

# Earth and Planetary Materials

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Spring 2013

Lecture 4

2013.01.16

# Example – Beryl $\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$



Goshenite



pure



Aquamarine



$\text{Fe}^{2+}$  &  $\text{Fe}^{3+}$



Emerald



$\text{Cr}^{3+}$



Heliodor



$\text{Fe}^{3+}$



Red beryl



$\text{Mn}^{3+}$



Morganite



$\text{Mn}^{2+}$



## Rules for ionic (atomic) substitution

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Size and charge matter!

# Victor M. Goldschmidt

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- 1888-1947
- Swiss-born Norwegian mineralogist and petrologist who laid the foundation of inorganic crystal chemistry and founded modern geochemistry

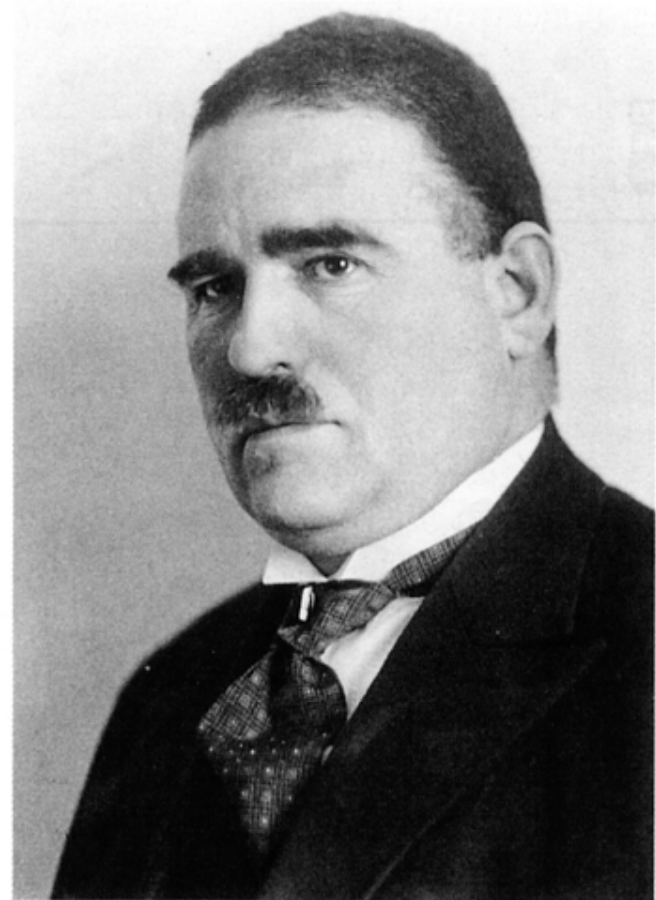


Fig. 1. V.M. Goldschmidt at Göttingen (ca. 1932)

## Goldschmidt's Rules – Size

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Atomic substitution is controlled by size (radii) of the ion

If size difference is

< 15%: free substitution

15 ~30%: limited substitution

> 30%: little to no substitution

If there is a small difference of ionic radius, the smaller ion enters the crystal preferentially

**Table 1-8**  
COMMON IONIC SUBSTITUTION PAIRS

<i>Ion</i>	<i>CN</i>	<i>Radius (Å)</i>	<i>Ion</i>	<i>CN</i>	<i>Radius (Å)</i>
Mg	VI	0.80	Fe <sup>2+</sup>	VI	0.86
Al	IV	0.47	Si	IV	0.34
F	VI	1.25	O	VI	1.32
Ba	IX	1.55	K	IX	1.63
Ge	IV	0.48	Si	IV	0.34
Ga	VI	0.70	Al	VI	0.61
Hf	VIII	0.91	Zr	VIII	0.92
Mn <sup>4+</sup>	VI	0.62	Fe <sup>3+</sup>	VI	0.73
Mn <sup>2+</sup>	VI	0.91	Fe <sup>2+</sup>	VI	0.86
La–Lu	VIII	1.26–1.05	Ca	VIII	1.20
Na	VIII	1.24	Ca	VIII	1.20

# Goldschmidt's Rules - Charge

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Atomic substitution is controlled by charge of the ions

If charge difference is:

= 1: substitute readily if electrical neutrality is maintained

>1: substitution is minimal

For ions of similar radius but different charges, the ion with the higher charge enters the crystal preferentially

