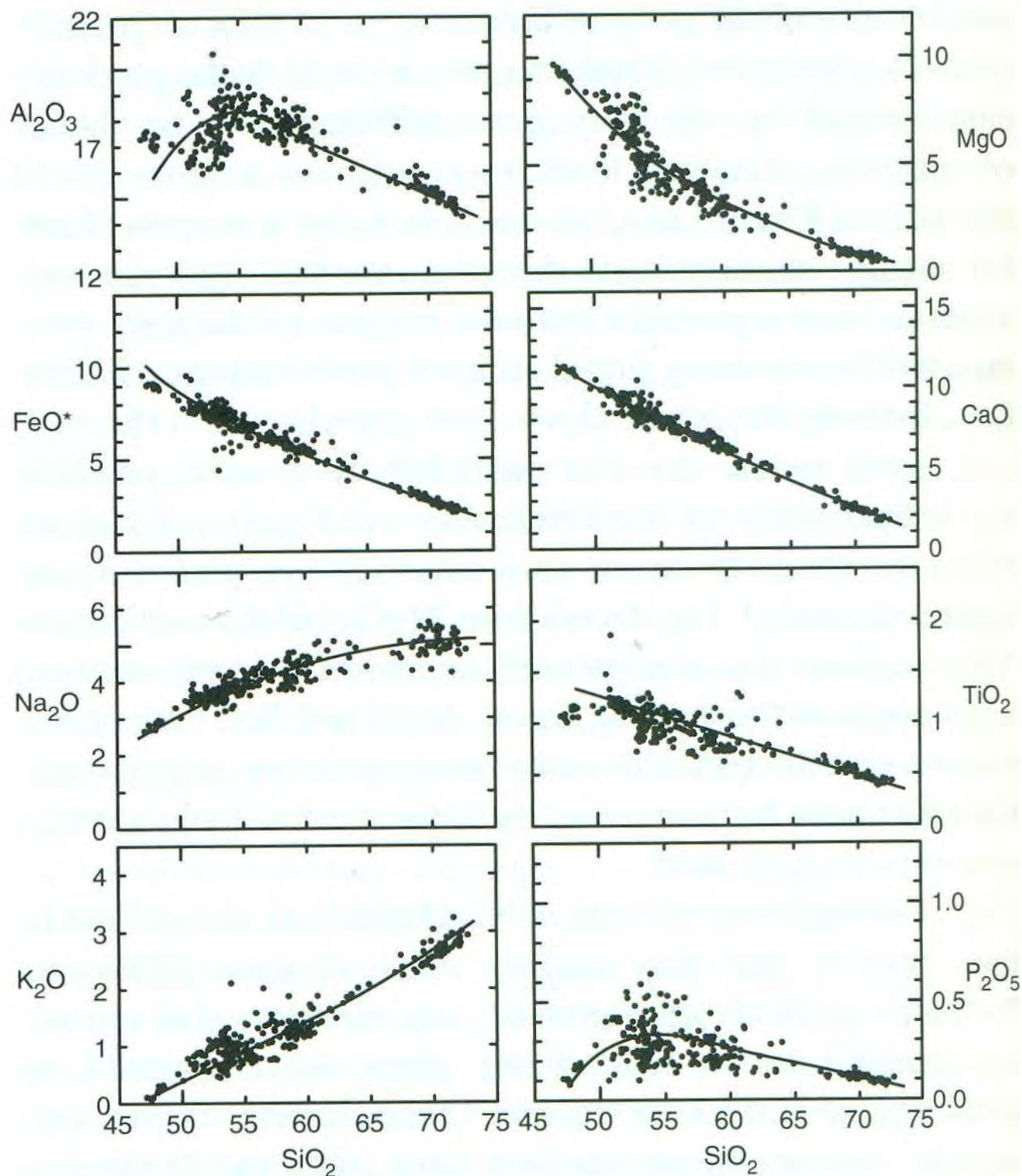
trends suggest that the magmas are related

**primary/primitive magma** – derived directly by partial melting of a source – no subsequent differentiation.

**evolved/derivative magma** – chemical differentiation

**parental magma** – most primitive magma found in a region

Harker (1909) suggested that  $\text{SiO}_2$  increased with magmatic evolution, thus the rock with the lowest  $\text{SiO}_2$  is regarded as the **parental magma** (not necessarily **primary magma**).



**FIGURE 8.2** Harker variation diagram for 310 analyzed volcanic rocks from Crater Lake (Mt. Mazama), Oregon Cascades. Data compiled by Rick Conrey (personal communication).

## Magmatic evolution (differentiation) can be caused by

crystal settling – fractional crystallization

mixing of two magmas

assimilation of the wall rocks

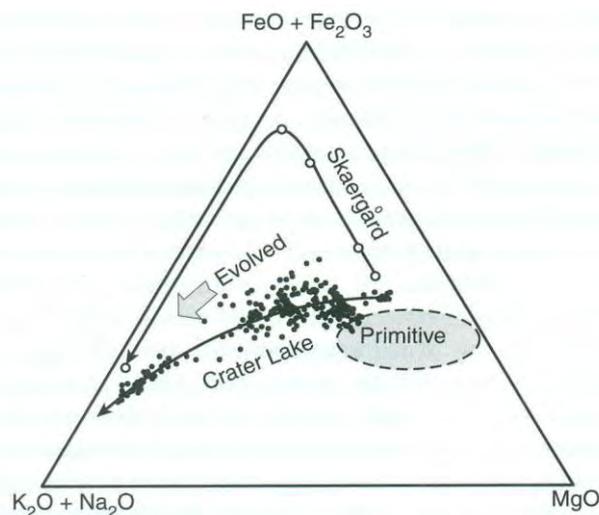
If crystal settling – fractional crystallization is assumed for the variation seen in Crater Lake than the changes in Mg, Fe, Ca can be explained by separation of olivine, pyroxene, calcic plagioclase from the magma.

The apparent increase in Na<sub>2</sub>O and K<sub>2</sub>O is an artifact of totaling the rock composition to 100 wt%.

Increase in Na<sub>2</sub>O and K<sub>2</sub>O in the diagrams shows that albite component in the plagioclase crystallized was low, and no K-feldspar crystallized.

Al<sub>2</sub>O<sub>3</sub> shows first increase then decrease – explanation pyroxene crystallized first followed by plagioclase.

## Triangular plots - AFM diagram



**FIGURE 8.3** AFM diagram for Crater Lake volcanics (data from Figure 8.2) and the Skaergård intrusion, eastern Greenland.

AFM diagrams are cast on wt%

In Fig. 8.3. two different trends are visible

Fractional crystallization depletes the melt in MgO and enriches in FeO – parental (primitive) magmas are closer to MgO corner.

Alkalis are enriched in evolved liquids and enter into solid phases only during the late stage crystallization.

## Magma series

A group of magmas that share some chemical characteristics and show a consistent pattern on variation diagrams

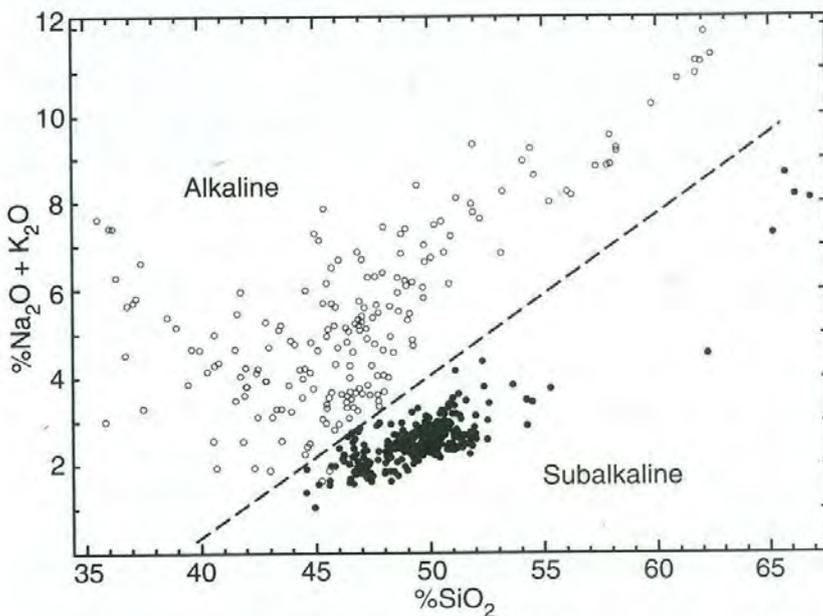
the most commonly used terms

alkali and subalkali series

subalkali series are divided into tholeiitic and calc-alkaline series

The alkali – subalkali division is based on alkali-silica diagram (see below for the Hawaii volcanic rocks)

The dividing line is by MacDonald (1968) and Irvine and Baragar (1971)



**FIGURE 8.11** Total alkalis versus silica diagram for the alkaline (open circles) and subalkaline rocks of Hawaii. After MacDonald (1968). Copyright © The Geological Society of America, Inc.

