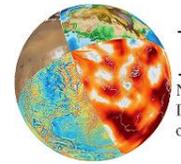




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**DEEP**  
Norwegian Research School for  
Dynamics and Evolution  
of Earth and Planets

# Geochemical constraints

From crystallography to the geochemical evolution of the planet

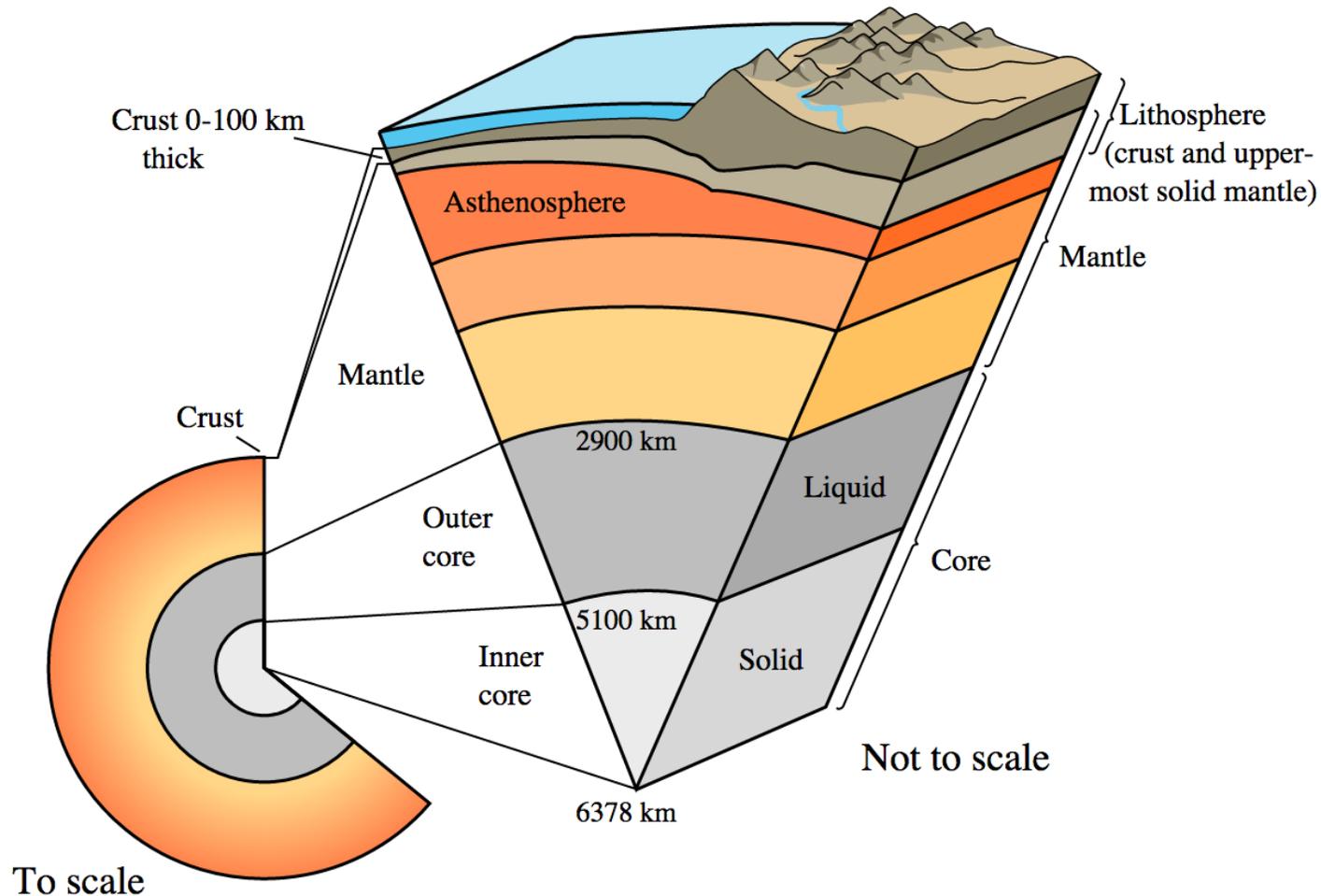
Maria Telmon, UiT – The Arctic University of Norway

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- Introduction – the Earth interior and differentiation
- How geologists use chemistry – major elements
- How geologists use chemistry – minor and trace elements
  - The Partition coefficient and its application
  - The REEs
- (How geologists use chemistry – isotopes)
- Lithosphere vs Asthenosphere