- Forms a stronger bond with the anions surrounding the site

## Ringwood's Modifications (1955)

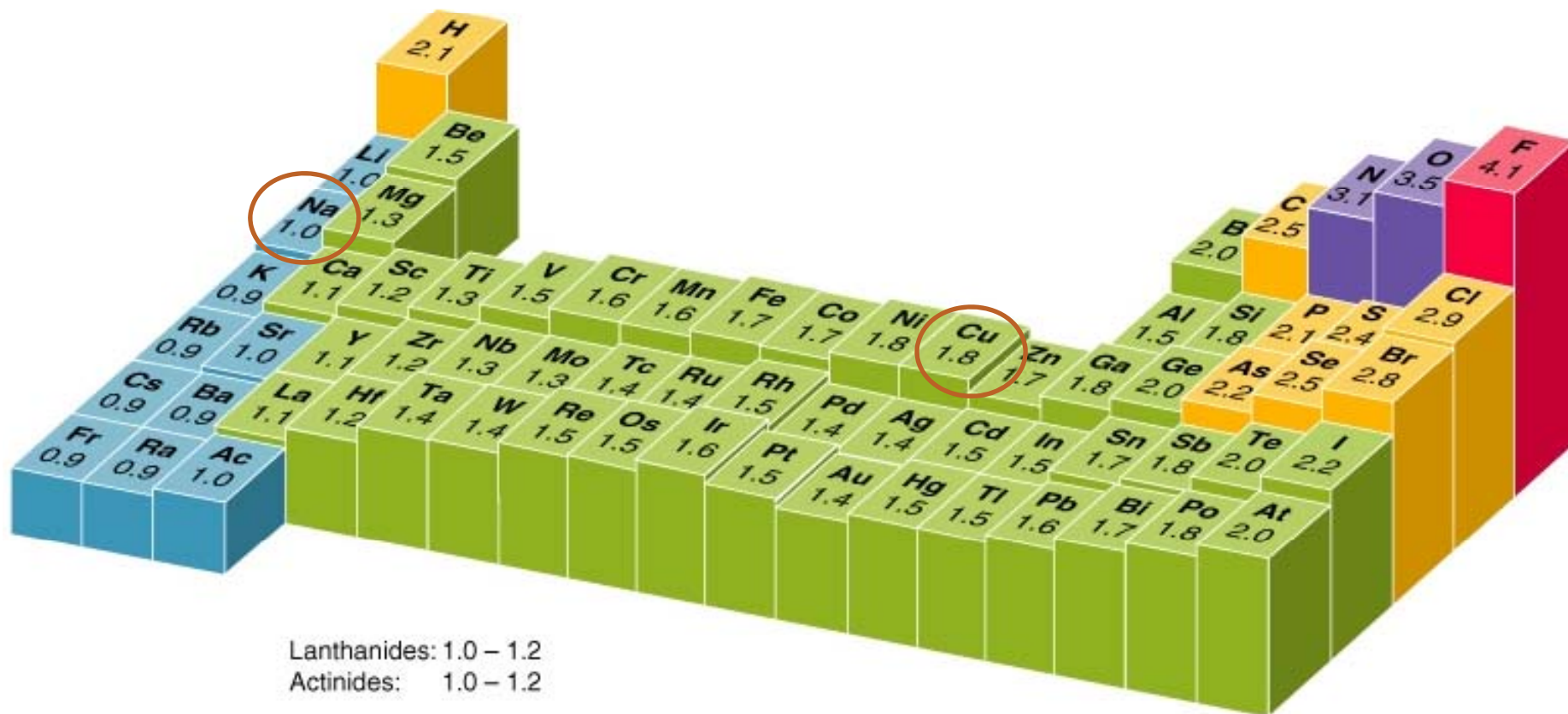
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- Substitutions may be limited, even when the size and charge criteria are satisfied, when the competing ions have different electronegativities and form bonds of different ionic character
- Explains discrepancies with respect to the Goldschmidt rules

### Example:

- $\text{Na}^+$  and  $\text{Cu}^+$  have the same radius and charge, but do not substitute for one another





## Other factors affecting substitution

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- Temperature
  - Minerals expand at higher T
  - Greater tolerance for ionic substitution at higher T
- Pressure
  - Increasing pressure causes compression
  - Less tolerance for ionic substitution at higher P
- Availability of ions – ions must be readily available for substitution to occur

