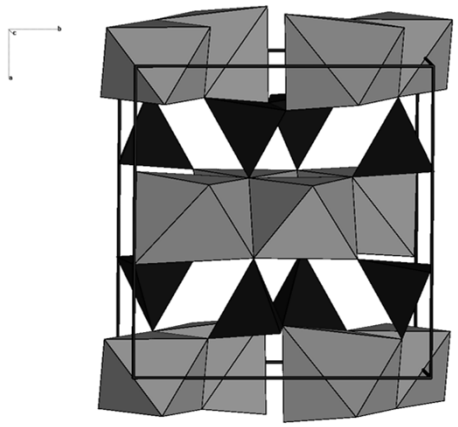
Stoichiometry

Chemical Analyses and Formulas

Enstatite Pbcn

- Cell a=9.306; b=8.892 c= 5.349 Å
- Mg1 (0, 0.1006, 0.25)
- Mg2 (0, 0.2625, 0.25)
- Si (0.2928, 0.0897,0.0739)
- O1 (0.1200, 0.0942, 0.0770)
- O2 (0.3773, 0.2463, 0.0677)
- O3 (0.3481, 0.9836, 0.3079)



Stoichiometry

- Chemical elements occur in specific integer ratios in minerals because of the crystal structure.
- Oxygen is the dominant anion in minerals of the crust and mantle.
- Elements (cations) of similar radius and charge can substitute at specific sites.

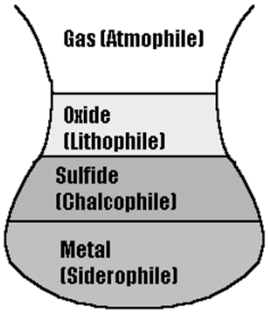
Stoichiometry

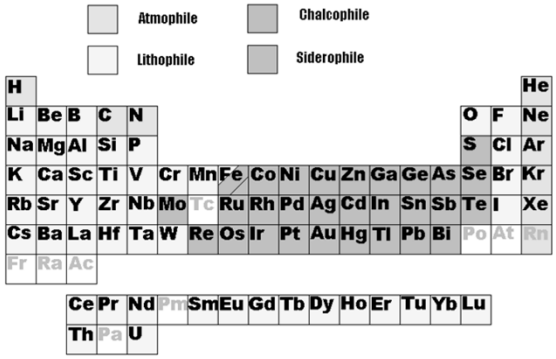
- Chemical analyses of oxygen bearing minerals are given as weight percents of oxides.
- We need to be able to recalculate oxide analyses to cations per given number of oxygens to derive a chemical formula.

Geochemical Classification of the Elements

- How do the elements partition between coexisting fluid (melt) phases?
  - Gas Phase : Atmophile : Van der Waals
  - Oxide phase: Lithophile : Ionic
  - Sulfide Phase: Chalcophile: Covalent
  - Metal Phase: Siderophile: Metallic

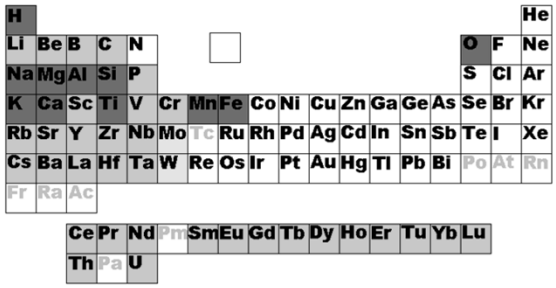
Geochemical Classification of the Elements





Oxides of Lithophile Cations

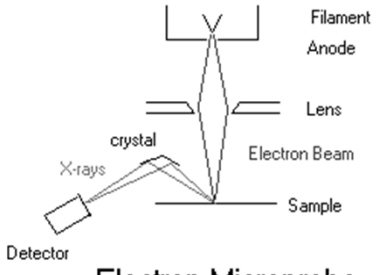
- SiO_2 TiO_2 (4+)
- Al_2O_3 Cr_2O_3 Fe_2O_3 (3+)
- MgO MnO FeO (2+)
- CaO (2+)
- Na_2O K_2O H_2O (1+)



