# Major and trace Element Geochemistry

Major Elements

- Comprise most of the rock, determines the proportions of rock-forming minerals such as feldspar, quartz, micas, olivine, pyroxenes and amphiboles

- Concentration in rock > 0.1wt. %

- 11 elements make up more than 99% of BSE: O, Na, Mg, Al, Si, P, K, Ca, Ti, Mn and Fe

Trace elements

- Concentration < 0.1 wt. %
- Not stoichiometric constituents of phases

- Do not affect chemical or physical properties of the system significantly

- Obey Henrys law (dilute solutions)

Fig. 1
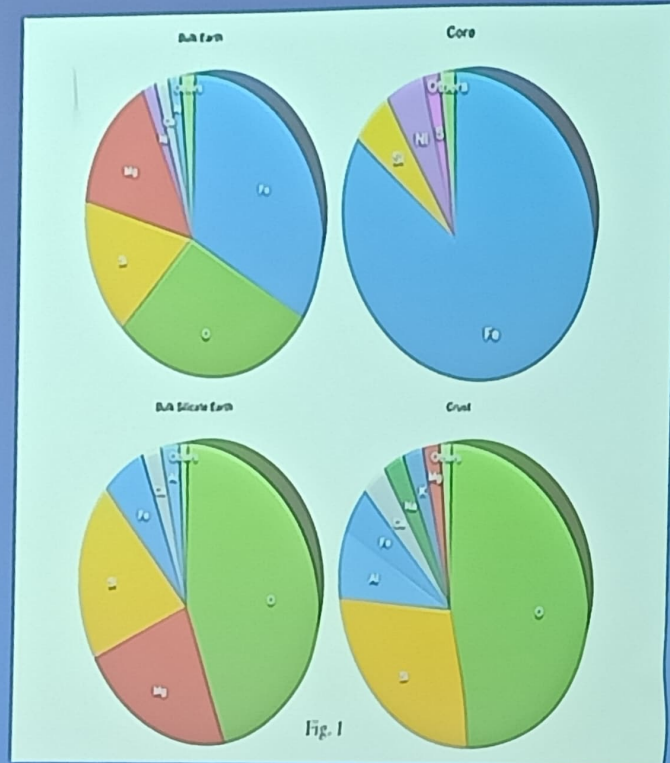
Incorporation of trace elements in minerals

Figure by MIT OpenCourseWare

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1. Direct substitution of TE into specific structural sites of minerals: e.g., Ni^{+2} in the site that contains Mg^{+2} in Mg_2SiO_4

2. Substitution in defect sites: Minerals do not have perfect arrangement of cations and anions, and there are defect sites such as:
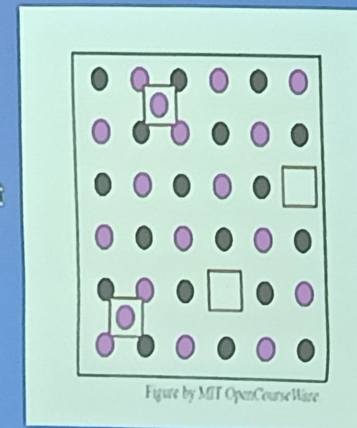
- Schottky defect: vacancy within the lattice created by transferring an atom from interior of crystal to the surface of the crystal

- Frenkel defect: whereby an atom is transferred to an interstitial position. These vacancies can be occupied by TE