The alkali rocks are in general richer in alkalis and poorer in silica

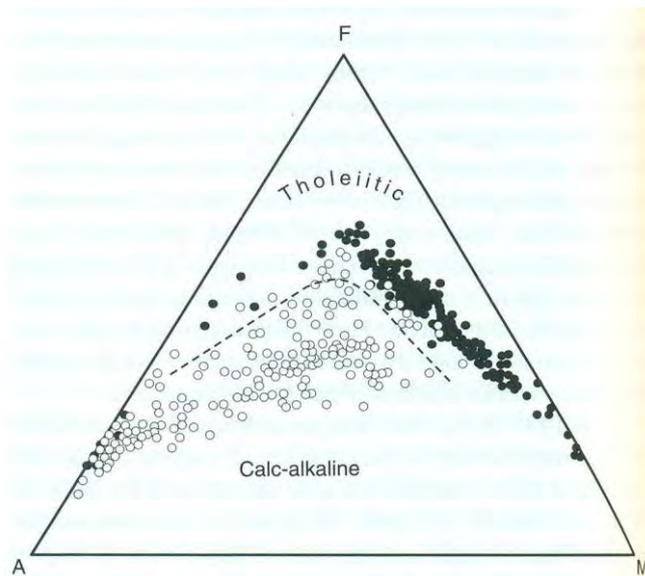
common evolutionary sequence in alkali series:

alkali olivine basalt → trachy basalt → trachyandesite → trachyte or phonolite

in subalkali series

basalt → andesite → dacite → rhyolite

The tholeiitic and calc-alkaline series cannot be distinguished on the alkali-silica diagram but plot on distinct fields in the AFM diagram.



**FIGURE 8.14** AFM diagram showing the distinction between selected tholeiitic rocks from Iceland, the Mid-Atlantic Ridge, the Columbia River Basalts, and Hawaii (solid circles) plus the calc-alkaline rocks of the Cascade volcanics (open circles). From Irving and Baragar (1971).

Each magma series is characterized by a particular parent basalt and shows a sequence of derivative magmas.

Correlation between the magma series and the tectonic setting

Characteristic Series	Plate Margin		Within Plate	
	Convergent	Divergent	Oceanic	Continental
Alkaline	yes	no	yes	yes
Tholeiitic	yes	yes	yes	yes
Calc-alkaline	yes	no	no	no

After Wilson (1989), p. 11.

calc-alkaline magmas are mostly restricted to subduction environments

divergent margins have only tholeiitic magmas

## Lecture 7

# Chemical Petrology

## Trace elements and isotopes

trace elements are far more sensitive to magmatic fractionation than major elements because different phases incorporate or exclude trace elements with much greater selectivity than major elements.

Most useful trace elements

transition metals – Sc, Ti, V, Cr, Mn, Co; Ni, Cu and Zn

REE

Rb, Sr, Y, Zr, Nb, Cs, Ba, Hf, Ta, Pb, Th and U.

### Element distribution

Goldschmidt rules

1. Two ions with the same radius and valence should enter into solid solution in amounts proportional to their concentration

Rb has similar ionic radius as K, should enter K-feldspars, micas, evolved melts

Ni should behave like Mg and should enter olivine and in the early formed crystals.

2. If two ions have a similar radius and the same valence, the smaller ion is preferentially incorporated into solid over liquid. Because Mg has smaller radius than Fe, it enters the solid (olivine) preferentially.

3. If two ions have similar radius but different valence, the ion with the higher charge is preferentially incorporated into solid over the liquid. Thus  $\text{Cr}^{3+}$  and  $\text{Ti}^{4+}$  are always preferred in solids as compared to liquids.

### Chemical fractionation

Uneven distribution of elements between phases

e.g., Ca/Na is always greater in plagioclase than the coexisting melt, Mg/Fe ditto in olivine.

Distribution coefficient (partition coefficient) D

$$D (K_D) = C_S/C_L$$

$C_S$  = concentration of trace element in solid (in ppm or wt%)

$C_L$  = same in liquid

The Table below shows the extensive fractionation shown by the trace elements (that is why there are petrogenetically so useful).

**TABLE 9.1** Partition Coefficients ( $C_S/C_L$ ) for Some Commonly Used Trace Elements in Basaltic and Andesitic Rocks

	Olivine	Opx	Cpx	Garnet	Plag	Amph	Magnetite
Rb	0.010	0.022	0.031	0.042	0.071	0.29	
Sr	0.014	0.040	0.060	0.012	1.830	0.46	
Ba	0.010	0.013	0.026	0.023	0.23	0.42	
Ni	<i>14</i>	<i>5</i>	<i>7</i>	0.955	<i>0.01</i>	6.8	29
Cr	0.70	10	34	1.345	0.01	2.00	7.4
La	0.007	0.03	0.056	0.001	0.148	0.544	2
Ce	0.006	0.02	0.092	0.007	0.082	0.843	2
Nd	0.006	0.03	0.230	0.026	0.055	1.340	2
Sm	0.007	0.05	0.445	0.102	0.039	1.804	1
Eu	0.007	0.05	0.474	0.243	0.1/1.5*	1.557	1
Dy	0.013	0.15	0.582	3.17	0.023	2.024	1
Er	0.026	0.23	0.583	6.56	0.020	1.740	1.5
Yb	0.049	0.34	0.542	11.5	0.023	1.642	1.4
Lu	0.045	0.42	0.506	11.9	0.019	1.563	

Data from Rollinson (1993) and <http://earthref.org>

\*Eu<sup>3+</sup>/Eu<sup>2+</sup>

*Italics indicate estimates.*

The partition coefficients in Table 9.1 are approximations because  $K_D$  varies by melt composition (considerably)

temperature

pressure (slightly)

Major elements do not fractionate extremely;  $K_D$  values of major elements are between 0.1 – 10, whereas for trace elements in garnet ranges from 0.001 to 11.9.

Trace elements are sensitive to distribution and fractionation processes.

**incompatible trace elements** are concentrated in the melt  $K_D \ll 1$ , for example Rb, Ba, K, Na for major elements

**compatible trace elements** concentrate in solids  $K_D \gg 1$ , e.g., Ni, Cr, Mg, Fe for major elements

Incompatible elements are subdivided into two groups based on the ratio of valence/ionic radius

### **high field strength elements (HFS)**

REE, Th, U, Ce,  $Pb^{4+}$ , Zr, Hf, Ti, Nb and Ta

the low-field strength **large ion lithophile (LIL)** elements (lithophile – preferring a silicate phase as opposed to chalcophile – preferring a sulphide phase)

K, Rb, Cs, Ba,  $Pb^{2+}$ , Sr and  $Eu^{2+}$

LIL elements are considered more mobile

### **bulk distribution coefficient $D_i$**

$$D_i = \sum W_A D_i^A$$

where  $W_A$  is the weight fraction of mineral A in the rock and  $D_i^A$  distribution coefficient for the element i in mineral A.

For example if we consider a garnet lherzolite with 69% olivine, 25% opx, 10% cpx and 5% garnet (all by weight) that  $D_i$  for erbium is

$$\begin{aligned} D_{Er} &= 0.6 * 0.026 + 0.25 * 0.23 + 0.10 * 0.583 + 0.05 * 6.56 \\ &= 0.459 \end{aligned}$$

high  $K_D$  for garnet affect the bulk distribution coefficient significantly.

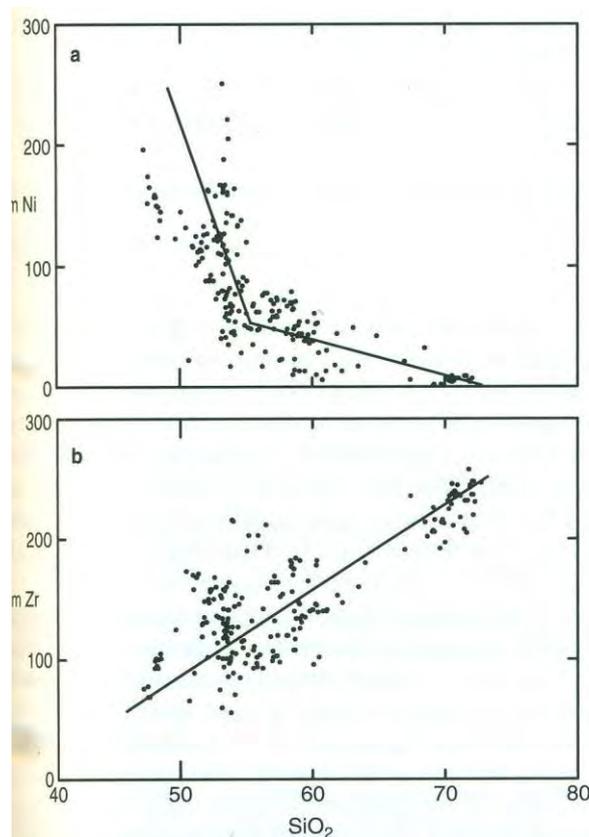
During the partial melting of this garnet-lherzolite, incompatible elements like Rb ( $D_{Rb} = 0.016$ ), Sr ( $D_{Sr} = 0.25$ ), Ba ( $D_{Ba} = 0.08$ ) and the REE will be concentrated in the

melt, whereas Ni ( $D_{Ni}=10.4$ ) and Cr ( $D_{Cr}=6.39$ ) will remain in the solid peridotite residua.

Because of higher fractionations (higher values of  $K_D$ ) trace elements provide a better measure of partial melting and crystallization than the major elements.

Moreover trace elements are preferentially concentrated in a single phase, e.g. Ni in olivine and will give a measure of the mineral that has fractionated.

The abrupt change in Ni in the diagram below indicates the end of olivine fractionation. Note also that the value of Ni changes from 250 ppm down to 0 ppm, two orders of magnitude – compare this with change in MgO.



**FIGURE 9.1** Harker diagrams of (a) Ni versus  $SiO_2$  and (b) Zr versus  $SiO_2$  for the Crater Lake suite of volcanic rocks in Figure 8.2.