Electron Microprobe

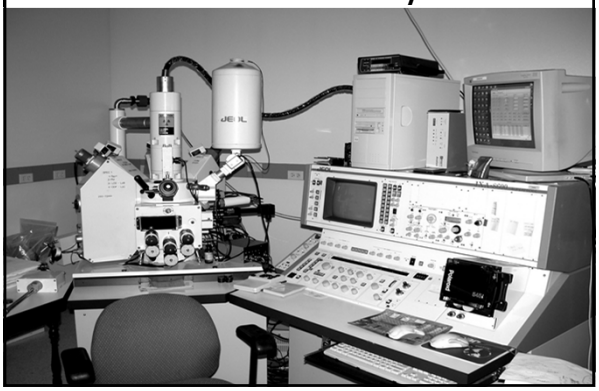
- *Quantitative Chemical analysis*
- *Major and minor element*
- *Uses electrons to excite secondary X-rays from sample.*
- *Electrons can be focussed onto a 10μm spot*
- *Sample is polished thin section*

Electron Microprobe



Electron Microprobe

Electron Microprobe



Example 1
Weight percents to formula

Oxide	Wt%	MolWt Oxide	Moles Oxide	Moles Cation	Moles Oxygen
SiO_2	59.85				
MgO	40.15				
	100.0				

Example 1
Weight percents to formula

Oxide	Wt%	MolWt Oxide	Moles Oxide	Moles Cation	Moles Oxygen
SiO_2	59.85	60.086			
MgO	40.15	40.312			
	100.0				

Example 1
Weight percents to formula

Oxide	Wt%	MolWt Oxide	Moles Oxide	Moles Cation	Moles Oxygen
SiO_2	59.85	60.086	.9960		
MgO	40.15	40.312	.9960		
	100.0				

Example 1
Weight percents to formula

Oxide	Wt%	MolWt Oxide	Moles Oxide	Moles Cation	Moles Oxygen
SiO_2	59.85	60.086	.9960	.9960	1.9920
MgO	40.15	40.312	.9960	.9960	.9960
	100.0				2.9980

Example 1
Weight percents to formula

Oxide	Wt%	MolWt Oxide	Moles Oxide	Moles Cation	Moles Oxygen
SiO_2	59.85	60.086	.9960	.9960	1.9920
MgO	40.15	40.312	.9960	.9960	.9960
	100.0				2.9980

- Mole ratios Mg : Si : O = 1 : 1 : 3
- $MgSiO_3$

Example 2
Formula to weight percents

- Kyanite is Al_2SiO_5
- Calculate the weight percents of the oxides:
  - SiO_2
  - Al_2O_3

Example 2
Formula to weight percents: Kyanite: Al_2SiO_5

Oxide	Moles PFU	MolWt Oxide	Grams Oxide	Wt% Percent
SiO_2				
Al_2O_3				
Formula weight				

Example 2
Formula to weight percents: Kyanite: Al_2SiO_5

Oxide	Moles PFU	MolWt Oxide	Grams Oxide	Wt% Percent
SiO_2	1			
Al_2O_3				
Formula weight				

Example 2
Formula to weight percents: Kyanite: Al_2SiO_5

Oxide	Moles PFU	MolWt Oxide	Grams Oxide	Wt% Percent
SiO_2	1			
Al_2O_3	1			
Formula weight				

Example 2
Formula to weight percents: Kyanite: Al_2SiO_5

Oxide	Moles PFU	MolWt Oxide	Grams Oxide	Wt% Percent
SiO_2	1	60.086	60.086	
Al_2O_3	1	101.963	101.963	
Formula weight				

Example 2
Formula to weight percents: Kyanite: Al_2SiO_5

Oxide	Moles PFU	MolWt Oxide	Grams Oxide	Wt% Percent
SiO_2	1	60.086	60.086	
Al_2O_3	1	101.963	101.963	
Formula weight			162.049	

Example 2
Formula to weight percents: Kyanite: Al_2SiO_5

Oxide	Moles PFU	MolWt Oxide	Grams Oxide	Wt% Percent
SiO_2	1	60.086	60.086	37.08
Al_2O_3	1	101.963	101.963	62.92
Formula weight			162.049	

Example 3: Solid Solutions Weight percents to formula

- Alkali Feldspars may exist with any composition between $NaAlSi_3O_8$ and $KAlSi_3O_8$.
- Formula has 8 oxygens: $(Na,K)AlSi_3O_8$
- The alkalis may substitute in any ratio, but total alkalis to Al is 1 to 1.

Example 3: Solid Solutions Weight percents to formula (8 oxygens).

Oxide	Wt%	MolWt Oxide	Moles Oxide	Moles Cation	Moles Oxygen
SiO_2	68.20	60.086			
Al_2O_3	19.29	101.963			
Na_2O	10.20	61.9796			
K_2O	2.32	94.204			
		100.00			

Example 3: Solid Solutions Weight percents to formula (8 oxygens).

