Illustrating mineral chemistry: graphical displays of multicomponent systems

Initial concepts: two freely substituting components

End-members: two idealized starting components (cations) that could ideally fill the same site in a mineral structure

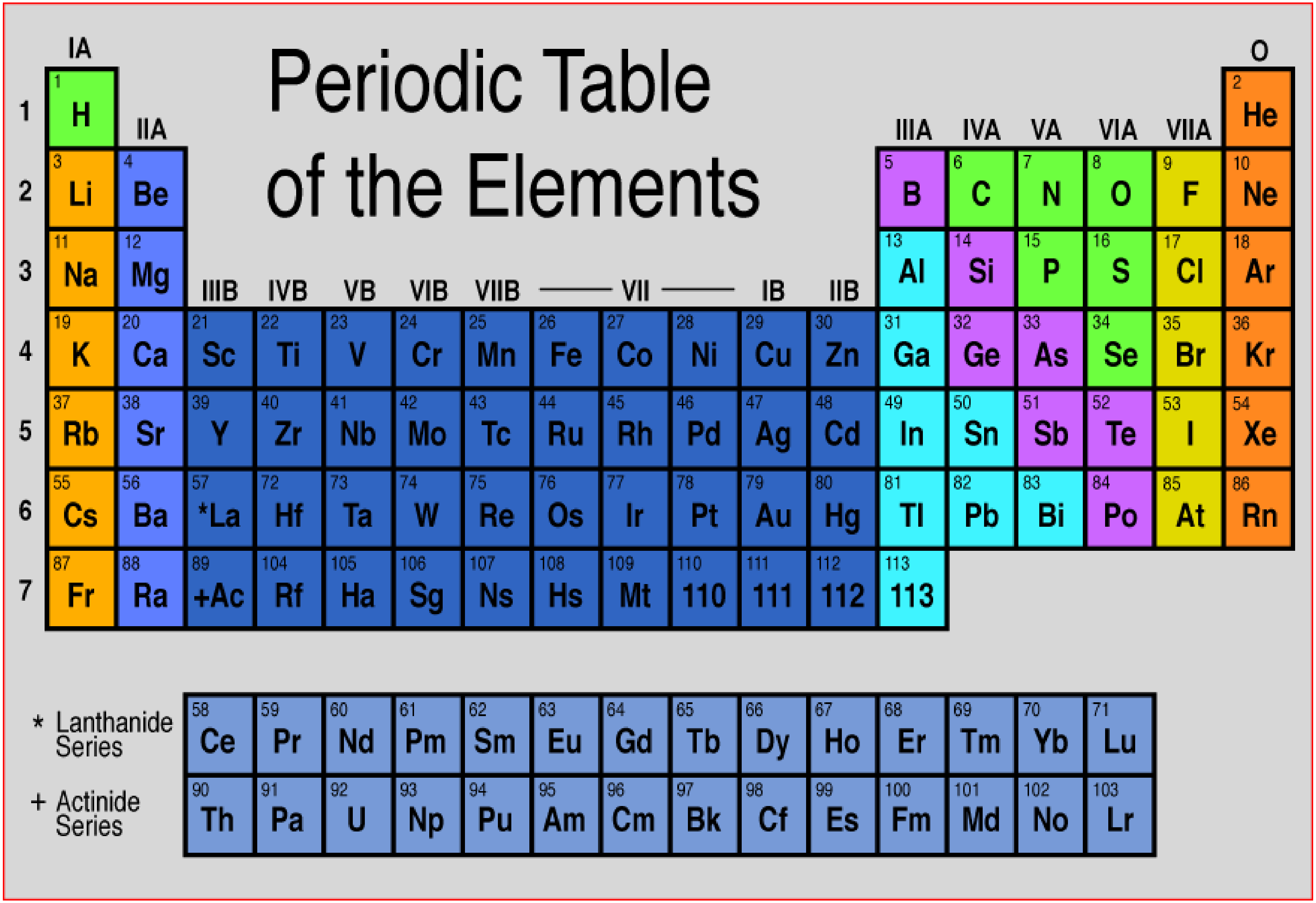
This leaves the possibility that a mixture of these components could occur