## Types of substitution

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Simple substitution

Interstitial substitution

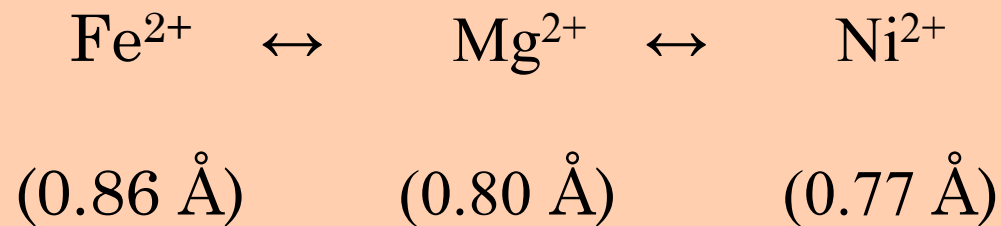
Vacancy substitution

## (1) Simple substitution

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- Involves the same sites in the crystal structure
- Type 1: Complete binary solid solution: ions have same charge and nearly same size, substitute freely

Example:



## Example – Olivine group

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- End members are forsterite ( $\text{Mg}_2\text{SiO}_4$ ; “Fo”) and fayalite ( $\text{Fe}_2\text{SiO}_4$ ; “Fa”)
- Any composition in between is possible:  $(\text{Mg}_x\text{Fe}_{1-x})_2\text{SiO}_4$
- $x = 0.7$  would be “70 mole percent forsterite”; or “Fo<sub>70</sub>”

## (1) Simple substitution

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- Type 2: Coupled substitution: ions have nearly same size, but different charge; balance charge by simultaneous substitution on a second site.

## Example

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- $\text{Si}^{4+}$  and  $\text{Al}^{3+}$  (CN = 4): balanced by also substituting  $\text{Ca}^{2+}$  for  $\text{Na}^+$  on a different site
- write as a charge-balanced reaction:  $\text{Si}^{4+} + \text{Na}^+ = \text{Al}^{3+} + \text{Ca}^{2+}$

Example – Plagioclase feldspars:



**Table 1-10**

**EXAMPLES OF COUPLED SUBSTITUTION**

Giving isomorphic “derivative structures”

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	Si	Si	O <sub>4</sub>	Quartz
	Al	P	O <sub>4</sub>	Berlinite
	Al	Al	O <sub>3</sub>	Corundum
	Fe	Ti	O <sub>3</sub>	Ilmenite
	Si	Si	Si <sub>2</sub> O <sub>8</sub>	Coesite
K	Al	Si	Si <sub>2</sub> O <sub>8</sub>	Sanidine
Na	Al	Si	Si <sub>2</sub> O <sub>8</sub>	Albite
Ca	Al	Al	Si <sub>2</sub> O <sub>8</sub>	Anorthite

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## (2) Interstitial substitution