## Models for solid-melt processes

### Batch melting model

Melt remains in equilibrium with the solid, until at some point, the melt is released and moves upward as an independent system.

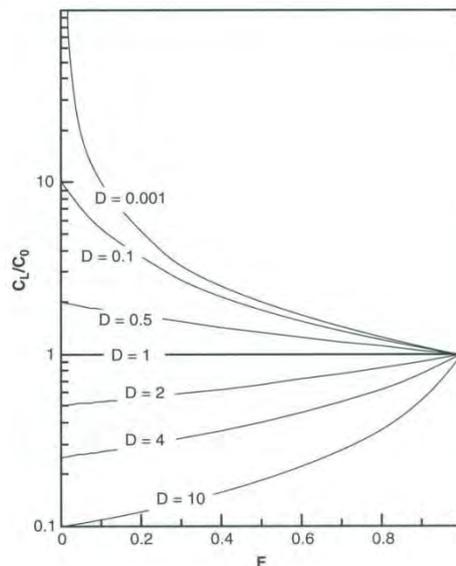
$$C_L/C_0 = 1/(D_i(1-F) + F) \quad (9.5)$$

$C_0$  = concentration of trace element in the original rock before melting

$C_L$  = concentration of trace element in the melt

$F$  = weight fraction of melt produced (melt/(melt+rock))

$D_i$  = bulk distribution coefficient



**FIGURE 9.2** Variation in the relative concentration of a trace element in a liquid versus source rock as a function of  $\bar{D}$  and the fraction melted, using Equation (9.5) for equilibrium batch melting.

Melt fraction more than 0.4 is unlikely for batch melting in the mantle.

The Figure shows that highly incompatible elements are highly concentrated in initial small melt fraction – dilution as melting proceeds.

as  $F \rightarrow 1$   $C_L/C_0 = 1$

as  $F \rightarrow 0$   $C_L/C_0 = 1/D_i$

If we know the concentration of a trace element in magma ( $C_L$ ) derived by a small degree of batch melting, and we know  $D_i$ , we can estimate the concentration of the element in the source region ( $C_0$ ).

## Rare Earth Elements

Also called lanthanide series

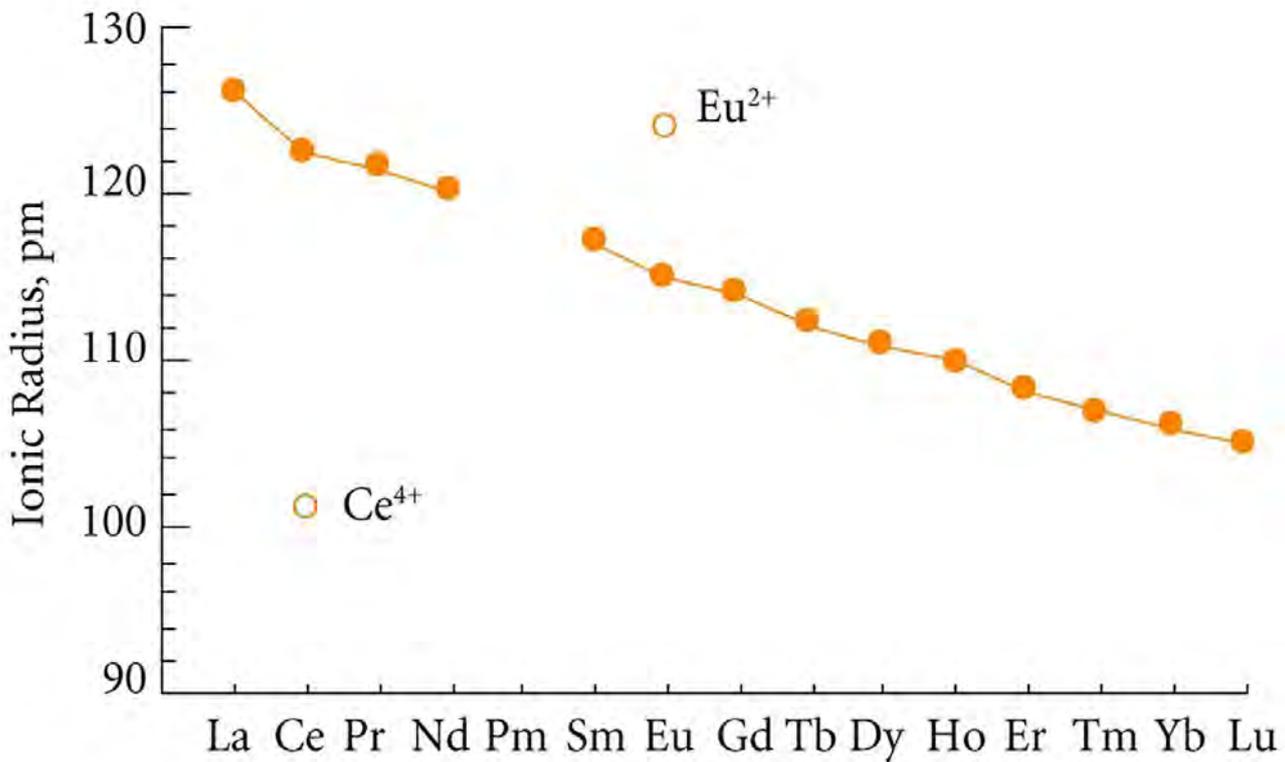
from lanthanum to lutetium, 15 elements (atomic numbers 57-71)

**La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu**

all have similar chemical and physical properties

all have 3+ oxidation state

their ionic radius decreases with increasing atomic number (lanthanide contraction); this results in the heavier REE to be more compatible.



**TABLE 9.1** Partition Coefficients ( $C_S/C_L$ ) for Some Commonly Used Trace Elements in Basaltic and Andesitic Rocks

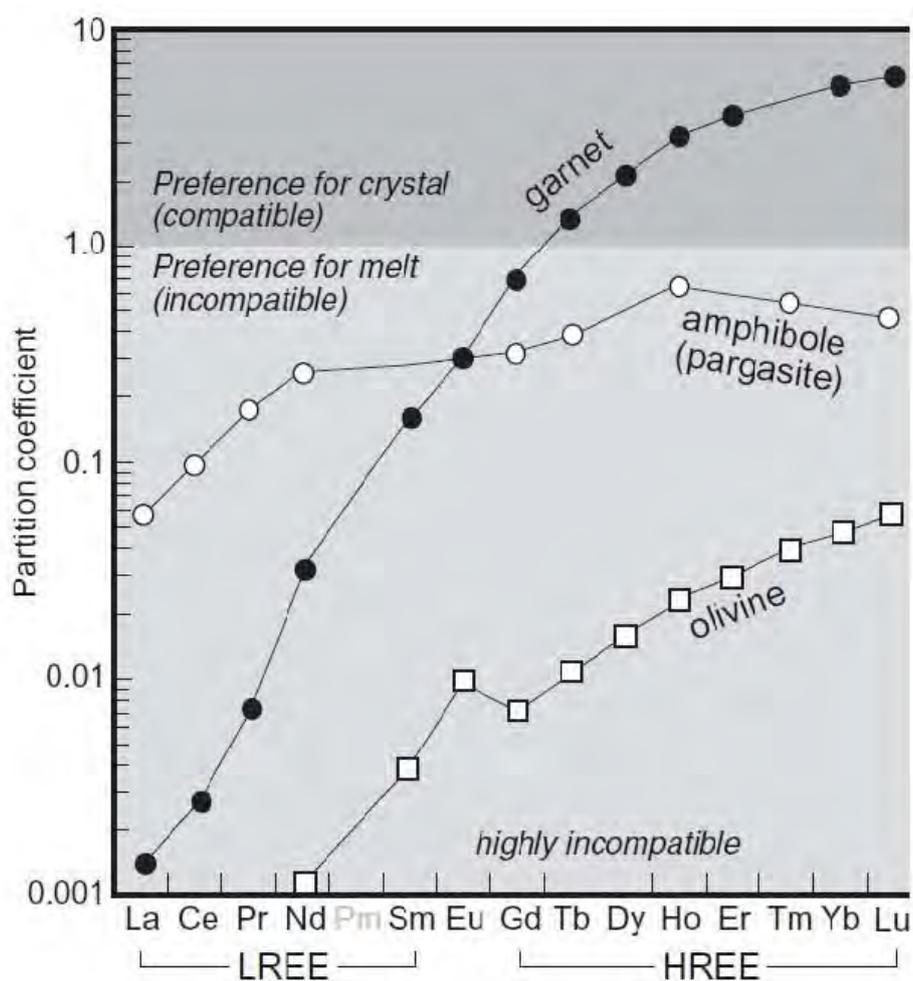
	Olivine	Opx	Cpx	Garnet	Plag	Amph	Magnetite
Rb	0.010	0.022	0.031	0.042	0.071	0.29	
Sr	0.014	0.040	0.060	0.012	1.830	0.46	
Ba	0.010	0.013	0.026	0.023	0.23	0.42	
Ni	<i>14</i>	5	7	0.955	<i>0.01</i>	6.8	29
Cr	0.70	10	34	1.345	0.01	2.00	7.4
La	0.007	0.03	0.056	0.001	0.148	0.544	2
Ce	0.006	0.02	0.092	0.007	0.082	0.843	2
Nd	0.006	0.03	0.230	0.026	0.055	1.340	2
Sm	0.007	0.05	0.445	0.102	0.039	1.804	1
Eu	0.007	0.05	0.474	0.243	0.1/1.5*	1.557	1
Dy	0.013	0.15	0.582	3.17	0.023	2.024	1
Er	0.026	0.23	0.583	6.56	0.020	1.740	1.5
Yb	0.049	0.34	0.542	11.5	0.023	1.642	1.4
Lu	0.045	0.42	0.506	11.9	0.019	1.563	

Data from Rollinson (1993) and <http://earthref.org>

\* $\text{Eu}^{3+}/\text{Eu}^{2+}$

*Italics indicate estimates.*

mineral specific fractionation among otherwise similar elements, e.g. garnet strongly favors heavy REE, plagioclase is insensitive to ionic radius – little fractionation except for Eu.