# How geologists use chemistry – introduction

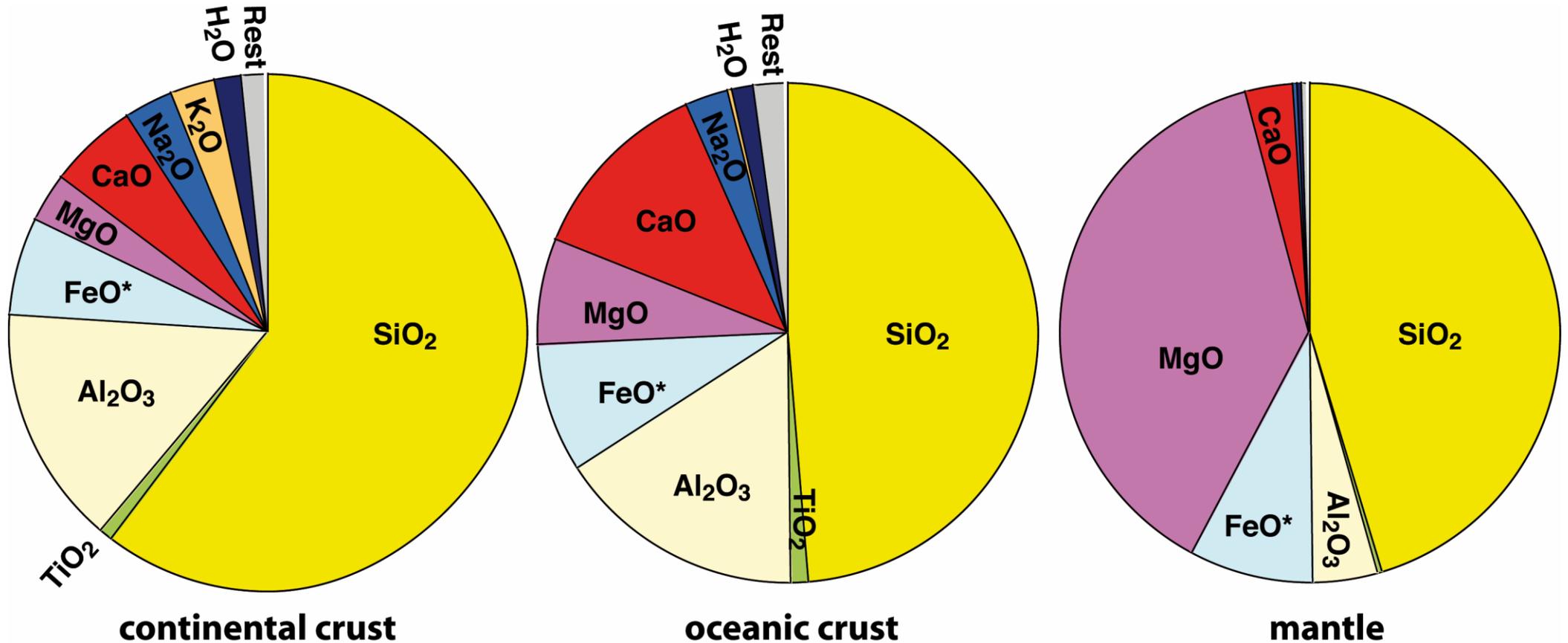
We know that the Earth has a certain internal structure:



But why? And what does it imply?

# How geologists use chemistry – introduction

Because the Earth underwent differentiation some Ga ago..



Differentiation pattern



# How geologists use chemistry – major elements

Differentiation affected the element abundances and distribution on the Earth:

| Element | Wt % Oxide | Atom % |
|---------|------------|--------|
| O       |            | 60.8   |
| Si      | 59.3       | 21.2   |
| Al      | 15.3       | 6.4    |
| Fe      | 7.5        | 2.2    |
| Ca      | 6.9        | 2.6    |
| Mg      | 4.5        | 2.4    |
| Na      | 2.8        | 1.9    |

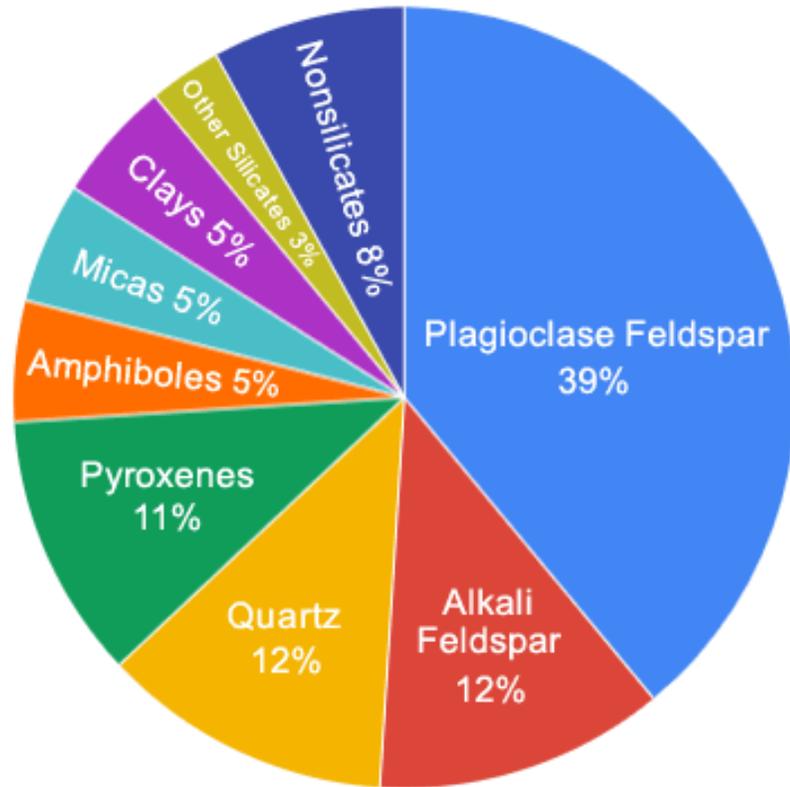
Element abundances on the Earth's crust

- **Major elements: > 1 wt%**  
SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, FeO\*, MgO, CaO, Na<sub>2</sub>O, K<sub>2</sub>O, H<sub>2</sub>O
- **Minor elements: 0.1 -1 wt %**  
TiO<sub>2</sub>, MnO, P<sub>2</sub>O<sub>5</sub>, CO<sub>2</sub>
- **Trace elements < 0.1 wt% (ppm)**