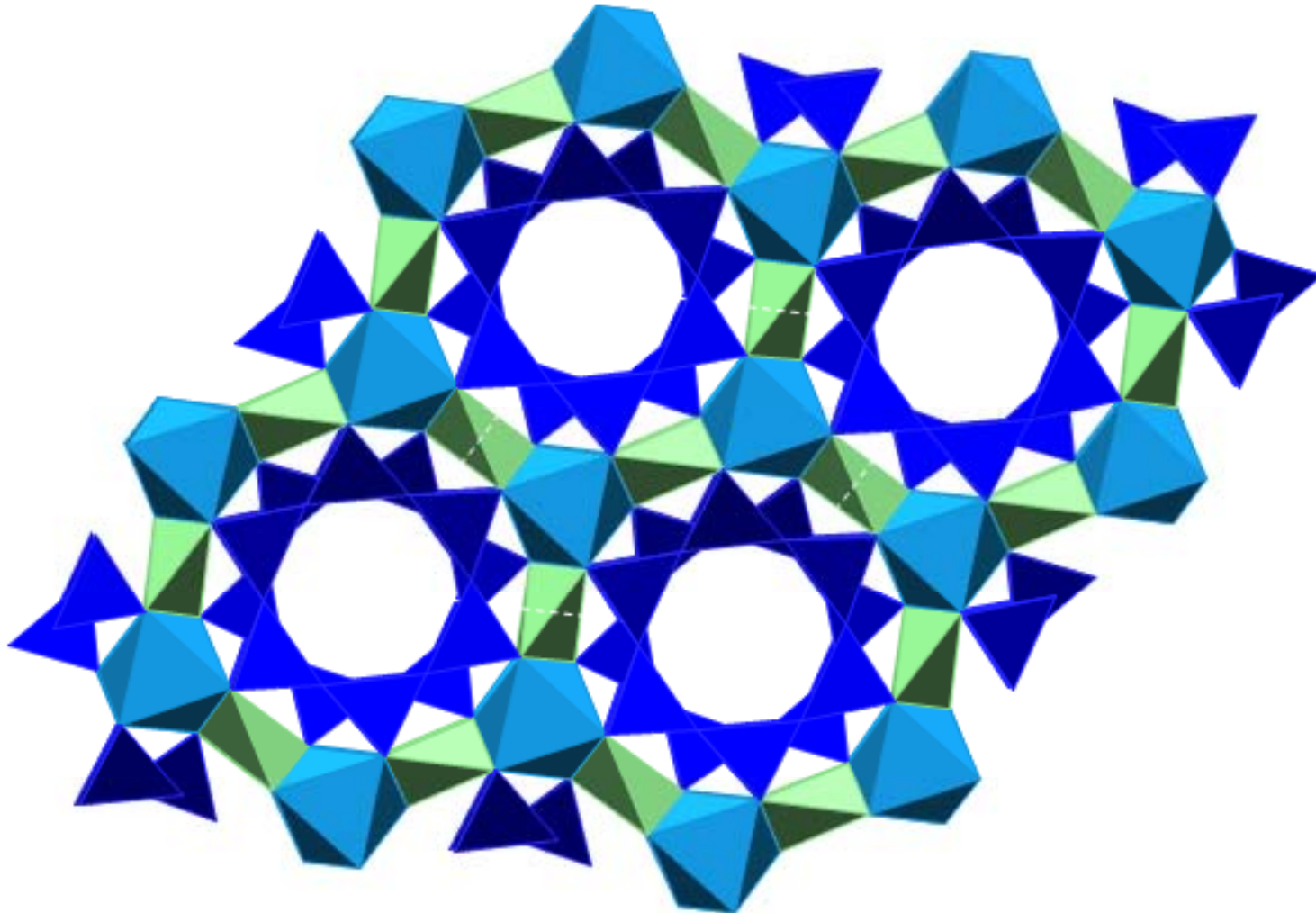
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- Coupled substitution where the charge balancing substitution is accommodated on a site normally vacant in the mineral
- Many minerals have large channels or space between layers that can accommodate cations

## Example – Beryl $\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$

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- Channels in beryl – accommodating charged ions