Oxide	Wt%	MolWt Oxide	Moles Oxide	Moles Cation	Moles Oxygen
SiO_2	68.20	60.086	1.1350		
Al_2O_3	19.29	101.963	0.1892		
Na_2O	10.20	61.9796	0.1646		
K_2O	2.32	94.204	0.0246		
		100.00			
					8.000

Example 3: Solid Solutions Weight percents to formula (8 oxygens).

Oxide	Wt%	MolWt Oxide	Moles Oxide	Moles Cation	Moles Oxygen
SiO_2	68.20	60.086	1.1350	1.1350	
Al_2O_3	19.29	101.963	0.1892	0.3784	
Na_2O	10.20	61.9796	0.1646	0.3291	
K_2O	2.32	94.204	0.0246	0.0493	
	100.00				
					8.000

Example 3: Solid Solutions Weight percents to formula (8 oxygens).

Oxide	Wt%	MolWt Oxide	Moles Oxide	Moles Cation	Moles Oxygen
SiO_2	68.20	60.086	1.1350	1.1350	2.2701
Al_2O_3	19.29	101.963	0.1892	0.3784	0.5676
Na_2O	10.20	61.9796	0.1646	0.3291	0.1646
K_2O	2.32	94.204	0.0246	0.0493	0.0246
	100.00				3.0269 x 2.6430=
					8.000

Example 3: Solid Solutions Weight percents to formula (8 oxygens).

Oxide	Wt%	MolWt Oxide	Moles Oxide	Moles Cation	Moles Oxygen	
SiO_2	68.20	60.086	1.1350	1.1350	2.2701	3.0
Al_2O_3	19.29	101.963	0.1892	0.3784	0.5676	1.0
Na_2O	10.20	61.9796	0.1646	0.3291	0.1646	0.87
K_2O	2.32	94.204	0.0246	0.0493	0.0246	0.13
	100.00				3.0269 x 2.6430=	
					8.000	

- Mole ratios $Na_{0.87}$ $K_{0.13}$ $Al_{1.00}$ $Si_{3.00}$ O_8
- calculated as cations per 8 oxygens

Simple Solid Solutions

- $NaAlSi_3O_8$ - $KAlSi_3O_8$ Alkali Feldspars
- $MgSiO_3$- $FeSiO_3$ Enstatite-Ferrosilite (pyroxene)
- $MgCaSi_2O_6$-$FeCaSi_2O_6$ Diopside-Hedenbergite
- Mg_2SiO_4- Fe_2SiO_4 Forsterite-Fayalite
- $Mg_3Al_2Si_3O_{12}$- $Fe_3Al_2Si_3O_{12}$ Pyrope - Almandine

Example 4 Weight Percent Oxides from Formula

- Given the formula $En_{70}Fs_{30}$ for an orthopyroxene, calculate the weight percent oxides.
- En = enstatite = $Mg_2Si_2O_6$
- Fs = ferrosilite = $Fe_2Si_2O_6$
- Formula is $(Mg_{0.7}Fe_{0.3})_2Si_2O_6$ = $(Mg_{1.4}Fe_{0.6})Si_2O_6$

Example 4 $(Mg_{1.4}Fe_{0.6})Si_2O_6$ Weight Percent Oxides from Formula

Oxide	Moles PFU	MolWt Oxide	Grams Oxide	Wt% Percent
SiO_2	2	60.086		
MgO	1.4	40.312		
FeO	0.6	71.846		
Formula weight				

Example 4 $(Mg_{1.4}Fe_{0.6})Si_2O_6$ Weight Percent Oxides from Formula

Oxide	Moles PFU	MolWt Oxide	Grams Oxide	Wt% Percent
SiO_2	2	60.086		
MgO	1.4	40.312		
FeO	0.6	71.846		
Formula weight				

Example 4 $(Mg_{1.4}Fe_{0.6})Si_2O_6$ Weight Percent Oxides from Formula

Oxide	Moles PFU	MolWt Oxide	Grams Oxide	Wt% Percent
SiO_2	2	60.086	120.172	
MgO	1.4	40.312	56.437	
FeO	0.6	71.846	43.108	
Formula weight			219.717	