The exception for 3+ rule is Eu, which commonly occurs as  $\text{Eu}^{2+}$  and substitutes for Ca in plagioclase (but not in cpx). Thus D for  $\text{Eu}^{2+}$  for plagioclase is very high.

Not all 15 RRE are determined but 9-10 is sufficient to show the trend.

REE are shown by normalizing it to a standard

two common standards are

primordial mantle

chondrite meteorite

## Meteorites

considered as samples from early solar system

three types irons, stony-irons and stones

iron meteorites are differentiated

stones are subdivided into chondrites and achondrites

chondrules are spherical silicate inclusions, 0.1-3.0 mm in diameter. They are considered as glass droplets that have crystallized to silicate minerals (olivine, opx, glass..)

**TABLE 1.1** Simplified Classification of Meteorites

Class	Subclass	# of Falls	% of Falls
Irons	All	42	5
Stony-irons	All	9	1
Stones	Achondrites		
	SNC's	4	8
	Others	65	
Chondrites	Carbonaceous	35	86
	Others	677	

After Sears and Dodd (1988).

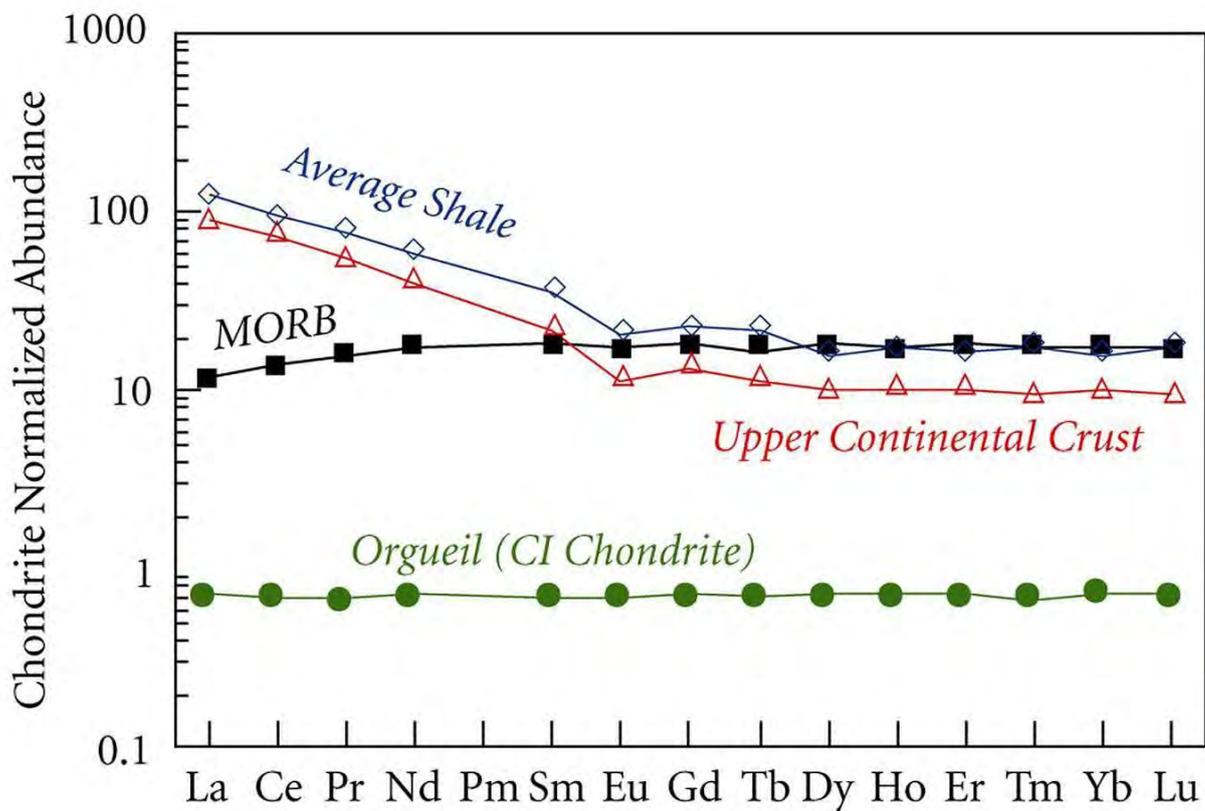
Chondrites are not differentiated (because otherwise chondrules will disappear) and are considered as closest to solar nebula.

It has been suggested that all inner planets have formed from a material of chondrite composition – Chondritic Earth Model (CEM).

**TABLE 9.4** Concentration of Selected REE in C-1 Chondrite Meteorites (in ppm)

Element	Z	Chondrite
La	57	0.237
Ce	58	0.612
Nd	60	0.467
Sm	62	0.153
Eu	63	0.058
Dy	66	0.254
Er	68	0.1655
Yb	70	0.170
Lu	71	0.0254

Data from Sun and McDonough (1989).



### Normalized multi-element diagrams

spider diagrams – spidergrams

involves also other elements Sr, Rb, K, Ba etc.

### Applications of trace elements to igneous systems

extend of partial melting

extend of fractional crystallization

identification of host rock

REE can be used to distinguish between high and low-pressure melting. At depths of over 70 km garnet and cpx are residual phases and melts (up to 10%) will be highly depleted in heavy REE (HREE)

At depths of lower than 40 km plagioclase is an important residual phase and can be detected by Eu anomaly in the melt.

**TABLE 9.6 A Brief Summary of Some Particularly Useful Trace Elements in Igneous Petrology**

Element	Use as a Petrogenetic Indicator
Ni, Co, Cr	Highly compatible elements. Ni and Co are concentrated in olivine, and Cr is concentrated in spinel and clinopyroxene. High concentrations indicate a mantle source, limited fractionation, or crystal accumulation.
Zr, Hf	Very incompatible elements that do not substitute into major silicate phases (although they may replace Ti in titanite or rutile). High concentrations imply an enriched source or extensive liquid evolution.
Nb, Ta	High-field-strength elements that partition into Ti-rich phases (titanite, Ti-amphibole, Fe-Ti oxides). Typically low concentrations in subduction-related melts.
Ru, Rh, Pd, Re, Os, Ir, Pd	Platinum group elements (PGEs) that are siderophile and used mostly to study melting and crystallization in mafic-ultramafic systems in which PGEs are typically hosted by sulfides. The Re/Os isotopic system is controlled by initial PGE differentiation and is applied to mantle evolution and mafic melt processes.
Sc	Concentrates in pyroxenes and may be used as an indicator of pyroxene fractionation.
Sr	Substitutes for Ca in plagioclase (but not in pyroxene), and, to a lesser extent, for K in K-feldspar. Behaves as a compatible element at low pressure, where plagioclase forms early, but as an incompatible element at higher pressure, where plagioclase is no longer stable.
REE	Myriad uses in modeling source characteristics and liquid evolution. Garnet accommodates the HREE more than the LREE, and orthopyroxene and hornblende do so to a lesser degree. Titanite and plagioclase accommodate more LREE. $\text{Eu}^{2+}$ is strongly partitioned into plagioclase.
Y	Commonly incompatible. Strongly partitioned into garnet and amphibole. Titanite and apatite also concentrate Y, so the presence of these as accessories could have a significant effect.