Schottky defect

Figure by MIT OpenCourseWare

Frenkel defect

Figure by MIT OpenCourseWare
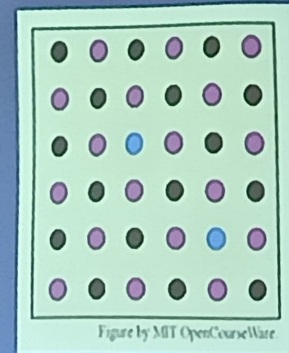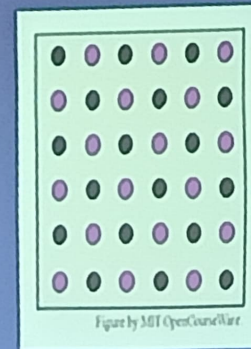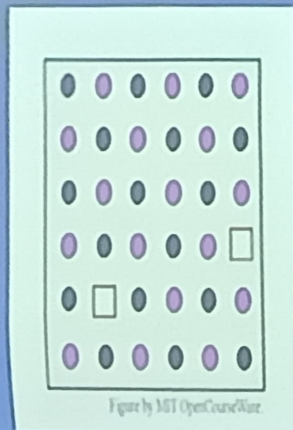
3. **Inclusions in minerals:** These may be melt, fluid or solid inclusions trapped within a growing mineral

Figure by MIT OpenCourseWare

Inclusions are not structural constituents

When inclusions can be recognized there are no problems in data interpretation, but it is likely that some inclusions are too small to readily recognize.

Figure by MIT OpenCourseWare
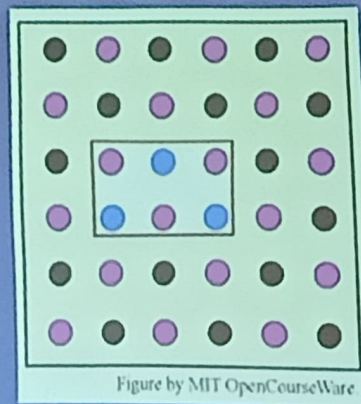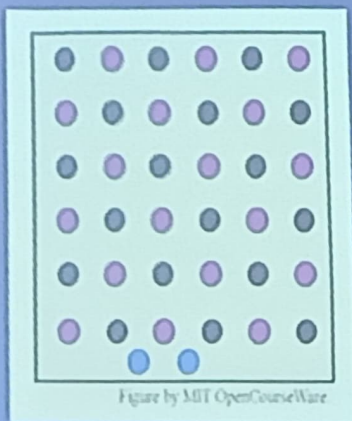
Adsorption on surfaces: The surfaces of phases have different bonding characteristics than interiors of phases, so grain boundaries may have different TE concentrations than the interiors

This can be evaluated by mild acid-leaching of silicate phases with analyses prior to and subsequent to leaching. Example: adsorption of Cu, Pb, Zn on FeO(OH) [goethite]

	Adsorption	Ion exchange	Surface reduction/oxidation
Surface Adsorption	Inner-sphere Outer-sphere	$\Leftrightarrow Cd^{2+}$	Metal redox Biodegradation
Structural Incorporation	Coprecipitation (amorphous) $Fe(OH)_3$-$H_xAs^VO_4$	Solid solution (crystalline) Apatite $Ca_5(PO_4)_3(OH, F, Cl)$	Micro-encapsulation Nanoparticle precipitation

Classification of element based on their geochemical affinity (Goldschmidt's classification)

- Siderophile → affinity for metal (usually Fe)
- Chalcophile → affinity for sulfide
- Lithophile → affinity for silicate
- Atmophile → extremely volatile elements → concentrated in hydrosphere and atmosphere

Table 7.1. Goldschmidt's Classification of the Elements

Siderophile	Chalcophile	Lithophile	Atmophile
Fe*, Co*, Ni*	(Cu), Ag	Li, Na, K, Rb, Cs	(H), N, (O)
Ru, Rh, Pd	Zn, Cd, Hg	Be, Mg, Ca, Sr, Ba	He, Ne, Ar, Kr, Xe
Os, Ir, Pt	Ga, In, Tl	B, Al, Sc, Y, REE	
Au, Re‡, Mo‡	(Ge), (Sn), Pb	Si, Ti, Zr, Hf, Th	
Ge*, Sn*, W‡	(As), (Sb), Bi	P, V, Nb, Ta	
Cl, Cu*, Ga*	S, Se, Te	O, Cr, U	
Ge*, As‡, Sb‡	(Fe), Mo, (Os)	H, F, Cl, Br, I	
	(Ru), (Rh), (Pd)	(Fe), Mn, (Zn), (Ga)	