Example 4 $(Mg_{1.4}Fe_{0.6})Si_2O_6$ Weight Percent Oxides from Formula

Oxide	Moles PFU	MolWt Oxide	Grams Oxide	Wt% Percent
SiO_2	2	60.086	120.172	54.69
MgO	1.4	40.312	56.437	25.69
FeO	0.6	71.846	43.108	19.62
Formula weight			219.717	100.00

Example 5 Weight Percent Oxides from Formula

- A pyroxene is a solid solution of 40% jadeite ($NaAlSi_2O_6$) and 60% acmite ($NaFeSi_2O_6$).
- Calculate the weight percent oxides
- Formula is $Na(Al_{0.4}Fe_{0.6})Si_2O_6$

Formula is $Na(Al_{0.4}Fe_{0.6})Si_2O_6$ Calculate Weight Percent Oxides

Oxide	Moles PFU	MolWt Oxide	Grams Oxide	Wt% Percent
SiO_2	2.0	60.086	120.172	54.76
Al_2O_3	0.2	101.963	20.393	9.29
Fe_2O_3	0.3	159.692	47.908	21.83
Na_2O	0.5	61.980	30.990	14.12
Formula weight			219.463	100.00

Coupled Substitutions

- Plagioclase feldspar $NaAlSi_3O_8$ - $CaAl_2Si_2O_8$
- Jadeite-diopside $NaAlSi_2O_6$ - $CaMgSi_2O_6$

Coupled Substitution 40% Anorthite; 60% Albite Calculate Weight percent Oxides

- First write the formula
- Anorthite is $CaAl_2Si_2O_8$
- Albite is $NaAlSi_3O_8$
- An_{40} Ab_{60} is $Ca_{.4}Na_{.6}Al_{1.4}Si_{2.6}O_8$

An_{40} Ab_{60} is $Ca_{.4}Na_{.6}Al_{1.4}Si_{2.6}O_8$

Oxide	Moles PFU	MolWt Oxide	Grams Oxide	Wt% Percent
SiO_2	2.6			
Al_2O_3	0.7			
CaO	0.4			
Na_2O	0.3			

$An_{40}\ Ab_{60}$ is $Ca_{.4}Na_{.6}Al_{1.4}Si_{2.6}O_8$

Oxide	Moles PFU	MolWt Oxide	Grams Oxide	Wt% Percent
SiO_2	2.6	60.086		
Al_2O_3	0.7	101.963		
CaO	0.4	55.96		
Na_2O	0.3	61.980		

$An_{40}\ Ab_{60}$ is $Ca_{.4}Na_{.6}Al_{1.4}Si_{2.6}O_8$

Oxide	Moles PFU	MolWt Oxide	Grams Oxide	Wt% Percent
SiO_2	2.6	60.086	156.22	
Al_2O_3	0.7	101.963	71.37	
CaO	0.4	55.96	22.38	
Na_2O	0.3	61.980	18.59	
Formula weight			268.58	

$An_{40}\ Ab_{60}$ is $Ca_{.4}Na_{.6}Al_{1.4}Si_{2.6}O_8$

Oxide	Moles PFU	MolWt Oxide	Grams Oxide	Wt% Percent
SiO_2	2.6	60.086	156.22	58.17
Al_2O_3	0.7	101.963	71.37	26.57
CaO	0.4	55.96	22.38	8.33
Na_2O	0.3	61.980	18.59	6.92
Formula weight			268.58	100.00

Example Given Analysis Compute Mole percents of Jadeite and Diopside

- Jadeite is $NaAlSi_2O_6$
- Diopside is $CaMgSi_2O_6$

Jadeite - Diopside

Oxide	Wt%	MolWt Oxide	Moles Oxide	Moles Cation	Moles Oxygen
SiO_2	56.64	60.086			
Al_2O_3	7.21	101.963			
MgO	13.30	40.312			
CaO	18.46	55.96			
Na_2O	4.38	94.204			
	99.99				
Normalize to 8 oxygens					

Jadeite - Diopside

Oxide	Wt%	MolWt Oxide	Moles Oxide	Moles Cation	Moles Oxygen
SiO_2	56.64	60.086	.9426		
Al_2O_3	7.21	101.963	.0707		
MgO	13.30	40.312	.3299		
CaO	18.46	55.96	.3299		
Na_2O	4.38	94.204	.0246		
	99.99				
Normalize to 6 oxygens					