### (3) Vacancy (Omission) substitution

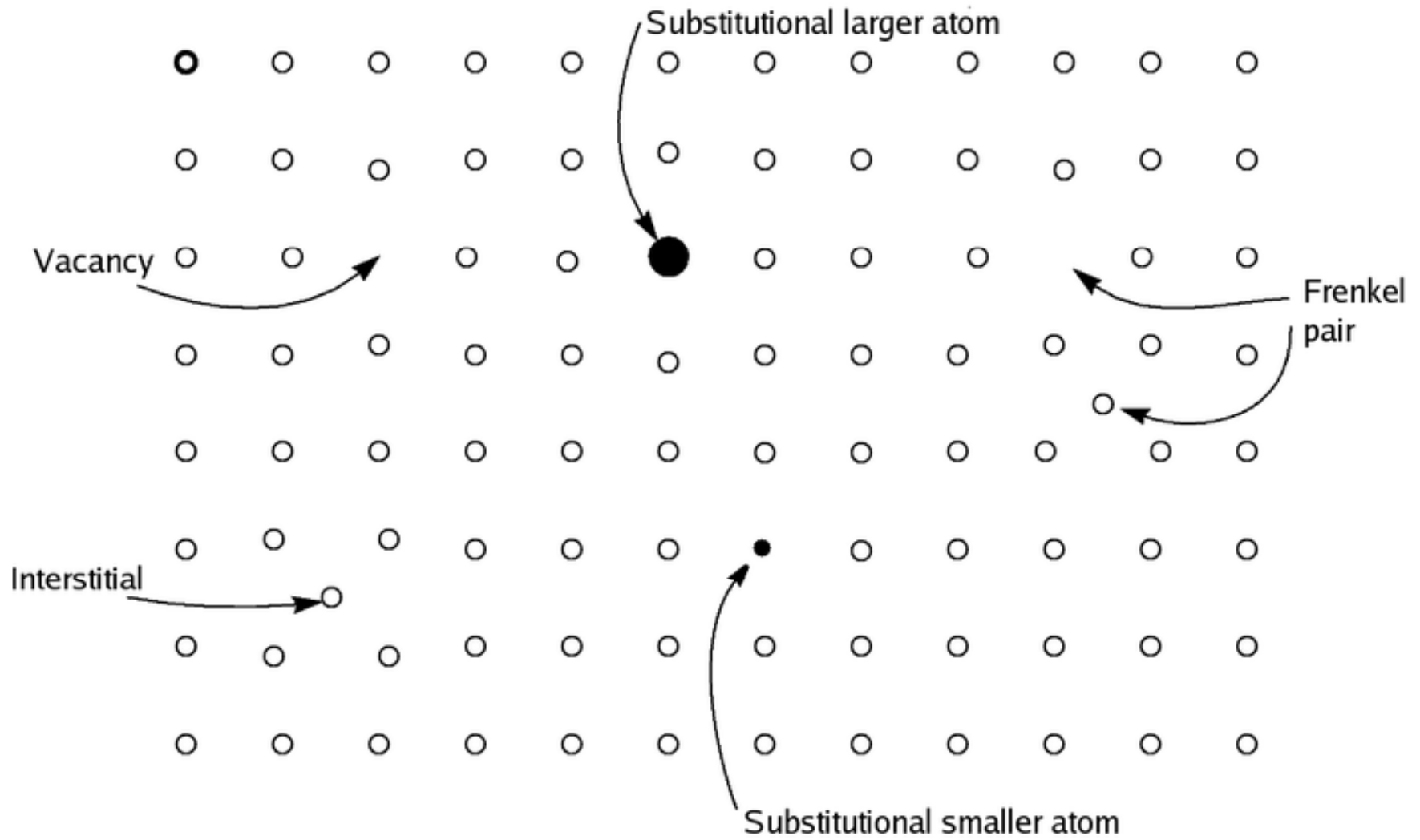
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Charge is balanced by leaving sites vacant