*Chalcophile and lithophile in the earth's crust
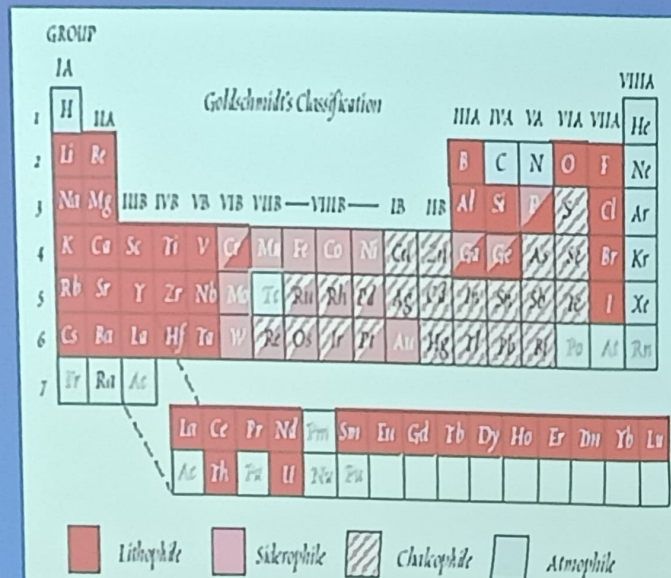‡Chalcophile in the earth's crust
‡Lithophile in the earth's crust

Figure 7.2. Goldschmidt's classification of the elements.

Classification of elements based on compatibility in mantle minerals

Elements can be classified into two groups based on their compatibility in mantle minerals during mantle melting.

Compatible elements → Mantle minerals (olivine, pyroxene, anorthite, spinel and garnet) are made up of Si, Al, Fe, Mg and Ca. These are the MRFE field (Mantle Rock Forming Elements). Include trace elements (Ni, Cr, Co, Cu, Ti, Sc, V, Co and Zn) readily incorporated in the lattice sites of mantle minerals (typically first series transition metals)—COMPATIBLE elements

Incompatible elements → Elements whose charge or size differs significantly from that of available lattice sites in mantle minerals and which are therefore not incorporated in mantle minerals are called INCOMPATIBLE elements → partition into the melt phase

Two subgroups:
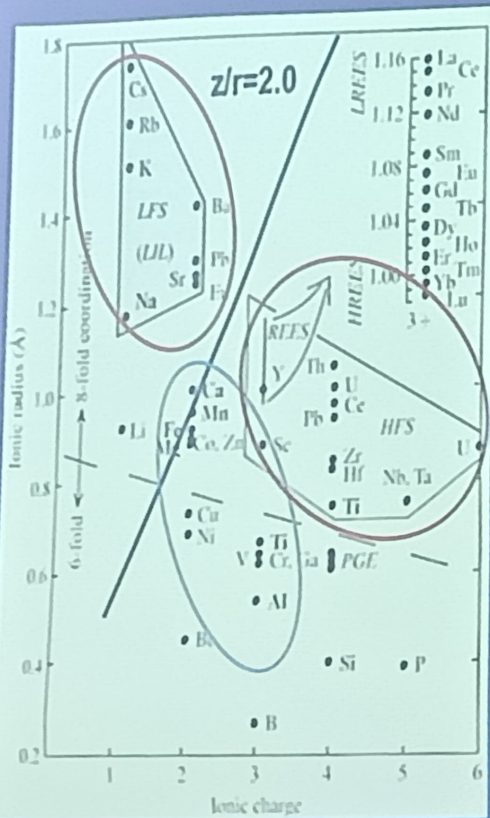HFSE (e.g., Zr, Hf, Nb, Ta, REE)
LFSE/ LILE (e.g., K, Rb, Cs, Ba, Sr)
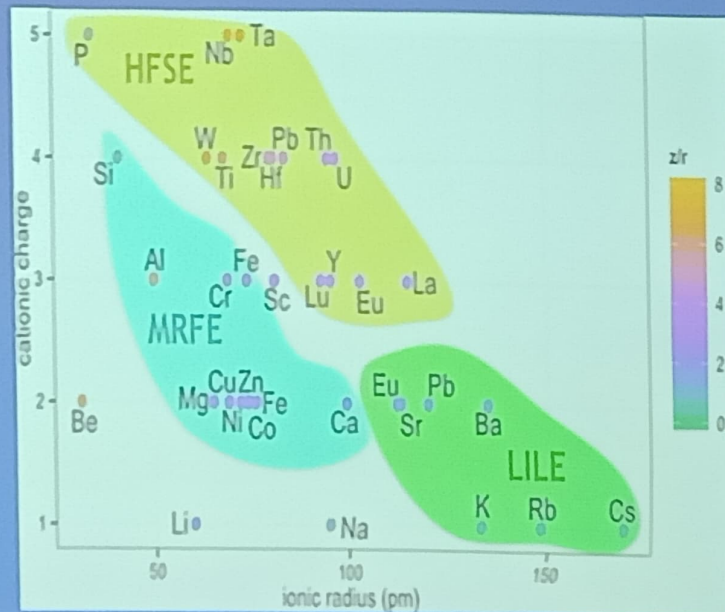
Classification of elements on the basis of ionic potential