Jadeite - Diopside

Oxide	Wt%	MolWt Oxide	Moles Oxide	Moles Cation	Moles Oxygen
SiO_2	56.64	60.086	.9426	.9426	1.8852
Al_2O_3	7.21	101.963	.0707	.1414	.2121
MgO	13.30	40.312	.3299	.3299	.3299
CaO	18.46	55.96	.3299	.3299	.3299
Na_2O	4.38	94.204	.0246	.0493	.0246
	99.99				
Normalize to 6 oxygens					

Jadeite - Diopside

Oxide	Wt%	MolWt Oxide	Moles Oxide	Moles Cation	Moles Oxygen	
SiO_2	56.64	60.086	.9426	.9426	1.8852	2.0
Al_2O_3	7.21	101.963	.0707	.1414	.2121	0.3
MgO	13.30	40.312	.3299	.3299	.3299	0.7
CaO	18.46	55.96	.3299	.3299	.3299	0.7
Na_2O	4.38	94.204	.0246	.0493	.0246	0.3
	99.99				2.8278 x 2.1218=	
Normalize to 6 oxygens					6.000	

- $Na_{.3}Ca_{.7}Al_{.3}Mg_{.7}Si_2O_6$ =
- 30% Jadeite 70% Diopside

Jadeite - Diopside

Oxide	Wt%	MolWt Oxide	Moles Oxide	Moles Cation	Moles Oxygen
SiO_2	56.64	60.086	.9426	.9426	1.8852
Al_2O_3	7.21	101.963	.0707	.1414	.2121
MgO	13.30	40.312	.3299	.3299	.3299
CaO	18.46	55.96	.3299	.3299	.3299
Na_2O	4.38	94.204	.0246	.0493	.0246
	99.99				2.8278 x 2.1218=
Normalize to 6 oxygens					6.000

- $Na_{.3}Ca_{.7}Al_{.3}Mg_{.7}Si_2O_6$ =
- 30% Jadeite 70% Diopside

Unit Cells and Mineral Density

- *Unit cell is basic repeat unit of structure.*
- *Parallel-piped box: a, b, c (Å), α, β, γ (°)*
- *Å = 10^{-8} cm*
- *Avogadro's number (# atoms / mole) = 6.02 x10^{23}*
- *If you know the contents of the box and the size of the box you can calculate the density.*

Cell Volume (1Å^3=10^{-24} cm^3)

- *Cubic* $V = a^3$
- *Tetragonal* $V = a^2c$
- *Hex/Trigonal* $V = a^2c \sin 120^o$
- *Orthorhombic* $V = abc$
- *Monoclinic* $V = abc \sin \beta$
- *Triclinic*
- $V = abc\,(1 + 2\cos\alpha\cos\beta\cos\gamma - \cos^2\alpha - \cos^2\beta - \cos^2\gamma)^{1/2}$

Avogadro's Number

- *The number of atoms in a mole.*
- *A mole of any compound is the molecular weight in grams.*
- *6.022 x 10^{23}*

Density

- Volume of Avogadro's number of unit cells = AV
- The number of formula units per unit cell = Z
  - Z is a small integer 1 to about 16.
- Weight of Avogadro's number of unit cells = Z* FW

$$\rho = \frac{Z \bullet FW}{A \bullet V}$$

Example Density Calculation

- *Calculate the density of ferberite ($FeWO_4$), which is monoclinic with*
- *a = 4.73; b = 5.70; c = 4.95; β = 90.01; Z = 2.*
- *Calculate the gram formula weight:*
  - *1 Fe (55.847) = 55.847*
  - *1 W (183.85) = 183.85*
  - *4 O (15.9995) 63.998*
  - *FW = 303.695 g*

Example Density Calculation: Ferberite $FeWO_4$

- *V = abc sin β = (4.73)(5.70)(4.95)(sin 90.01º)*
- *V = 133.46 Å³*
- *V = 1.335 x 10^{-22} cm³*
- *ρ = ZFw/AV = 2 (303.70) / 6.02 10^{23} *1.335 10^{-22}*
- *ρ = 7.56 g/cm³*

Example Density Calculation: Witherite $BaCO_3$

- *Witherite is orthorhombic Pmcn*
- *a = 5.316; b = 8.892; c = 6.428*
- *V = 303.85*
- *Z = 4*
- *FW = 197.34g*

Example Density Calculation: Witherite $BaCO_3$

V = 303.85 Å³

- *V = 3.0385 x 10^{-22} cm³*
- *ρ = ZFw/AV = 4 (197.34) / 6.02 10^{23} *3.038 10^{-22}*
- *ρ = 4.31 g/cm³*