For example, the alkali-feldspars

$NaAlSi_3O_8$ ---------------------- $KAlSi_3O_8$

Exchange of Na^{+1} and K^{+1} can occur regularly

Plotting the ratio of the cations can be done independently or the relationship can be plotted based on the relative wt% of each species



Periodic Table of the Elements

	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	O
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 *La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 +Ac	104 Rf	105 Ha	106 Sg	107 Ns	108 Hs	109 Mt	110 110	111 111	112 112	113 113					

* Lanthanide Series	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
+ Actinide Series	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

3 ways of expressing mineral composition

Talc (sheet silicate usually formed from metamorphosed ultramafics)

I1

In terms of weight percent oxides (wt%)

Chemical formula	MgO	SiO2	H2O	MgO	SiO2	H2O
$Mg_3[Si_4O_{10}](OH)_2$	31.88	63.37	4.75	3	4	1

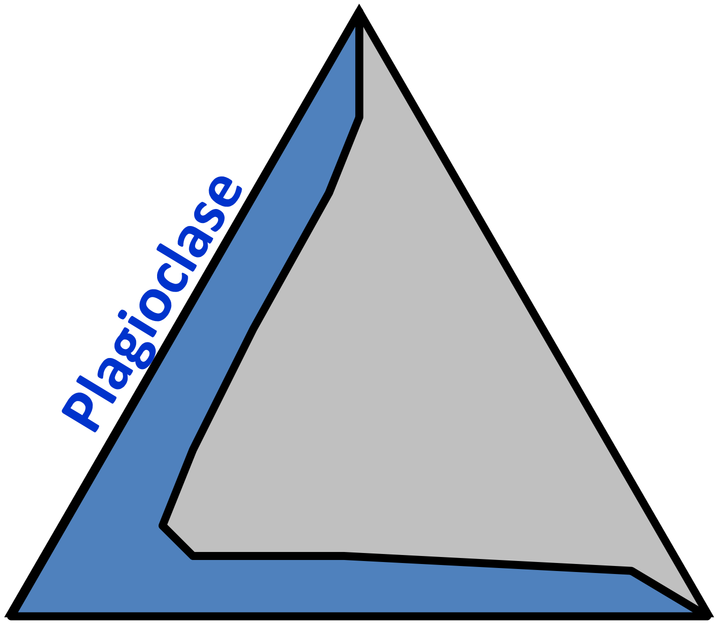
In terms of wt% elements and apfu'

Mg	Si	O	H	Mg	Si	O	H
19.23	29.62	50.62	0.53	3	4	12	2

Feldspar Group

Feldspars are the most common silicates in the Earth’s Crust.

$CaAl_2Si_2O_8$
Anorthite (An)



$NaAlSi_3O_8$
Albite (Ab)

Alkali Fsp

$KAlSi_3O_8$
Orthoclase (Or)

There is an “old” system for feldspar nomenclature, based on composition.

$Or_{37\text{-}100}$ = Sanidine
$Or_{10\text{-}37}$ = Anorthoclase
$Ab_{90\text{-}70}$ = Oligoclase
$Ab_{70\text{-}50}$ = Andesine
$Ab_{50\text{-}30}$ = Labradorite
$Ab_{50\text{-}10}$ = Bytownite