Ionic potential (IP) = Ionic charge / Ionic radius
- Rough index for mobility (solubility) in aqueous solutions: Low ionic potential → more mobile

(1) MRFE: low ionic charge and radius-elements Si, Al, Fe, Mg, Ca making up olivine, pyroxene, anorthite, spinel and garnet (mantle peridotite) + trace elements (Ni, Cr, Co, Cu, Zn) incorporated in these minerals

(2) LFSE/LILE (IP<2): lithophile trace elements having a large ionic radius to charge ratio (ionic radii greater than those of Ca^{2+} and Na^{1+}). By this definition, LILE are K, Rb, Cs, Sr, Ba, Pb and Eu^{+2}

(3) HFSE (IP>2): due to high charge, typically incompatible. Usually HFSE is used to designate Ti, Zr, Hf, Nb, Ta, REE, U, and Th

Thermodynamic considerations of TE solid solutions

1) Thermodynamic considerations show that TE are soluble to variable extents in different phases

2) Important characteristics of solutions involving TE in minerals:

(a) TE often strongly prefers a specific phase and display order of magnitude variation in abundance in co-existing phases

Large abundance variation significantly exceeds that of most major elements in rocks. This makes TE more sensitive monitors of igneous differentiation processes.
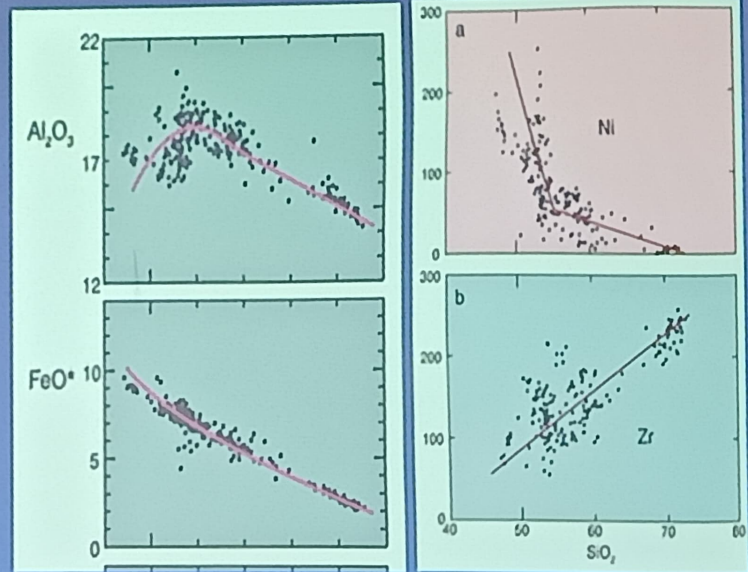
For example, consider partitioning of TE in a partially molten basaltic system composed of co-existing melt, olivine, plagioclase and clinopyroxene. At equilibrium we will find that La and Th are concentrated in melt, Ni in olivine, Sr in plagioclase, and Sc in clinopyroxene