## Tectonic discrimination diagrams

trace elements correlate with particular tectonic settings such as

CAB – calc-alkaline basalts

MORB – mid-ocean ridge basalts

IAB – island arc basalts

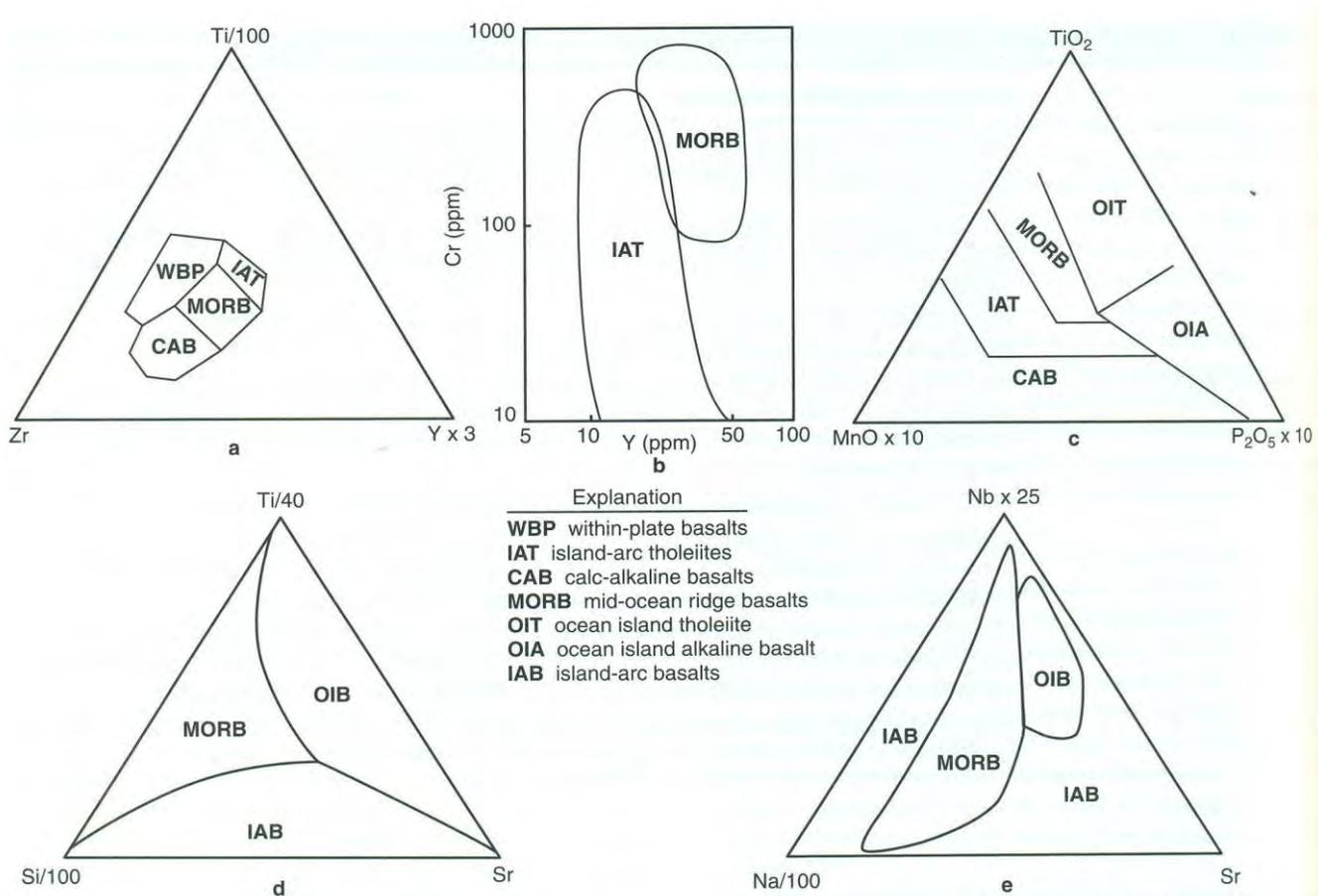
IAT – island arc tholeiites

OIT – ocean island tholeiite

OIA – ocean island alkaline basalt

WPB – within-plate basalts

empirical diagrams



**FIGURE 9.8** Examples of discrimination diagrams used to infer tectonic setting of ancient (meta-) volcanics. (a) After Pearce and Cann (1973), (b) after Pearce (1982), Coish et al. (1986). Reprinted by permission of the *American Journal of Science*, (c) after Mullen (1983) Copyright © with permission from Elsevier Science, (d) and (e) after Vermeesch (2005) © American Geophysical Union with permission.

used in determining the tectonic setting of metamorphosed, deformed old magmatic rocks

the usage and results are ambiguous because several factors affect the magma chemistry

extent of partial melting

fractional crystallization

magma mixing

wall-rock assimilation

metamorphism,

metasomatism

use mafic volcanic rocks to eliminate the first four factors

use elements considered immobile in metamorphism (usually Ti, Cr, Zr, Hf and Y)

rocks may plot in contradictory fields in different diagrams

## Lecture 8

### Isotopes

Atom consists of protons, neutrons and electrons.

Protons and neutrons are located in the nucleus, which makes up the bulk of the mass of an atom.

mass of a proton	1832	electrical charge positive
mass of a neutron	1833	no electrical charge
mass of an electron	1	electrical charge negative

The physical and chemical features of an atom is determined by the number of protons in the nucleus by the atomic number, e.g.,  ${}_{19}\text{K}$ .

The mass number is the number of protons plus neutrons in an atom, e.g.,  ${}^{40}\text{K}$

Isotopes are variants of the same element differentiated by different number of neutrons.

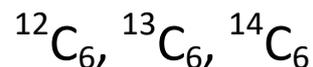
All atoms with 6 protons are carbon, 7 are nitrogen – however the number of neutrons in the nucleus may change without affecting the chemical characteristics of the element except its mass.



6 is the atomic number - number of protons in the nucleus

12 is the mass number – number of protons plus neutrons

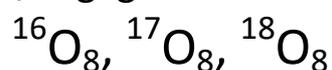
Three natural carbon isotopes are



atomic mass of C is 12.01

${}^{12}\text{C}_6$  – 98.93% of natural carbon

${}^{13}\text{C}_6$  – 1.07% of natural carbon,  ${}^{14}\text{C}_6$  negligible



${}^{16}\text{O}_8$  – 99.76 % of natural oxygen

${}^{17}\text{O}_8$  – 0.04 % of natural oxygen

${}^{18}\text{O}_8$  – 0.20 % of natural oxygen

Most commonly used isotopes: H, C, O, S, K, Ar, Rb, Sr, U, Pb, Th, Sm and Nd

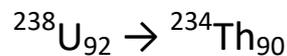
**Stable isotopes** – remain indefinitely

**Unstable or radioactive isotopes** – unstable, undergone radioactive decay to produce another nuclide (element) plus a particle (alpha  ${}^4\text{He}_2$  or beta – electron) or gamma ray and energy.

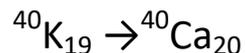
## Radioactive decay

three ways

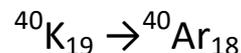
1. Ejection of  $\alpha$  particles from the nucleus –  $\alpha$  particles are the nucleus of helium atom  ${}^4\text{He}_2$



2. Ejection of  $\beta$  particles (electrons from the nucleus), so that a neutron becomes a proton and the atomic number increases.



3. Capture of  $\beta$  particles (electrons), proton turns into a neutron, and the atomic number decreases.



During radioactive decay  $\gamma$ -rays are also produced – high-energy electro-magnetic rays.

## Three types of radioactive decay



branched decay  ${}^{40}\text{K}_{19}$  decays either  ${}^{40}\text{Ar}_{18}$  or to  ${}^{40}\text{Ca}_{20}$ . 12% decays to Ar, 88% to Ca.

## parent – daughter isotopes

daughter isotopes are called radiogenic isotopes

**nuclear fission** - a parent isotope produces two daughter isotopes

the decay is specific for the radioactive isotope

${}^{24}\text{Na}_{11}$  created in nuclear reactors lasts only a few days or weeks; its half-life is 15 hours

${}^{238}\text{U}_{92}$  has a long half-life (4 468 million years) about half of the Earth's original  ${}^{238}\text{U}_{92}$  has decayed so far.

According to the theory of radioactive decay – the rate of decay is proportional to the number of parent atoms existing at that time

$$-dN/dt \propto N \quad \text{or}$$

$$-dN/dt = \lambda N$$

where

$N$  = number of parent atoms

$t$  = time

$\lambda$  = decay constant

$dN/dt$  = change in  $N$  w.r.t. time, or rate of decay at a particular time.

We can rearrange and integrate this equation to

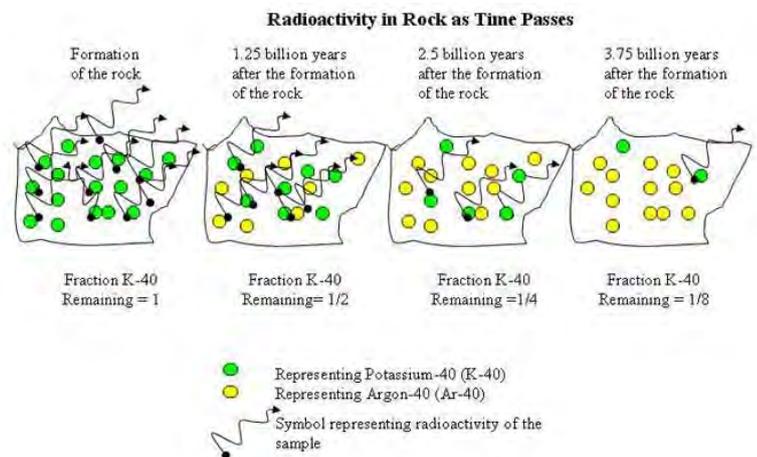
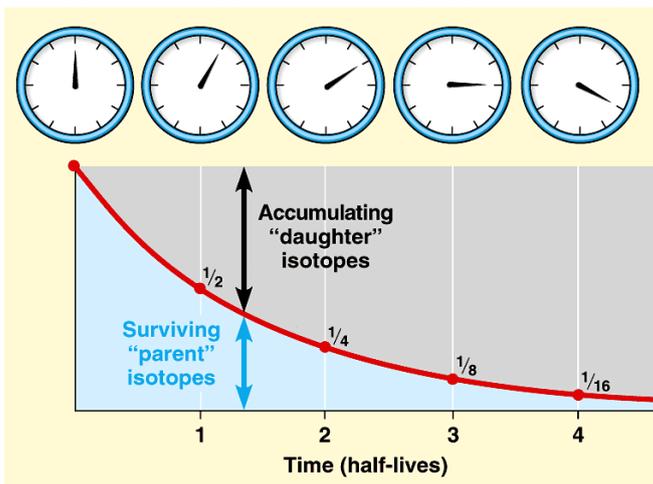
$$N/N_0 = e^{-\lambda t} \quad (8.1)$$

where

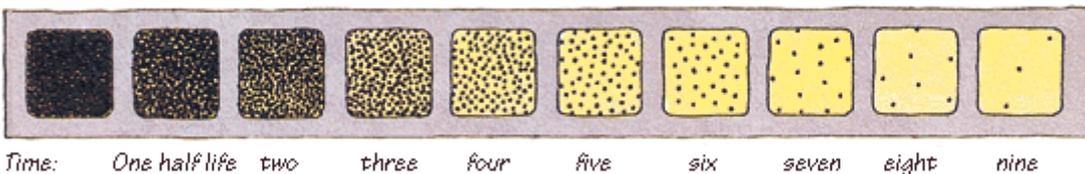
$N_0$  = original number of radioactive atoms

$N$  = number of atoms after some time  $t$  (in years) has passed

$t_{1/2}$  – **half-life** – time required for half of the unstable atoms to decay.