The Ternary diagram

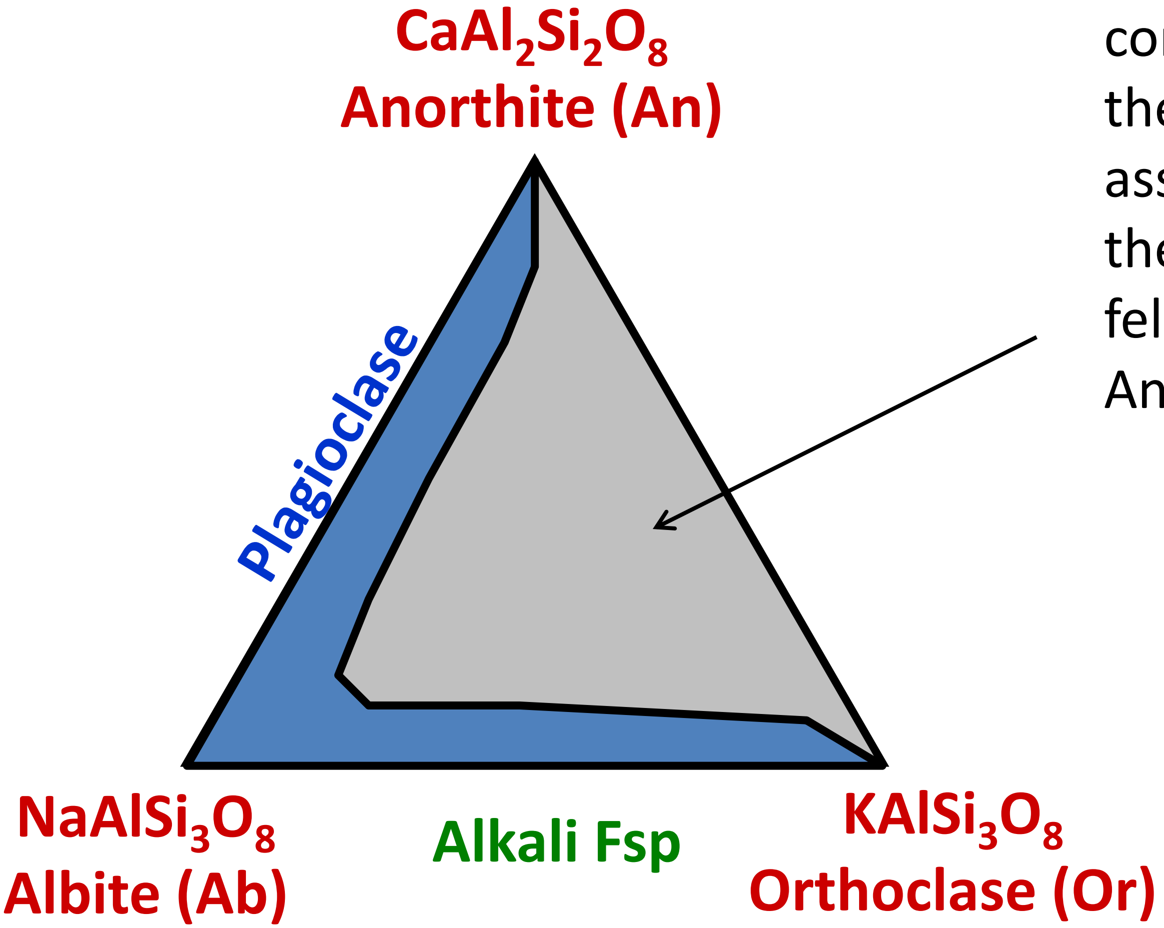
Three distinct end-members: each corner of the diagram is 100% of one component and 0% of the other two

Usually ternary plots are divided into a triangular gridded set with each line representing a 10% composition change

Returning to the feldspars:

CaAl2Si2O8------------$NaAlSi_3O_8$ ------------ $KAlSi_3O_8$

In this case, the ternary diagram represents two distinct but inherently linked solid-solution series



Miscibility gap: range of composition(s) where there are no stable assemblages in nature. In the example of the feldspars, there is no Or – An solid-solution series