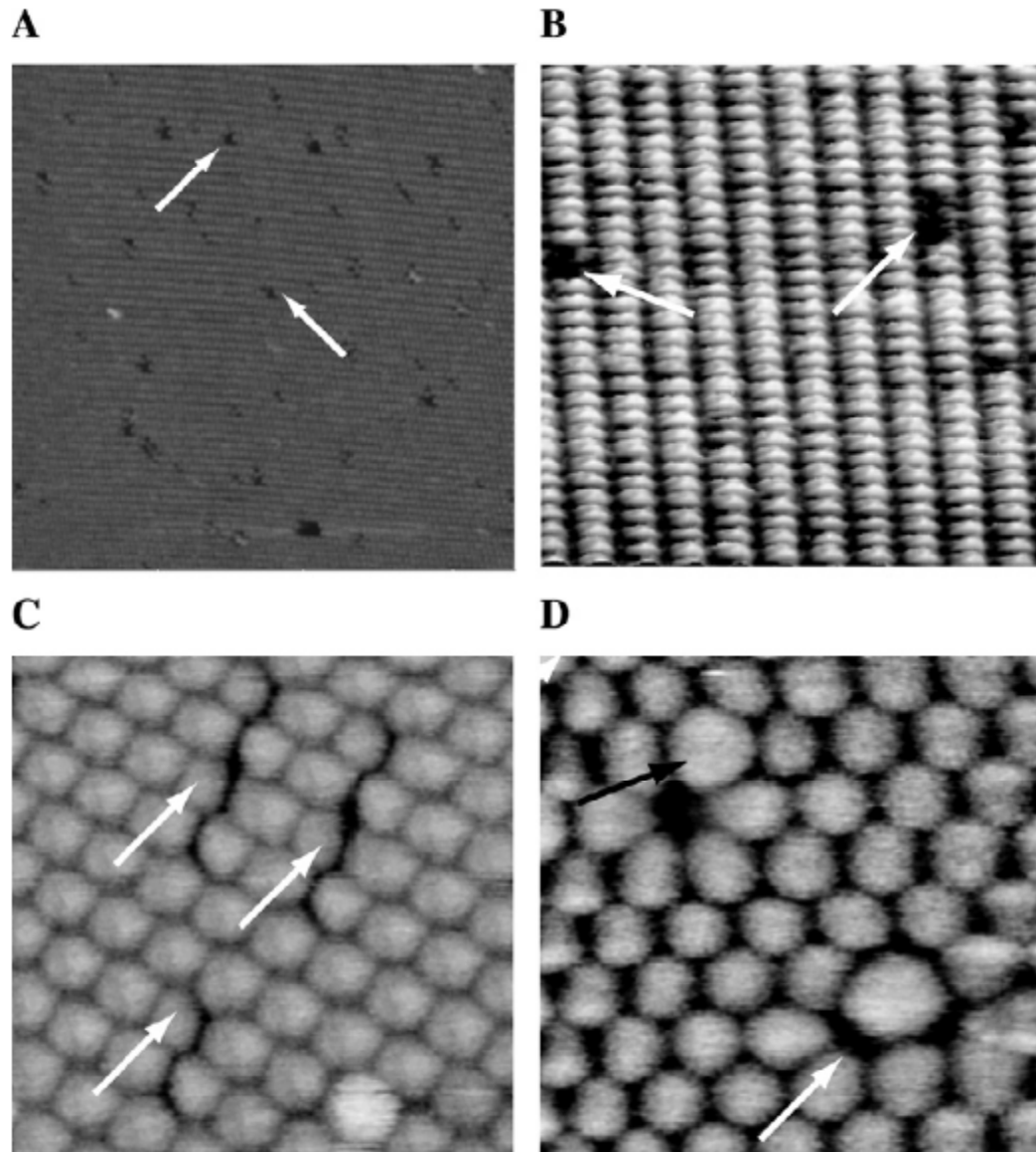
- Example: pyrrhotite:  $\text{Fe}_{(1-x)}\text{S}$  contains both  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$
- For charge balance  $3(\text{Fe}^{2+}) = 2(\text{Fe}^{3+}) + \square$   
where “ $\square$ ” represents an Fe-site that is vacant.
- Another way to represent the formula is:  $(\text{Fe}^{2+})_{1-3x}(\text{Fe}^{3+})_{2x}\square_x\text{S}$

# Point defects

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# Point defects under microscope



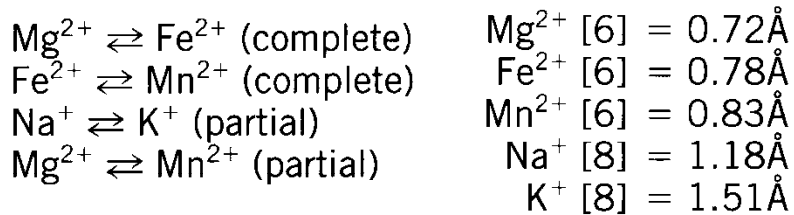
*A.J. Malkin, R.E. Thorne / Methods 34 (2004) 273–299*

Fig. 10. (A) Point defects in the crystalline lattice of CMV crystals. Two empty lattice sites (indicated with arrows) formed by missing virions ( $3.4 \times 3.4 \mu\text{m}$ ). (B) Vacancies of by one or more unit cells (indicated with arrows) on the surface of a thaumatin crystal ( $540 \times 540 \text{ nm}$ ). (C) Incorporation of abnormal CMV virions with diameters in the range of 22–26 nm (indicated with arrows) results in defect formation. (D) Incorporation of two abnormally large virions into the crystalline lattice. Anomalous particle incorporation can proceed either without visible defect formation, as in the example indicated by a white arrow, or with the formation of a point defect (where a black arrow indicates the aberrant particle).