# How geologists use chemistry – major elements

Abundance of the elements reflects the mineral assemblages:

Most Abundant Minerals in Earth's Crust



The rock forming minerals all contain Oxygen (O) and/or Silicon (Si).

Most of them are organized in **Silicates**, assemblages of Si and O (the Silica;  $\text{SiO}_4$ ) and other elements that can fit the **crystal lattice**.

*isolated  
silicate  
structure*



example:  
**olivine**

*single  
chain  
structure*



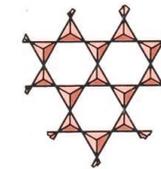
example:  
**pyroxenes**  
(augite is most common)

*double  
chain  
structure*



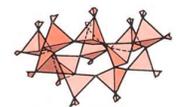
example:  
**amphiboles**  
(hornblende is most common)

*sheet  
silicate  
structure*



example:  
**micas**  
(biotite & muscovite are most common)  
& clay minerals

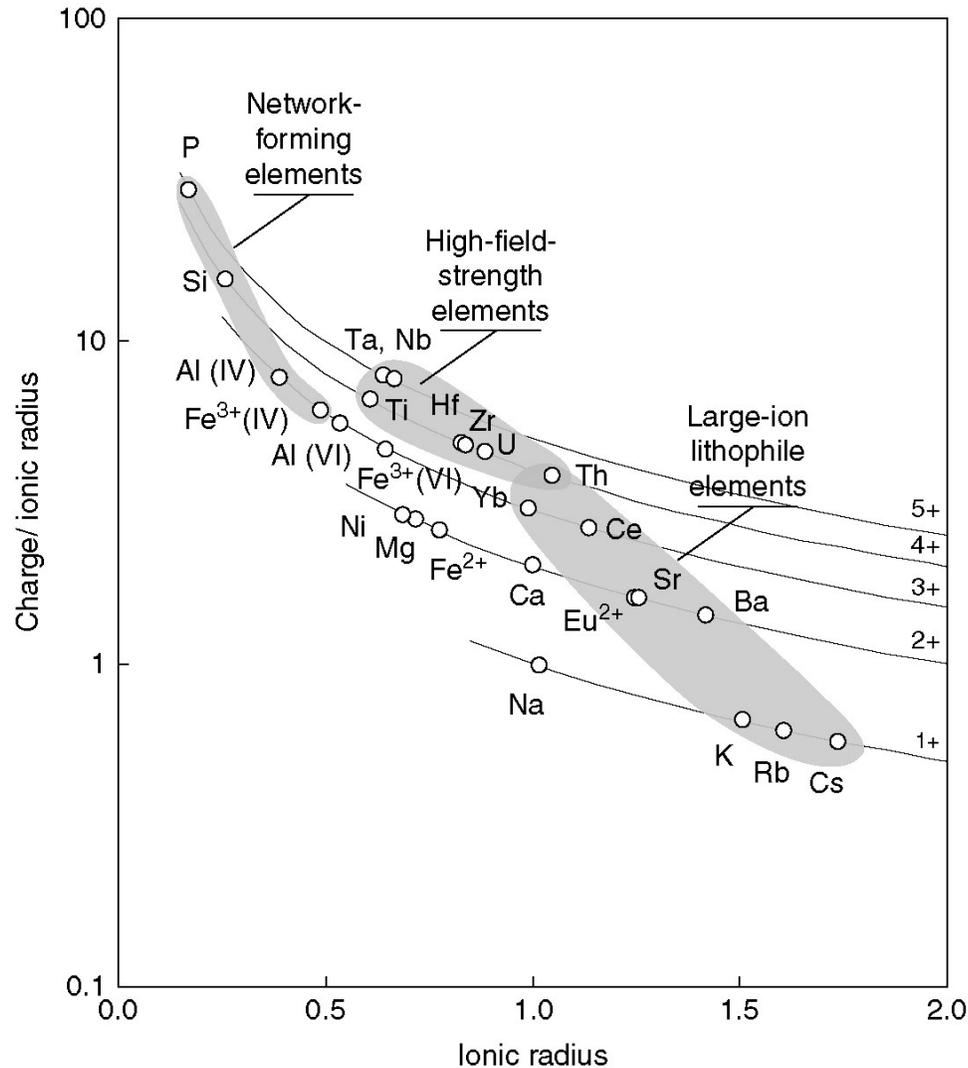
*framework  
silicate  
structure*



examples:  
**feldspar**  
(plagioclase, K-feldspar)  
& quartz

# How geologists use chemistry – major elements

The better fit of the elements in the crystal lattice is related to their **ionic radius**:



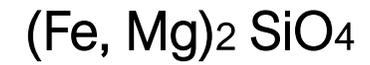
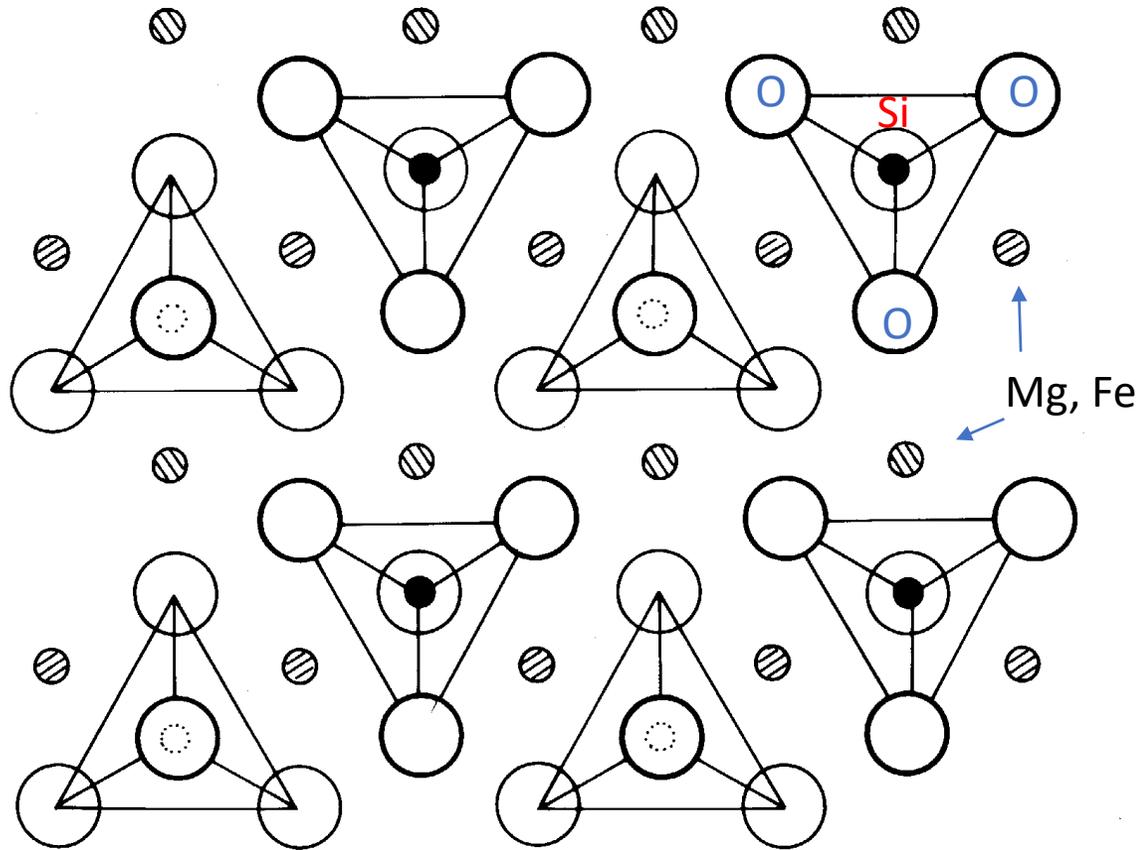
The graph gives us **two important pieces of information**:

1. Which **ion** can fit the specific internal structure of the mineral;
2. Which ion can substitute a **major element** in a certain structure.

Generally, one ion will readily substitute for another if the radii are within about 15% of one another, and if the valences are not different by more than one unit.

# How geologists use chemistry – major elements

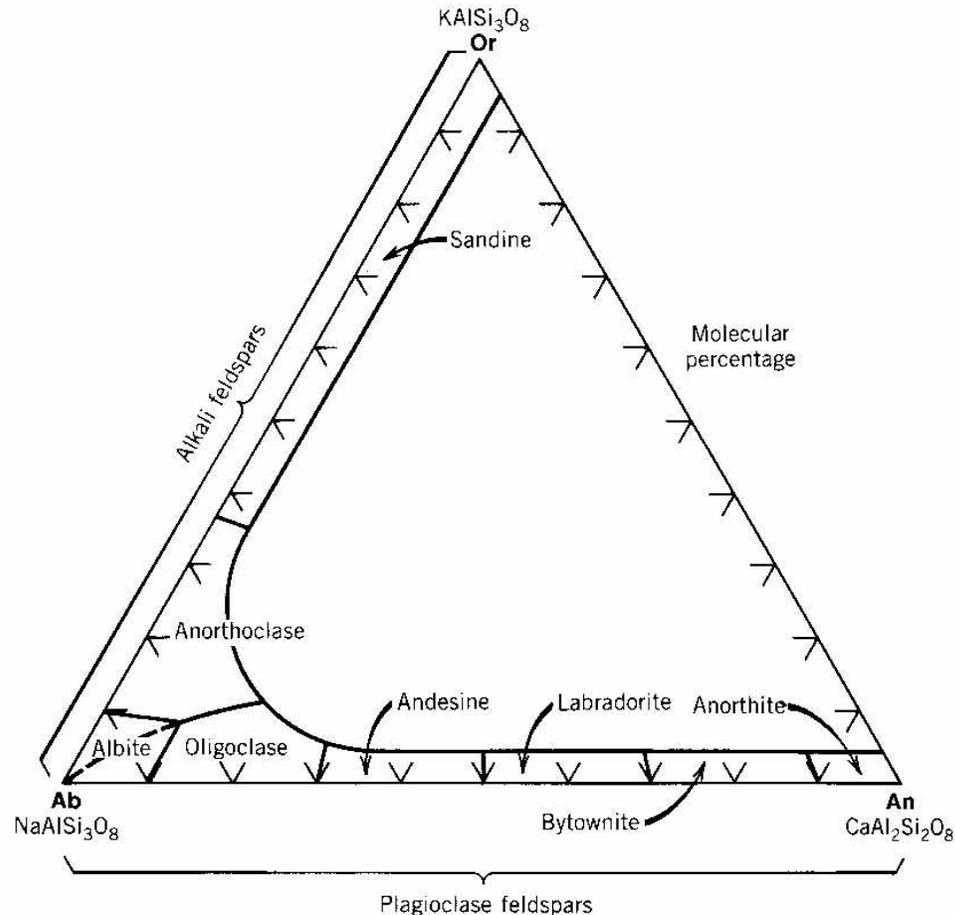
The example of Olivine:



The major elements govern the appearance of a phase

# How geologists use chemistry – major elements

## The example of Plagioclase:



**Albite** ( $\text{NaAlSi}_3\text{O}_8$ ) and **Anorthite** ( $\text{CaAl}_2\text{Si}_2\text{O}_8$ )

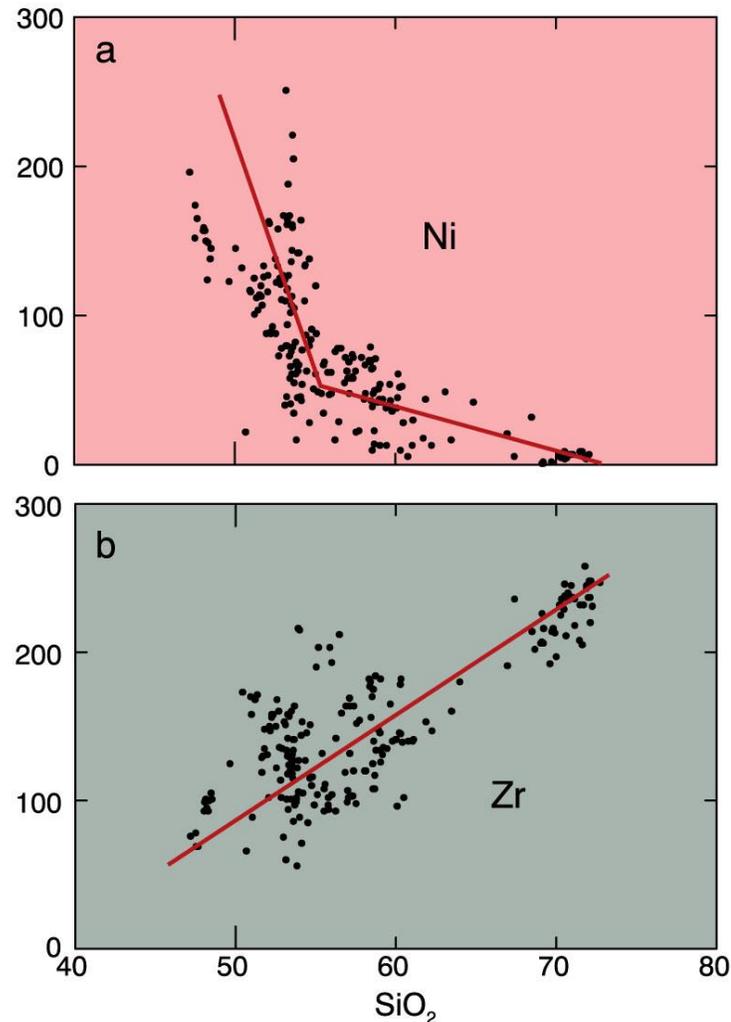


Double substitution of Sodium and one of the Silicons for Calcium and Aluminum (similar radii).

Valence differences also compensate:  $\text{Na}^+$  and  $\text{Si}^{4+}$  have the same positive valence as  $\text{Ca}^{2+}$  and  $\text{Al}^{3+}$ .

# How geologists use chemistry – trace elements

Also a trace element can enter a mineral phase by substitution:



1. Trace elements **do not govern** the appearance of a phase (E.g. Not like Mg or Fe in Olivine, or K in K-Feldspar)
2. Their distribution follows **certain rules**
3. Trace elements to help unravel the histories of igneous rocks.

