

Goldschmidt's rules

2. If 2 ions have a similar radius and the same valence: the smaller ion is preferentially incorporated into the solid over the liquid

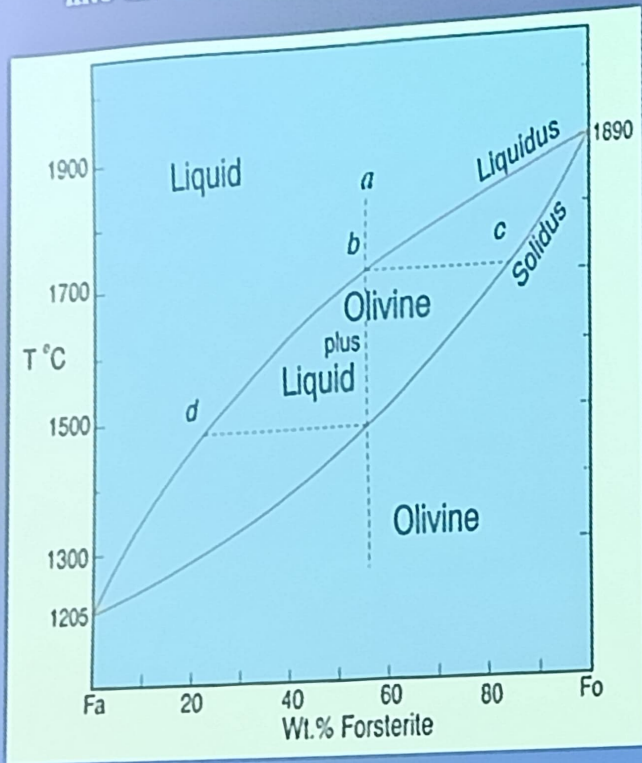


Fig. 6.10 Isobaric T-X phase diagram at atmospheric pressure After Bowen and Shairer (1932), Amer. J. Sci. 5th Ser., **24**, 177-213. From Winter (2001) An Introduction to Igneous and Metamorphic Petrology. Prentice Hall

smaller ion preferentially \rightarrow solid (Mg is smaller than Fe so more Mg in Ol than in melt)

3. If 2 ions have a similar radius, but different valence: the ion with the higher charge is preferentially incorporated into the solid over the liquid
4. Whenever a substitution is possible between two ions with significantly different electro negativities ($\Delta > 0.1$), the ion whose electronegativity is closer to that of the ion it is substituting will be preferentially incorporated

Goldschmidt's rules originate from a simple ionic model whereby solids (minerals) are viewed as an array of cations and anions with attractive and repulsive forces - **CONTROLS LATTICE ENERGY**

The concept of lattice energy, U , is a measure of the forces within an ionic crystal

It is a sum of attractive and repulsive forces

We have,

$$U = N_A \left[-\frac{MZ_1Z_2e^2}{4\pi\epsilon_0 r} + \frac{B}{r^n} \right] \quad \& \quad B = \frac{MZ_1Z_2e^2 r_0^{n-1}}{4\pi\epsilon_0 n}$$

Substituting the value of B and putting $r = r_0$

$$U_0 = N_A \left[-\frac{MZ_1Z_2e^2}{4\pi\epsilon_0 r_0} + \frac{1}{r_0^n} \frac{MZ_1Z_2e^2 r_0^{n-1}}{4\pi\epsilon_0 n} \right]$$

$$\text{or,} \quad U_0 = N_A \left[-\frac{MZ_1Z_2e^2}{4\pi\epsilon_0 r_0} + \frac{MZ_1Z_2e^2}{4\pi\epsilon_0 r_0 n} \right]$$

$$U_0 = -\frac{N_A MZ_1Z_2e^2}{4\pi\epsilon_0 r_0} \left(1 - \frac{1}{n} \right) \quad \text{Where,} \quad U_0 = \text{lattice energy}$$

Derivation of Born-Landé equation

Applying the minimization condition, $\frac{dU(r)}{dr} = 0$, then $r = r_0$

$$\frac{dU(r)}{dr} = \frac{z^2 e^2}{4\pi\epsilon_0 r^2} A - \frac{nB}{r^{n+1}} = 0$$