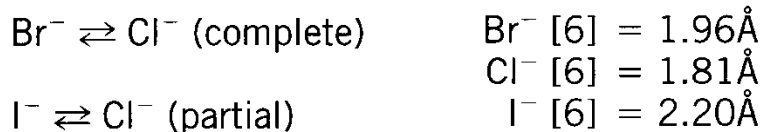
# Summary on substitution

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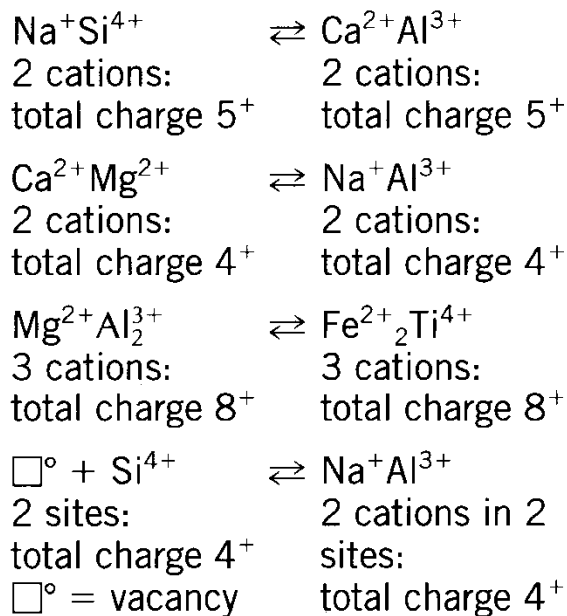
## Simple cationic:



## Simple anionic:



## Coupled cationic:



## Extent of solid solution:

complete at high temperature in plagioclase

limited, as in omphacite, a member of the pyroxene group

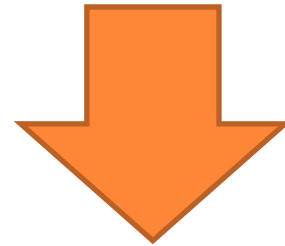
extensive, as in the spinel group

extensive, as in arfvedsonite, a sodium amphibole

# Summary on substitution

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- Simple substitution
  - Complete binary substitution
  - Coupled substitution
- Interstitial substitution
- Vacancy substitution



Varied composition

# Chemical composition

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## Isomorphs and derivative structures

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- Isomorphs: minerals that have same crystal structure but different chemical composition
- Example: berlinite is  $\text{AlPO}_4$  with the “quartz structure” (substitute  $\text{Si}^{4+} + \text{Si}^{4+} = \text{Al}^{3+} + \text{P}^{5+}$  )

## Isomorphs – Examples

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- $\text{KMg}_3(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$  - phlogopite
- $\text{K}(\text{Li,Al})_{2-3}(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$  – lepidolite
- $\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$  – muscovite

Amphiboles:

- $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$  – tremolite
  - $\text{Ca}_2(\text{Mg,Fe})_5\text{Si}_8\text{O}_{22}(\text{OH})_2$  – actinolite
- } Actinolite series minerals

$(\text{K,Na})_{0-1}(\text{Ca,Na,Fe,Mg})_2(\text{Mg,Fe,Al})_5(\text{Si,Al})_8\text{O}_{22}(\text{OH})_2$  – Hornblende

# From chemical composition to formula

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Or vice versa

## Reporting a mineral/rock composition

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- Element weight %: e.g. 5 g Fe in 100 g sample
- Oxide weight %: Majority of minerals contain large quantities of oxygen, e.g. silicates, oxides, carbonates
- Number of atoms → mineral chemical formula

Relating all elements to one: normalization

## From element wt% to formula – Example

A wet chemical analysis:

Na = 32.8 %

Al = 12.8 %

F = 54.4 %

What is the unknown mineral?

	wt	Atomic weight	wt / atomic weight	mole	normalization	mole ratio
Na	32.8	22.99	→ 32.8/22.99 →	1.4267	→ 1.4267/0.4744 →	3.007 ~3
Al	12.8	26.98	→ 12.8/26.98 →	0.4744	→ 0.4744/0.4744 →	1.000 ~1
F	54.4	19.00	→ 54.4/19.00 →	2.8631	→ 2.8631/0.4744 →	6.035 ~6



## Report as oxides

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- Mineral composition reported as oxides, e.g. Al as  $\text{Al}_2\text{O}_3$
- $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  often reported together as FeO (i.e., all  $\text{Fe}^{2+}$ )

### Conventional order

$\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{Cr}_2\text{O}_3$ , FeO

MnO, MgO, CaO, BaO,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ , F, Cl

## Between oxide and element wt% – Example

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Molecular weight:

$$\text{Mg} = 24.3 \quad \text{MgO} = 24.3 + 16 = 40.3$$

4.55 wt % Mg  $\rightarrow$  ?? wt% MgO

Step 1: Assuming 100 g of sample,  
mole of Mg:  $4.55 / 24.3 = 0.187$

Step 2: weight of MgO =  $40.3 \times 0.187 = 7.54$  g in 100g sample  
 $\rightarrow$  wt% = 7.54%