(b) TE solutions are non-ideal and obey Henrys law

Ideal Solutions: A solution is ideal if the activity of every component (i) in phase (j) is proportional to its mole fraction/partial pressure ($a_i^j = x_i^j$) **(Obey RAOULT'S LAW)**

Thus, the chemical potential (μ) of every component (i) in phase (j) is a linear function of the natural log of its mole fraction, (x_i) i.e.

$$\mu_i^j = \mu_i^{j0} + RT \ln x_i^j$$

μ_i^{j0} = chemical potential at some standard state

Three characteristics of ideal behavior are:

(1) $\Delta H_{mix} = 0$, i.e., no heat released upon mixing

(2) $\Delta V_{mix} = 0$, i.e., no volume change upon mixing

(3) Raoult's law is valid; i.e., $a_i^j = x_i^j$, where i = element, j = phase, x = mole fraction, a = activity

Non-ideal behavior follows Henry's law at low con, and Ideal behavior at high con

If there are two components A and B forming an ideal solution, then A—A, B—B, and A—B interactions would have similar energies
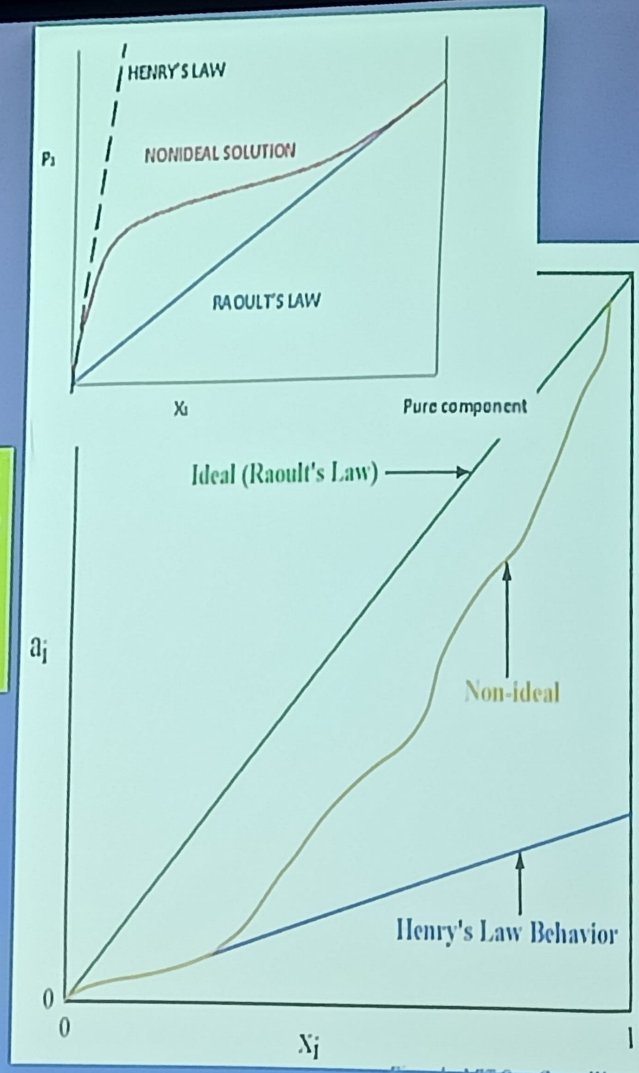
Non-ideal solutions: A factor must be introduced to account for non-ideal behavior. It is γ_i, the activity coefficient, in the relationship $a_i^j = \gamma_i^j x_i^j$ so that

$$\mu_i^j = \mu_i^{j0} + RT \ln a_i^j = RT \ln \gamma_i^j x_i^j$$

In a non-ideal solution of two components A and B, A— A interactions and B—B interaction energies would be different from A—B interaction energies

Dilute solutions-a special type of non-ideal behavior: By definition a trace element forms dilute solutions when Henry's Law is obeyed, i.e.

$a_i^j = k_i^j x_i^j$ as x_i^j tends towards 0