$$r_0 = \left(\frac{4\pi\epsilon_0 n B}{z^2 e^2 A} \right)^{\frac{1}{n-1}}$$

$$B = \frac{z^2 e^2 A}{4\pi\epsilon_0 n} r_0^{n-1}$$

$$U(r_0) = -\frac{Az^2 e^2}{4\pi\epsilon_0 r_0} \left(1 - \frac{1}{n} \right)$$

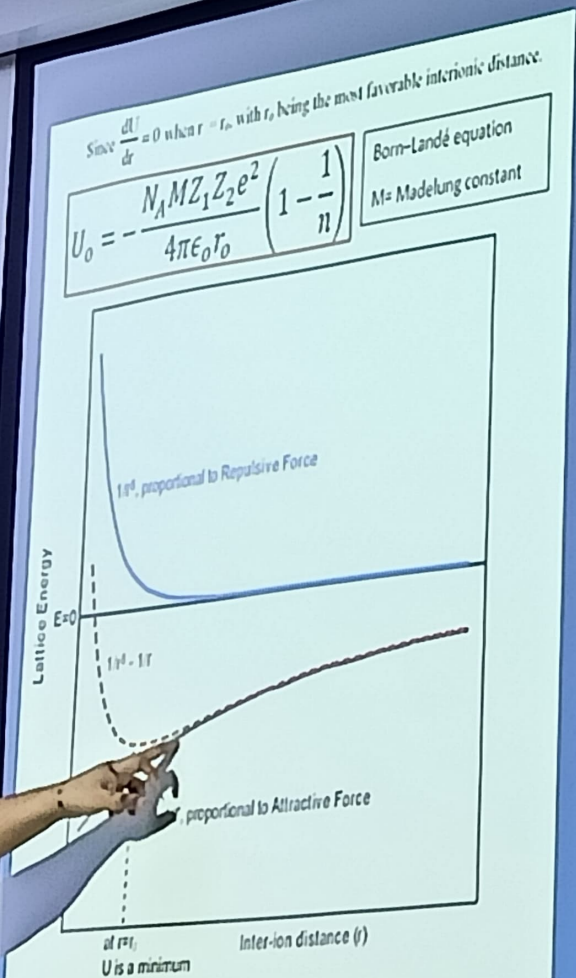
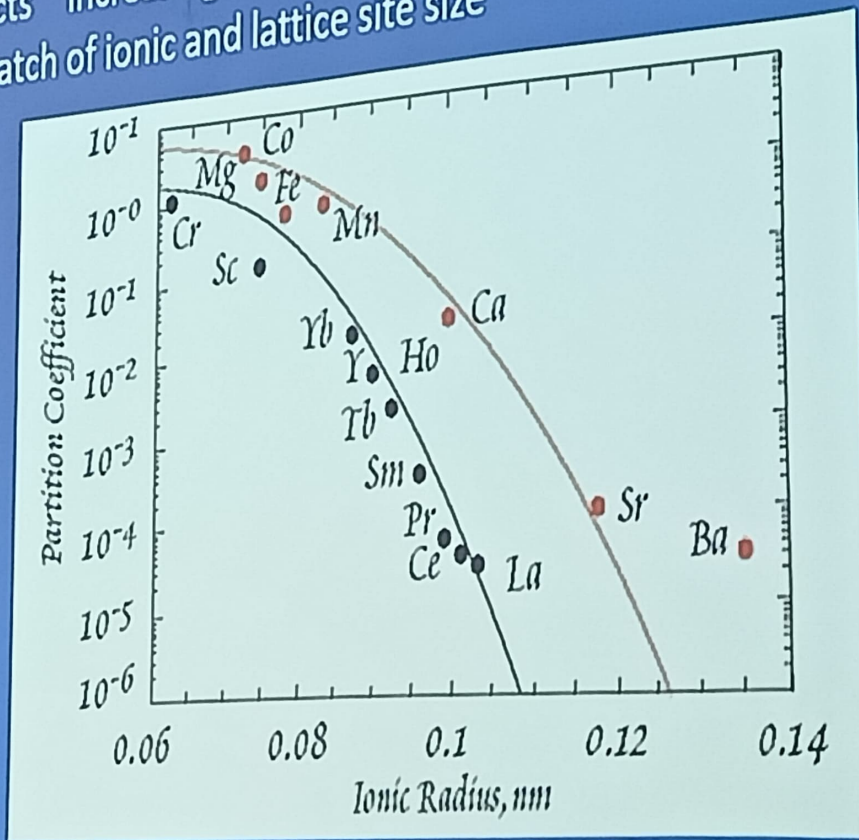


Figure 4: A plot of the two terms in the Lattice Energy equation, i.e. the attractive force varying as $1/r$ and the electron repulsion force varying as $1/r^4$, showing that there is an interionic distance (r_0) where the lattice energy is a minimum.