## From oxide wt% to formula – Example

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Again, assuming 100 g of sample

	wt%	m.w.		Moles oxide	Moles cation	Moles anion
SiO <sub>2</sub>	42.7	60.086	→ 42.7/60.086 →	0.7106	0.7106	1.4213
MgO	57.3	40.312	→ 57.3/40.312 →	1.4214	1.4214	1.4214
						<b>2.8427</b>

Atomic ratio

$$\text{Mg} : \text{Si} : \text{O} = 1.4214 : 0.7106 : 2.8427 = 2 : 1 : 4$$





## Step 1 - Moles of oxide

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	A	B	C
oxide	weight percent (g oxide / 100 g mineral)	Molecular weight (g oxide / mol oxide)	A / B (mol oxide / 100 g mineral)
<b>SiO<sub>2</sub></b>	48.0	60.084	0.80
<b>Al<sub>2</sub>O<sub>3</sub></b>	33.7	101.961	0.33
<b>CaO</b>	17.3	56.079	0.31
<b>Na<sub>2</sub>O</b>	0.63	61.9756	0.00
<b>K<sub>2</sub>O</b>	0.02	94.196	0.01
<b>Total</b>	99.7		

## Step 2 - Normalize Oxygens

	C	D	E
oxide	A / B (mol oxide / 100 g mineral)	Oxygen s / oxide	C * D (Oxygens / 100 g mineral)
<b>SiO<sub>2</sub></b>	0.80	2	1.598
<b>Al<sub>2</sub>O<sub>3</sub></b>	0.33	3	0.992
<b>CaO</b>	0.31	1	0.308
<b>Na<sub>2</sub>O</b>	0.00	1	0.000
<b>K<sub>2</sub>O</b>	0.01	1	0.010
<b>Total</b>			2.908

- 2.908 = Number of oxygens per 100 g mineral
- We know one formula unit of mineral contains 8 oxygens (for a feldspar)
- So we renormalize column E to eight total oxygens, giving us one formula unit of mineral.
- Multiply each value by the ratio:  
8 oxygens per formula unit  
/ 2.908 oxygens per 100 g mineral

## Step 2 - Normalize Oxygens

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	C	D	E	F
oxide	A / B (mol oxide / 100 g mineral)	Oxygens / oxide	C * D (Oxygens / 100 g mineral)	E * (8/2.908) (Oxygens / formula unit)
<b>SiO<sub>2</sub></b>	0.80	2	1.598	4.395
<b>Al<sub>2</sub>O<sub>3</sub></b>	0.33	3	0.992	2.728
<b>CaO</b>	0.31	1	0.308	0.849
<b>Na<sub>2</sub>O</b>	0.00	1	0.000	0.001
<b>K<sub>2</sub>O</b>	0.01	1	0.010	0.028
<b>Total</b>			2.908	8.000

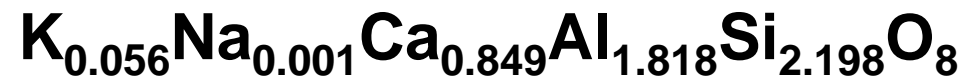
## Step 3 - Calculate Cations

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	D	F	G	H
oxide	Ox / oxide	$E * (8/2.908)$ (Oxygens / formula unit)	Cations / oxide	$(F/D)*G$ (Cations / formula unit)
<b>SiO<sub>2</sub></b>	2	4.395	1	2.198
<b>Al<sub>2</sub>O<sub>3</sub></b>	3	2.728	2	1.818
<b>CaO</b>	1	0.849	1	0.849
<b>Na<sub>2</sub>O</b>	1	0.001	2	0.001
<b>K<sub>2</sub>O</b>	1	0.028	2	0.056
<b>Total</b>		8.000		4.922

## Step 4 - Allocate cations to sites

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	H
oxide	(F/D)*G (Cations / formula unit)
<b>SiO<sub>2</sub></b>	2.198
<b>Al<sub>2</sub>O<sub>3</sub></b>	1.818
<b>CaO</b>	0.849
<b>Na<sub>2</sub>O</b>	0.001
<b>K<sub>2</sub>O</b>	0.056