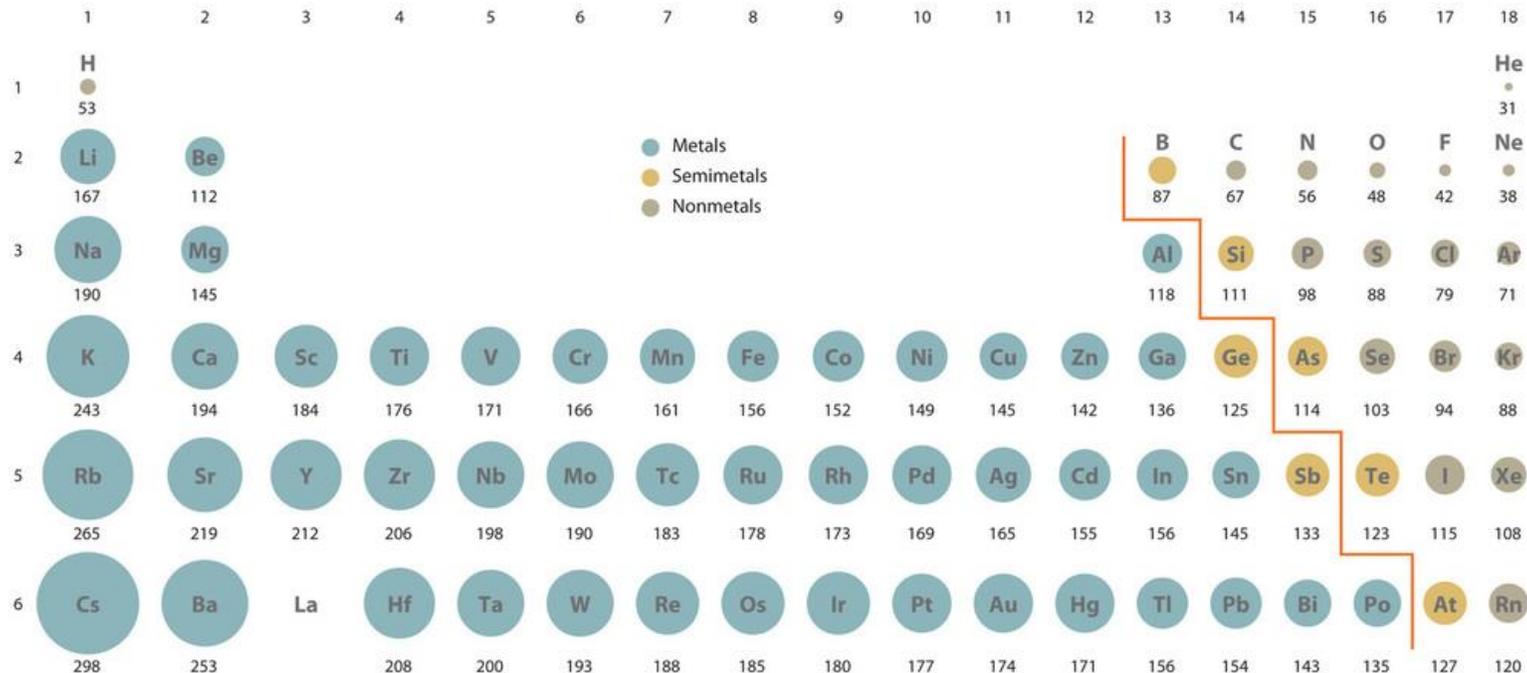
<https://www.science.smith.edu/~jbrady/petrology/igrocks-topics/trace/trace-figure00.php>

# How geologists use chemistry – trace elements

## Goldschmidt's Rules :

1. Two cations with the **same valence & ionic radius** exchange easily and enter a solid solution in amounts equal to their overall proportions:

Rb→K, Sr→Ca, Eu→Ca, Ni→Mg...



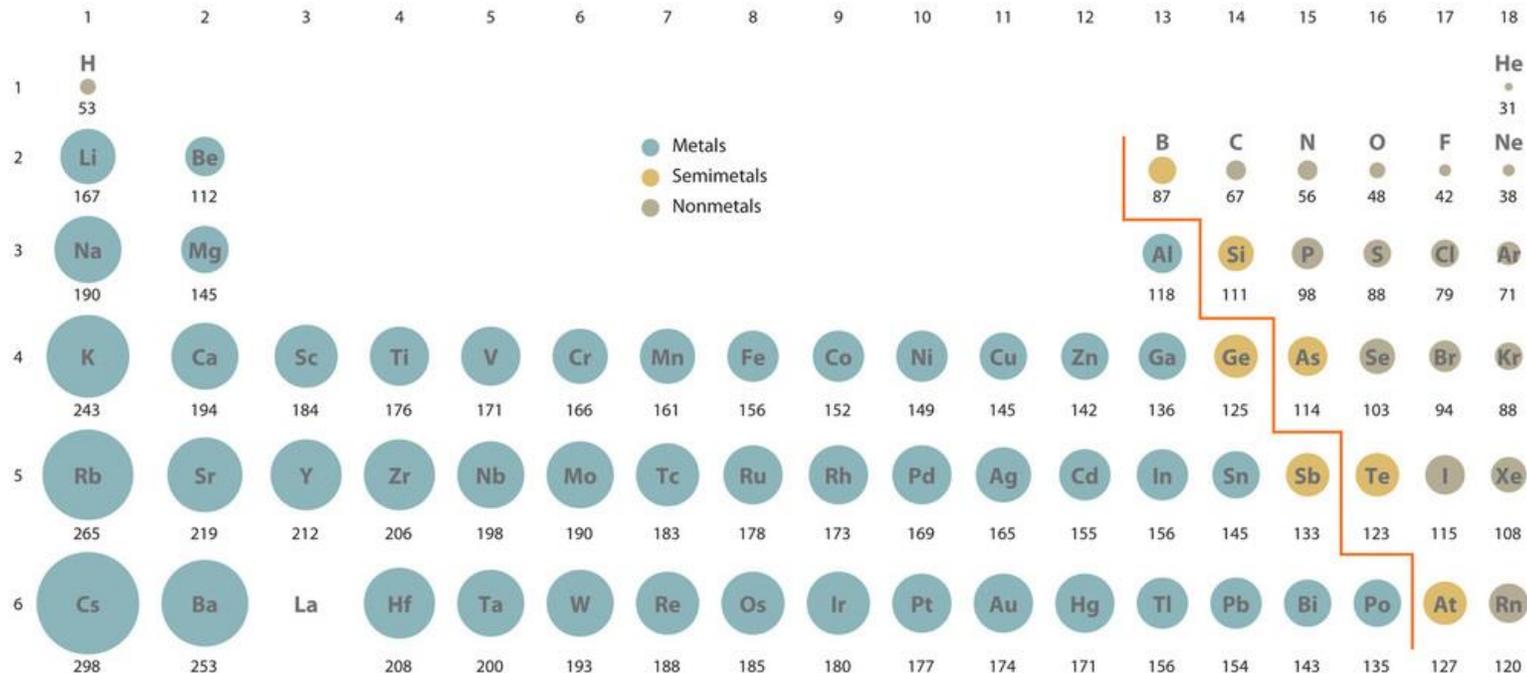
→ certain Trace Elements follow similar Major Elements