Decay rate of radioactivity: After ten half lives, the level of radiation is reduced to one thousandth



We can substitute  $t_{1/2}$  into the equation (8.1):

$$1/2 N_0 = N_0 e^{-\lambda t_{1/2}}$$

$$1/2 = e^{-\lambda t_{1/2}}$$

$$\begin{aligned} \ln 1/2 &= -\lambda t_{1/2} \\ \ln 2 &= \lambda t_{1/2} \\ t_{1/2} &= \mathbf{0.693 / \lambda} \quad (8.2) \end{aligned}$$

some radioactive half-times

$^{14}\text{C} \rightarrow ^{14}\text{N}$	5730 years
$^{238}\text{U} \rightarrow ^{206}\text{Pb}$	4400 million years
$^{40}\text{K} \rightarrow ^{40}\text{Ar}$	11 930 million years
$^{87}\text{Rb} \rightarrow ^{87}\text{Sr}$	48 800 million years
$^{147}\text{Sm} \rightarrow ^{143}\text{Nd}$	106 000 million years
$^{176}\text{Lu} \rightarrow ^{176}\text{Hf}$	35 700 million years

In order to calculate the age of the rock, we have to know the initial number of radioactive parent atoms. We can determine this number from the radiogenic daughter isotopes produced, because:

$$\begin{aligned} D^* &= N_0 - N \\ D^* &= N e^{\lambda t} - N \\ \mathbf{D^*} &= \mathbf{N(e^{\lambda t} - 1)} \quad (8.3) \end{aligned}$$

Thus we need to know the amount of remaining parent, the amount of daughter produced and the decay constant  $\lambda$  to calculate the age of the rock.

The main problem is to distinguish between radiogenic daughter isotopes and the same isotopes which are not a product of radioactive decay.

The age range of the radiometric dating techniques determined by the half-life of the radioactive element:

**TABLE 22.2** Half-lives of Some Useful Radioisotopes

Radioisotope	Symbol	Radiation	Half-life	Use
Tritium	${}^3_1\text{H}$	$\beta^-$	12.33 years	Biochemical tracer
Carbon-14	${}^{14}_6\text{C}$	$\beta^-$	5730 years	Archaeological dating
Phosphorus-32	${}^{32}_{15}\text{P}$	$\beta^-$	14.26 days	Leukemia therapy
Potassium-40	${}^{40}_{19}\text{K}$	$\beta^-$	$1.28 \times 10^9$ years	Geological dating
Cobalt-60	${}^{60}_{27}\text{Co}$	$\beta^-, \gamma$	5.27 years	Cancer therapy
Technetium-99m <sup>+</sup>	${}^{99\text{m}}_{43}\text{Tc}$	$\gamma$	6.01 hours	Brain scans
Iodine-123	${}^{123}_{53}\text{I}$	$\gamma$	13.27 hours	Thyroid therapy
Uranium-235	${}^{235}_{92}\text{U}$	$\alpha, \gamma$	$7.04 \times 10^8$ years	Nuclear reactors

\*The m in technetium-99m stands for metastable, meaning that it undergoes gamma emission but does not change its mass number or atomic number.

## K-Ar system

Three isotopes of K

stable  $^{39}\text{K}$  (93.3%)

unstable  $^{40}\text{K}$  (6.7%)

stable  $^{41}\text{K}$  (0.012%).

$^{40}\text{K}$  decays to stable  $^{40}\text{Ar}$  (10.72% of the decays) by electron capture and to  $^{40}\text{Ca}$  by beta decay (89.28%).

branching decay

The ratio of electron captures to beta decays is called branching ration R

$$R = \lambda_e / \lambda_\beta$$

$$\lambda_e = 0.581 \times 10^{-10}$$

$$\lambda_\beta = 4.962 \times 10^{-10}$$

The total decay constant for  $^{40}\text{K}$  is

$$\lambda = \lambda_e + \lambda_\beta = 5.543 \times 10^{-10}$$

Ar is a gas – no problem with inherent Ar in the rock.

$$^{40}\text{Ar} = ^{40}\text{Ar}_0 + (\lambda_e / \lambda) ^{40}\text{K} (e^{\lambda t} - 1)$$

where  $^{40}\text{Ar}_0 = 0$

$$t = 1/\lambda \ln ((^{40}\text{Ar}^* / ^{40}\text{K} \times \lambda / \lambda_e) + 1)$$

## Closure temperature (Blocking temperature)

Temperature at which a system has cooled so that there is no longer any significant diffusion of parent and daughter isotopes out of the system. For example, the temperature, when argon gas is started to be retained in biotite - 300° C.

Closure temperatures

zircon U-Pb

>750° C

hornblende Ar-Ar	530 ± 40° C
muscovite Ar-Ar	~350° C
biotite Ar-Ar	280 ± 40° C
muscovite Rb-Sr	~500° C
biotite Rb-Sr	~320° C
zircon fission track	175-225° C
apatite fission track	105 ± 10° C
apatite U-Th/He	~70° C

Blocking temperature is influenced by cooling rate and crystal size.

## The Rb-Sr system

Four Sr isotopes

$^{88}\text{Sr}$  :  $^{87}\text{Sr}$  :  $^{86}\text{Sr}$  :  $^{84}\text{Sr}$  in ratios of 10 : 0.7 : 1 : 0.07

$^{87}\text{Sr}$  is created by the breakdown of  $^{87}\text{Rb}$

$^{87}\text{Rb} \rightarrow ^{87}\text{Sr} + \text{a beta particle} - \lambda = 1.42 \cdot 10^{-11} \text{ a}^{-1}$

$^{86}\text{Sr}$  is a stable isotope

Rb behaves like K – concentrates in micas, amphiboles and to a lesser extent in K-feldspar

Sr behaves like Ca concentrates in plagioclase and apatite not in cpx.

total  $^{87}\text{Sr}$  in a rock = radiogenic  $^{87}\text{Sr}$  +  $^{87}\text{Sr}$  already in the rock

To separate the two, one uses the isochron technique utilizing two or more samples.

$^{86}\text{Sr}$  is not radiogenic and the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio at the time of crystallization is the same in all minerals in a rock (no fractionation).

The amount of  $^{87}\text{Sr}$  and thus the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio will increase in the minerals which have Rb but will stay as it is in minerals free of Rb.

If we divide equation 8.3 by  $^{86}\text{Sr}$ :

$$D^* = N(e^{\lambda t} - 1)$$

$$^{87}\text{Sr}/^{86}\text{Sr} = (^{87}\text{Sr}/^{86}\text{Sr})_0 + (^{87}\text{Rb}/^{86}\text{Sr})(e^{\lambda t} - 1)$$

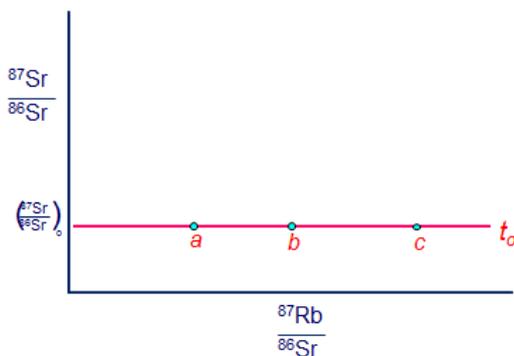
$\lambda$  for the Rb-Sr system is  $1.42 \cdot 10^{-11} \text{ a}^{-1}$ . For values of  $\lambda t$  less than 0.1,  $(e^{\lambda t} - 1) = \text{approx. } \lambda t$

Thus for ages less than 70 Ga

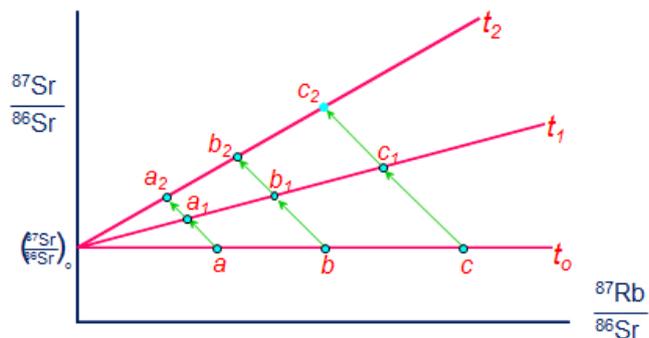
$$^{87}\text{Sr}/^{86}\text{Sr} = (^{87}\text{Sr}/^{86}\text{Sr})_0 + (^{87}\text{Rb}/^{86}\text{Sr})\lambda t$$

This is the equation of a straight line ( $y = b + mx$ ) in a  $^{87}\text{Rb}/^{86}\text{Sr}$  versus  $^{87}\text{Sr}/^{86}\text{Sr}$  plot and the slope gives the age.