COMMON SUBSTITUTIONS
$Si^{4+} \leftarrow\rightarrow Al^{3+}$
$Al^{3+} \leftarrow\rightarrow Mg^{2+}$
$Mg^{2+} \leftarrow\rightarrow Fe^{2+}$
$Na^{1+} \leftarrow\rightarrow K^{1+}$
$Na^{1+} \leftarrow\rightarrow Ca^{2+}$
$K^{1+} \leftarrow\rightarrow Ca^{2+}$
$Na^{1+}Si^{4+} \leftarrow\rightarrow Ca^{2+}Al^{3+}$
$Na^{1+}Al^{3+} \leftarrow\rightarrow 2Mg^{2+}$
$3Mg^{2+} \leftarrow\rightarrow \square + 2Al^{3+}$
$OH^{1-} \leftarrow\rightarrow Cl^{1-} + \square$
$OH^{1-} \leftarrow\rightarrow F^{1-} + \square$
$OH^{1-} \leftarrow\rightarrow 0^{2-} + \square$
$F^{1-} \leftarrow\rightarrow Cl^{1-} \leftarrow\rightarrow \square$

One for one cation substitution are a very common manner by which chemical formulas can be altered; however, notice the charge balance is often not maintained.

In these cases, additional cation substiutions and/or a change in the number of anions present in the formula is necessary to re-achieve an equilibrium electrical state.

Structural sites in minerals

Based on the size and charge of cations, we already know that there are particular types of coordination polyhedra based on the size of the cation(s) that must be accomodated, there are specific locations in a mineral where particular species will and will not fit.

Just as with creating or individual coordination polyhedra, there are specific sites in a mineral assemblage that are the appropriate size and capacity for a specific set of elements

These locations are given notations so that we can write generalized mineral formulas for a related mineral family irrespective of the specific mineral composition

Returning again to the feldspars:

$$M_{1\text{-}2}T_4O_8$$

Structural sites in minerals

Most simply the terms we will use for the major sites are:
M (1-4): "metal" cation site
T: tetrahedral site
A, B, C: interstitial sites between coordinated locations

Returning again to the feldspars:

$$M_{1\text{-}2}T_4O_8$$

Plagioclase: $Ca_xNa_{1-x}Al_{1+x}Si_{3-x}O_8$

Generalize formulas and sites for the major minerals

Garnet:

$A_2B_2Si_4O_{12}$

A > B and

$A = Ca^{2+}, Mg^{2+}, Fe^{2+}, Mn^{2+}$

$B = Al^{3+}, Fe^{3+}, Cr^{3+}$

Generalize formulas and sites for the major minerals

Olivine:

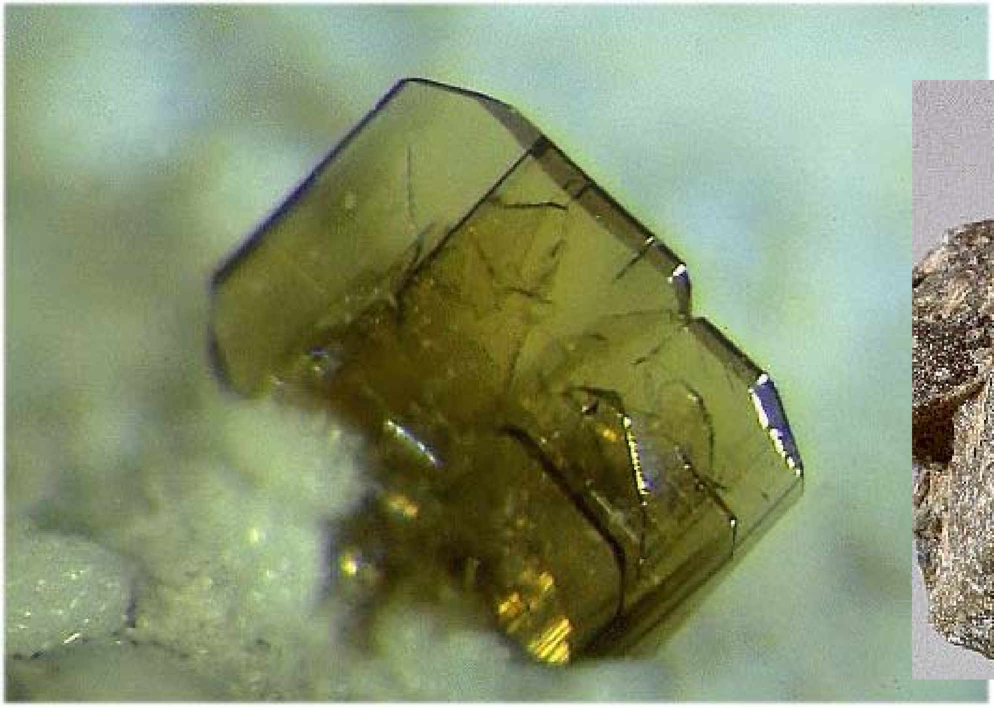
$M_2M_1SiO_4$

M2 > M1 and

M2 = Ca^{2+}, Mg^{2+}, $Fe^{2+/3+}$, Mn^{2+}

M1 = Mg^{2+}, $Fe^{2+/3+}$, Mn^{2+}

fayalite (Fe_2SiO_4) vs. monticellite ($CaFeSiO_4$)



An example from the Olivines

Olivine is a solid solution series between an Mg and Fe rich set of end-members: Forsterite and Fayalite

The general formula for Olivine is: $(Mg, Fe)_2[SiO]_4$

Chemical analysis (from Floran & Papike, 1973)

SiO2	TiO2	Al2O3	Fe2O3	FeO	MnO	MgO	CaO
30.09	0	0	0	69.42	0.28	0.91	0.08

Which Olivine is this an analysis of?

How can we calculate the formula in apfu'?

How many oxygen atoms will we need to base the calculation on?

An example from the Olivines

Olivine is a solid solution series between an Mg and Fe rich set of end-members: Forsterite and Fayalite

The general formula for Olivine is: $(Mg, Fe)_2[SiO]_4$

Based on the general formula, we can now assign a new formula to this specific species of Olivine:

$$(Mg_{0.0453}Fe_{1.937}Mn_{0.008}Ca_{0.003})[Si_{1.004}O_1]_4$$

Sum of M1 and M2 cations: 0.0453+1.937+0.008+0.003 = 1.9933 (~2)

Octahedral coordination polyhedra of the mineral fayalite

Generalize formulas and sites for the major minerals

Pyroxene:

$M_2M_1Si_2O_6$

M2 > M1 and

M2 = Ca^{2+}, Na^{1+}, Fe^{2+}, Mg^{2+}

M1 = Mg^{2+}, $Fe^{2+/3+}$, Mn^{2+}, Al^{3+}, Cr^{3+}, Ti^{4+}

enstatite ($Mg_2Si_2O_6$) vs. diopside ($CaMgSi_2O_6$)

Generalize formulas and sites for the major minerals

Amphibole:

$A_{0\text{-}1}M4_2M3M2_2M1_2Si_8O_{22}(OH)_2$

$A_{0\text{-}1}B_2C_5T_8O_{22}(OH)_2$

A > M4 > M3 ~> M2 = M1 **or** A > B > C > T **and**

$A = K^{1+}, Na^{1+}$

$B = Na^{1+}, Ca^{2+}, Mg^{2+}, Fe^{2+}, Mn^{2+}$

$C = Mg^{2+}, Fe^{2+/3+}, Mn^{2+}, Al^{3+}, Cr^{3+}$

$T = Si^{4+}, Al^{3+}, Ti^{4+}$

$OH = (OH)^{1-}, F^{1-}, Cl^{1-}, O^{2-}$

Anthrophyllite ($Mg_7Si_8O_{22}(OH)_2$) vs. Tremolite ($Ca_2Mg_5Si_8O_{22}(OH)_2$) vs. Richterite ($Na(CaNa)Mg_5Si_8O_{22}(OH)_2$)