- Mineral-melt partition coefficients for series of isovalent cations show near-parabolic smooth dependence on cation radius—**Onuma curves**
- Curves for elements having different ionic charge tend to be parallel to each other for the same mineral—melt system
- Reflects increasing lattice strain with increasing mismatch of ionic and lattice site size



Onuma curves explained through

Lattice strain model: The lattice strain model assumes that the principal energetic term controlling the incorporation of a misfit cation into a lattice site is the elastic strain energy, ΔG_{strain} required to displace the surrounding atoms. The expression representing this strain energy is:

$$\Delta G_{\text{strain}} = 4\pi EN_A \left[\frac{r_0}{2} (r_i - r_0)^2 + \frac{1}{3} (r_i - r_0)^3 \right] \quad (1)$$

where r_0 is the radius of the crystallographic site, r_i is the radius of the substituent cation, N_A is Avogadro's number and E is the Young's modulus of the site. Blundy and Wood (1994) assumed ΔG_{strain} to be the dominant energy term determining mineral-melt partitioning and linked the partition coefficient for element i , D_i , to ΔG_{strain} as follows

$$D_i = D_0 \exp \left(\frac{-4\pi EN_A \left[\frac{r_0}{2} (r_i - r_0)^2 + \frac{1}{3} (r_i - r_0)^3 \right]}{RT} \right) \quad (2)$$

where D_0 is the partition coefficient for an element with ideal radius r_0 . We have fitted equation (2) to all REE data reported

Also lattice energy is at a minimum in a system of spherical ions when each ion is surrounded by as many ions of opposite charge as possible

This increases the attractive forces relative to the repulsive forces, thereby lowering the lattice energy

Use of Ionic radii to predict coordination number of cations in silicate minerals

Cation coordination number (CN) for silicate minerals is the number of oxygen anions surrounding a cation

If we assume that 1) cations and anions are rigid spheres, and 2) ionic radii are constant, the concept of **radius ratio (Pauling's first rule)**

i.e. (cation ionic radii) / (oxygen ionic radii) can be used to predict cation coordination number

Radius ratio	Anion arrangement around cation	Cation coordination number	Example
<0.155	Linear	2	
0.155 to 0.225	Corners of equilateral triangle	3	B ₂ CO ₃
0.225 to 0.414	Corners of tetrahedron	4	ZnS, CuCl
0.414 to 0.732	Octahedral	6	NaCl, MgO
0.732-1.0	Cubic		CsCl
>1	Midpoint of cube edges	12 (close packing)	

Major element	Substituting trace element
Si	Ge, P
Ti	V
Al	Ga
Fe	Cr, Co, Ni
Mg	Cr, Co, Ni
Ca	Sr, Eu, REE
Na	Eu
K	Rb, Ba, Sr, Eu

We now know that Goldschmidt's Rules are not rigorously correct:

- (1) We have learnt that for a given structural site in a mineral, there is an optimal ionic radius and ions that are too large or too small are less readily incorporated into the mineral than an ion of optimal size
- (2) Highly charged ions not always preferentially incorporated into solids, e.g., there are charge balance considerations
- (3) Partitioning involves two phases, and in solid-melt partitioning, the effects of melt composition cannot be ignored; Goldschmidt's Rules consider only the crystal phase
- (4) In fluids, the partitioning of trace elements is often controlled by the complexation/chelation characteristics of the cation. This is primarily controlled by the electronic configuration and not the ionic charge and radius

Trace element fractionation during partial melting and crystallization

- **Batch Melting**

- Equilibrium partial melting

Melt continuously reacts & equilibrates with the solid residue at the site of melting until mechanical conditions allow it to escape as a single 'batch' of magma

Batch melting can be modal and non modal

- Modal batch melting

Minerals melt in the proportion in which they exist in the rock

- Non modal batch melting

Minerals melt in a proportion different from that of their mode in the rock

Batch melting equation-derivation

C_L = concentration of element in melt

C_O = starting concentration of element in un-melted source

C_S = concentration of element in un-melted residue

F = weight fraction of melt produced (wt. of melt/wt. of melt + wt. of residual rock)

For closed system equilibrium melting, simple mass balance between the phases yields:

$$C_O = F * C_L + (1-F) * C_S$$

$$\text{Since } D_{RS} = C_S / C_L$$

$$\text{So, } C_S = D_{RS} * C_L$$

Substituting C_S in the mass balance equation gives:

$$C_O = F * C_L + (1-F) * D_{RS} * C_L$$

$$C_O = C_L [F + (1-F) * D_{RS}]$$

$$C_L / C_O = 1 / [F + (1-F) * D_{RS}]$$

$$C_L / C_O = 1 / [F + D_{RS} - F * D_{RS}]$$

$$C_L / C_O = 1 / [F * (1 - D_{RS}) + D_{RS}]$$

$$\frac{C_L}{C_O} = \frac{1}{D_{RS}(1-F) + F}$$

$$C_S / C_O = D_{RS} / [D_{RS} + F (1 - D_{RS})] \quad D_{RS} \rightarrow \text{bulk partition co-efficient of residual solid}$$