Begin with 3 rocks plotting at a b c at time  $t_0$



At time  $t_2$  each rock system has evolved  $\rightarrow$  new line  
Again still linear and steeper line



a, b, c could be three different minerals in a rock or three rocks from an intrusion.  
 $t_0$  is the time when the rocks and minerals have crystallized.

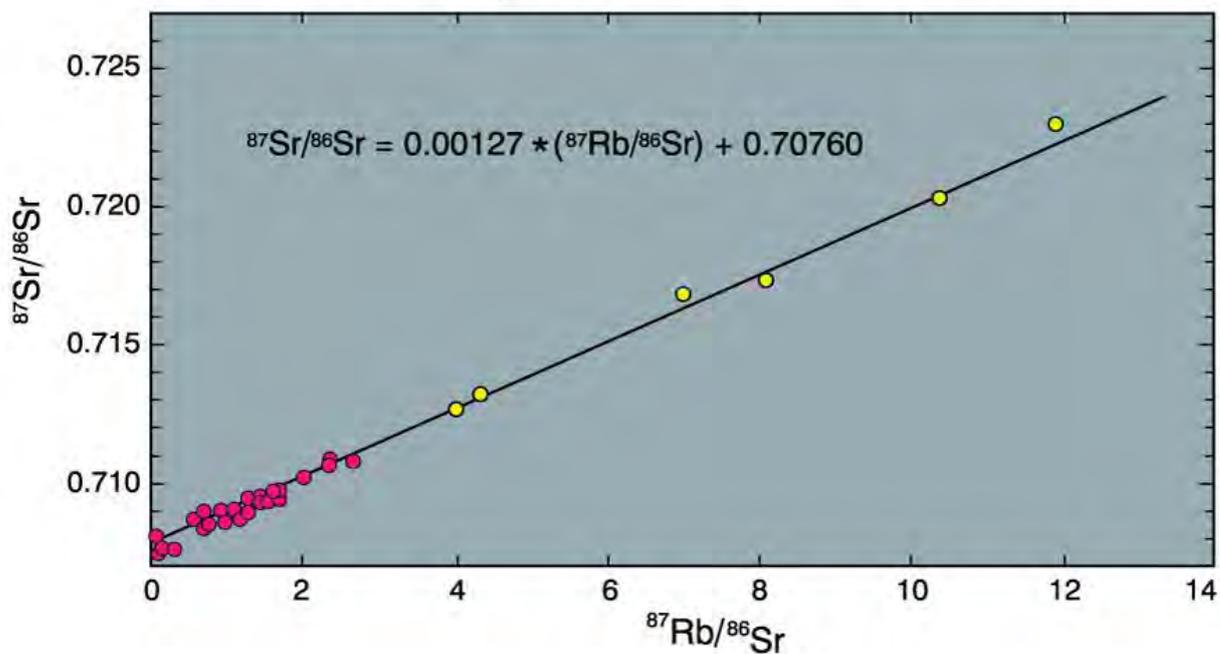
The isochron will give us two pieces of information:

1. the age of the rock from the slope of the isochron and the decay constant  $\lambda$ .
2. The original  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio  $(^{87}\text{Sr}/^{86}\text{Sr})_0$  at the time of crystallization, as well as the solid source of the melts (since Sr isotopes do not fractionate)

Example of Rb-Sr isochron on whole rock and hornblende from the Eagle Creek Pluton from the Sierra Nevada batholith.

The data fall on a slope, which give an age of 91 Ma.

### Rb-Sr Isochron, Eagle Peak Pluton, Sierra Nevada Batholith



Rb-Sr isochron for the Eagle Peak Pluton, Central Sierra Nevada Batholith, California, USA. Filled circles are whole-rock analyses, open circles are hornblende separates. After Hill et al. (1988). *Amer. J. Sci.*, 288-A, 213-241.

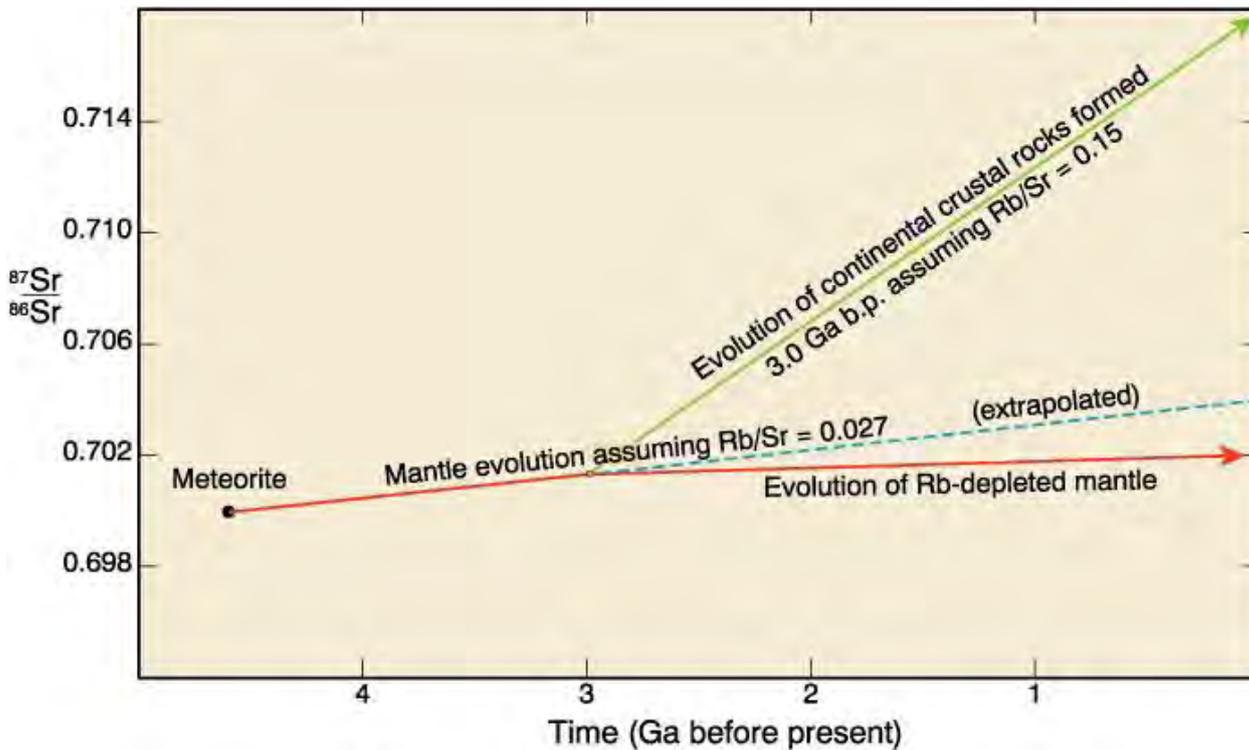
### Initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio

Model for the long-term Sr isotopic evolution of the mantle.

$^{87}\text{Sr}/^{86}\text{Sr}$  value at 4.6 Ga was about 0.699 and since then has slowly increased because of the small quantity of Rb in the mantle.

If at any time the mantle melts to form continental crust, Rb will fractionate into the melt.

Figure below shows a hypothetical melting at 3.0 Ga, after this event the mantle growth curve will have a lower slope because Rb has gone to the melt, whereas the crustal growth curve will have a higher slope.



Estimated Rb and Sr isotopic evolution of the Earth's upper mantle, assuming a large-scale melting event producing granitic-type continental rocks at 3.0 Ga b.p. After Wilson (1989).

The extrapolated original mantle growth curve evolves to a modern mantle with  $^{87}\text{Sr}/^{86}\text{Sr}$  value of 0.704. The present day residual upper mantle has  $^{87}\text{Sr}/^{86}\text{Sr}$  values of 0.703.

With the initial ratio one can tell whether the melt comes from the mantle or from the crust.

As a general rule

Initial  $^{87}\text{Sr}/^{86}\text{Sr}$  value less than 0.706 mantle origin, more of crustal origin or contaminated by crust.

Eagle Creek pluton has  $(^{87}\text{Sr}/^{86}\text{Sr})_0$  of 0.7076 indicating involvement of crustal components.



## Phase rule

### System

a portion of the universe that we want to study, e.g. water in a beaker

open system – energy and matter can be transferred

closed system – only energy can exchange

isolated – system neither energy nor matter can be transferred.

parameters of the system – T, P, composition, mass, density etc. – not all independent

### Phase

physically distinct material, mineral, liquid, gas...

### Component

chemical constituent, SiO<sub>2</sub>, O<sub>2</sub>, Si, H<sub>2</sub>O, NaAlSi<sub>3</sub>O<sub>8</sub>

For the purposes of the phase rule the components are defined as the minimum number of chemical species to completely define the system and its phases

For example – ice and water – two phases and one component (H<sub>2</sub>O) – not H<sub>2</sub> and O<sub>2</sub>.

albite – one component NaAlSi<sub>3</sub>O<sub>8</sub>

plagioclase – two components – NaAlSi<sub>3</sub>O<sub>8</sub> and CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>

### variables in a system

extensive variables – depends on the quantity of material, e.g., mass, volume

intensive variables – outside the system, does not depend on the quantity, e.g., P, T, density

How many intensive variables must be specified before the others are constrained and the state of the system is known?

The answer is given by the Phase Rule of Gibbs (1928)

$$F = C - n + 2$$

F number of degrees of freedom (number of intensive variables P, T)

C number of components

n number of phases

example H<sub>2</sub>O

one component H<sub>2</sub>O

C = 1

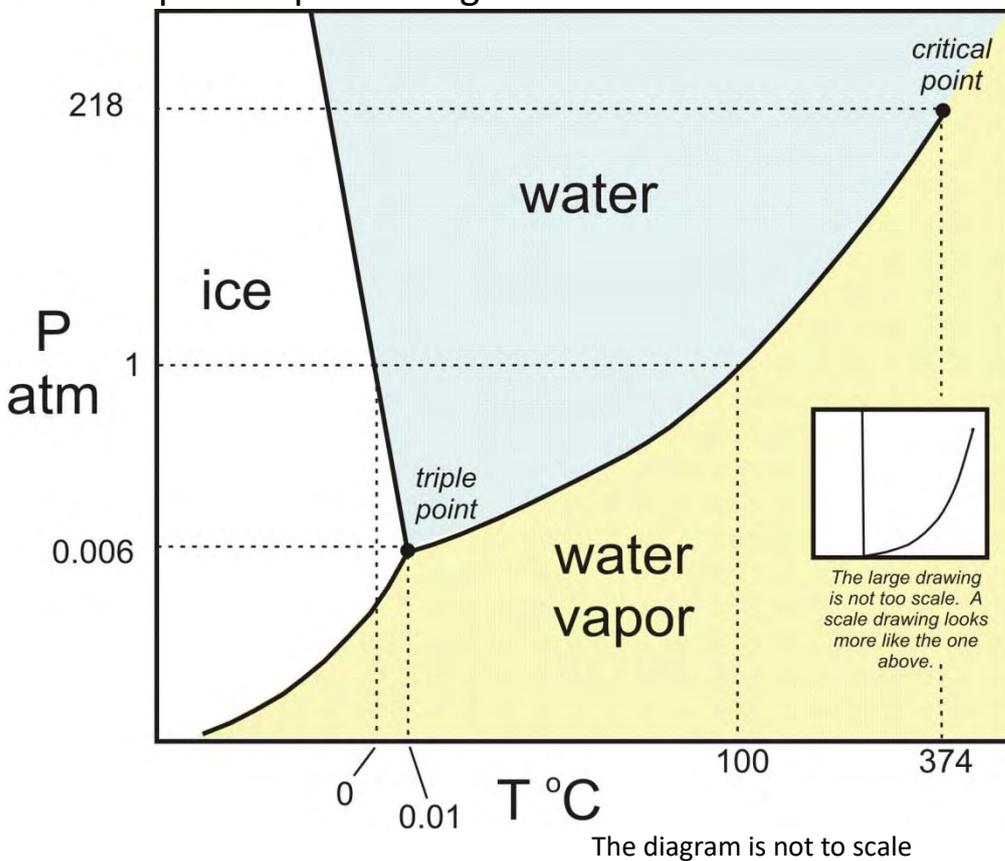
three phases water, vapor and ice

n = 3

applies to systems in chemical equilibrium

## phase diagrams

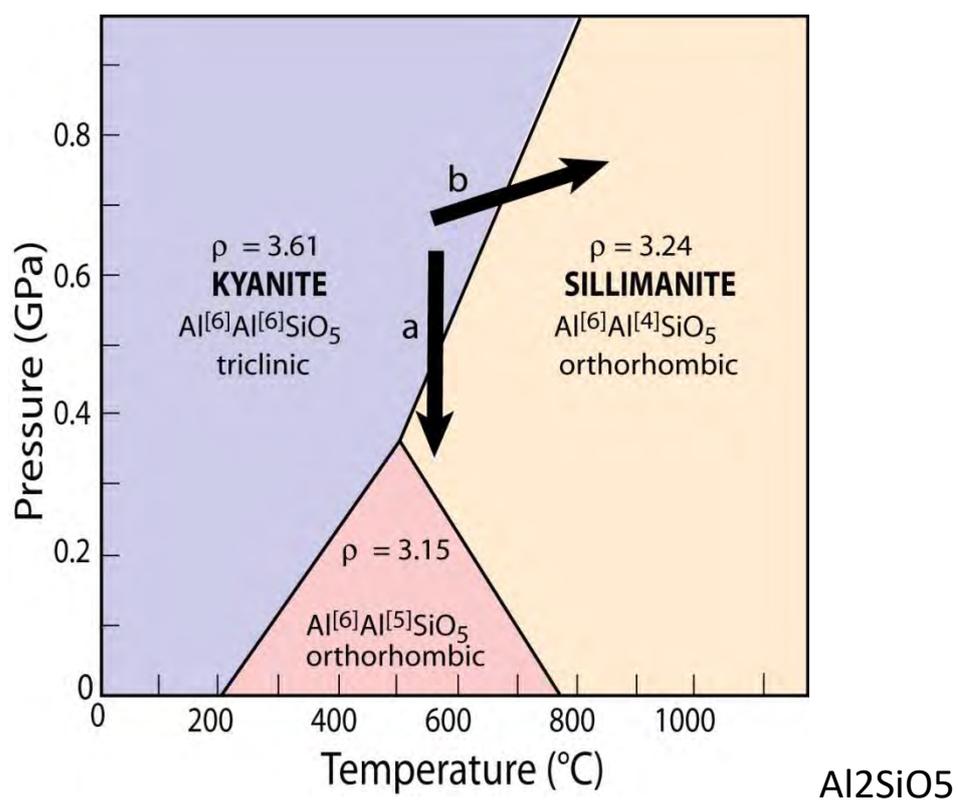
one component phase diagrams



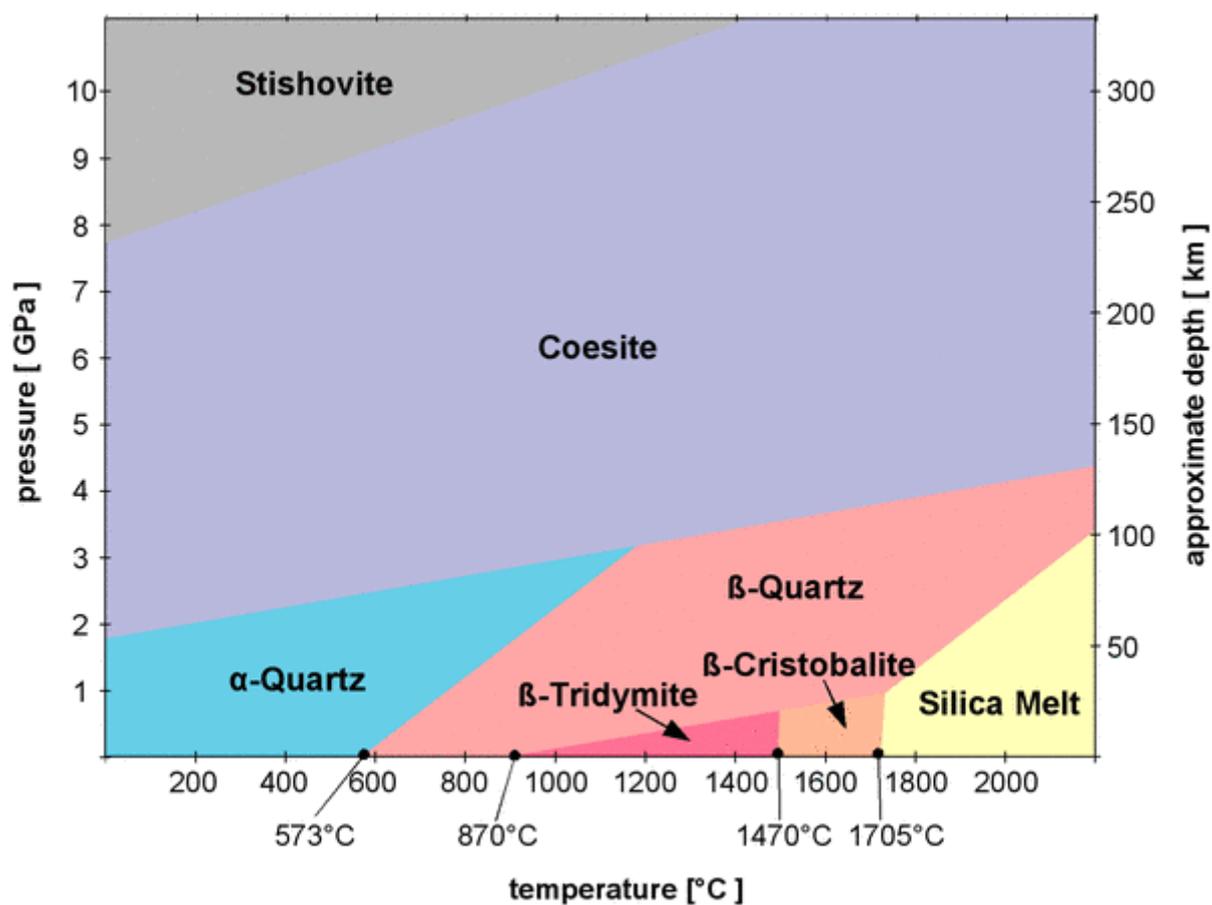
Above critical point no difference between water and vapor – super critical fluid, or just fluid

Difference between heat  $q$  and temperature. You can pump heat in the system of water and ice (in equilibrium) or water and vapor (in equilibrium) but that does not change its temperature.

pressure cooker increases  $P$  and thus  $T$



Divariant fields, univariant lines and invariant points



**Most of the lecture notes above have been compiled from**

Winter, J.D., 2010, Principles of igneous and metamorphic petrology. Prentice Hall, 702 s, ISBN 13: 978-0-321-68132-4.