# How geologists use chemistry – trace elements

## Goldschmidt's Rules :

- If two ions have a **similar radius**, but **different valence**, then *the ion with the higher charge is preferentially incorporated* into the solid over the liquid:

$\text{Li}^+ \rightarrow \text{Ni}^{2+}$  (olivine),  $\text{Zr}^{4+} \rightarrow \text{Nb}^{5+}$  (rutile, ilmenite)...



→ certain Trace Elements are fractionated by certain minerals

## Partition coefficient ( $K_D$ ):

The distribution of a trace element between two phases (solid and liquid) is regulated by the Equilibrium constant:

$$K_D = \frac{C_{(i)S}}{C_{(i)L}}$$

This value is constant and it depends principally on the mineral and liquid composition.

Where:

- $K_D$  = partition coefficient
- $C_{(i)S}$  = weight percent concentration of a trace element (i) in the solid
- $C_{(i)L}$  = weight percent concentration of a trace element (i) in the liquid

## Partition coefficient ( $K_D$ ):

$$K_D = \frac{C_S}{C_L}$$

So:

- If  $K_D = 1$  the trace element can stay either in the mineral or the liquid.
- If  $K_D \gg 1$  the trace element is said to be **COMPATIBLE** (with the mineral)
- If  $K_D \ll 1$  the trace element is said to be **INCOMPATIBLE** (with the mineral)

# How geologists use chemistry – trace elements

Going back to the previous diagram:

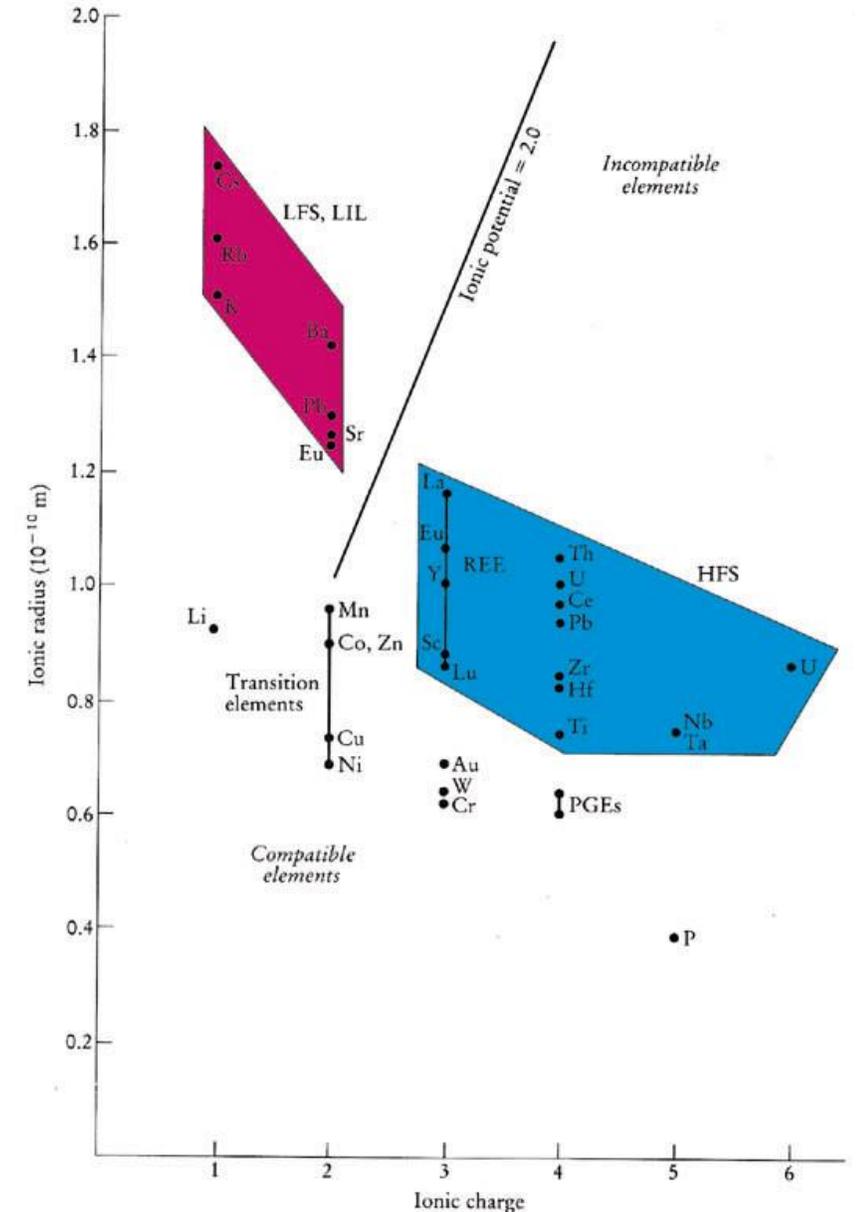
## Two Subgroups:

### 1. High Field Strength Elements (*HFSE*)

- REE, Th, U, Ce, Pb<sup>4+</sup>, Zr, Hf, Ti, Nb, Ta
- Small ionic radius, highly charged

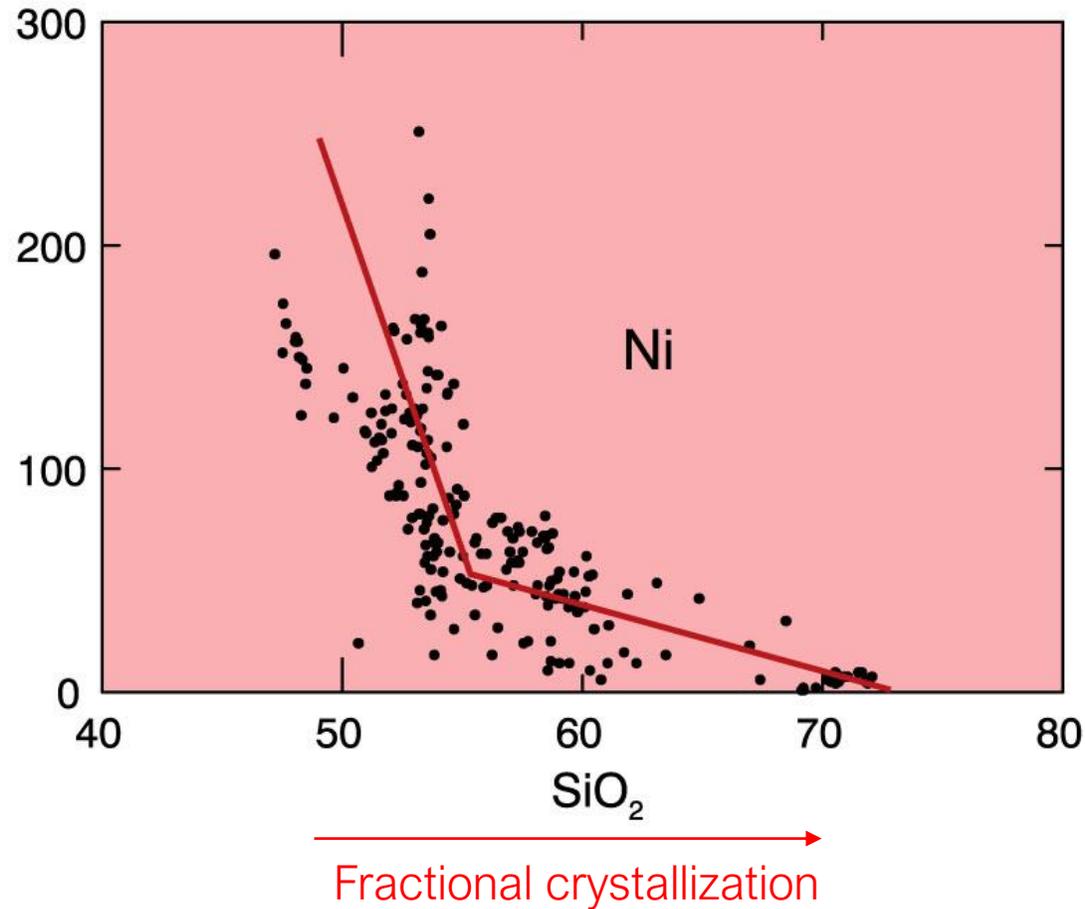
### 2. Low Field Strength Elements (*LFSE=LILE*)

- K, Rb, Cs, Ba, Pb<sup>2+</sup>, Sr, Eu<sup>2+</sup>
- more mobile in rocks
- **Large Ion Lithophile Elements**



# How geologists use chemistry – trace elements

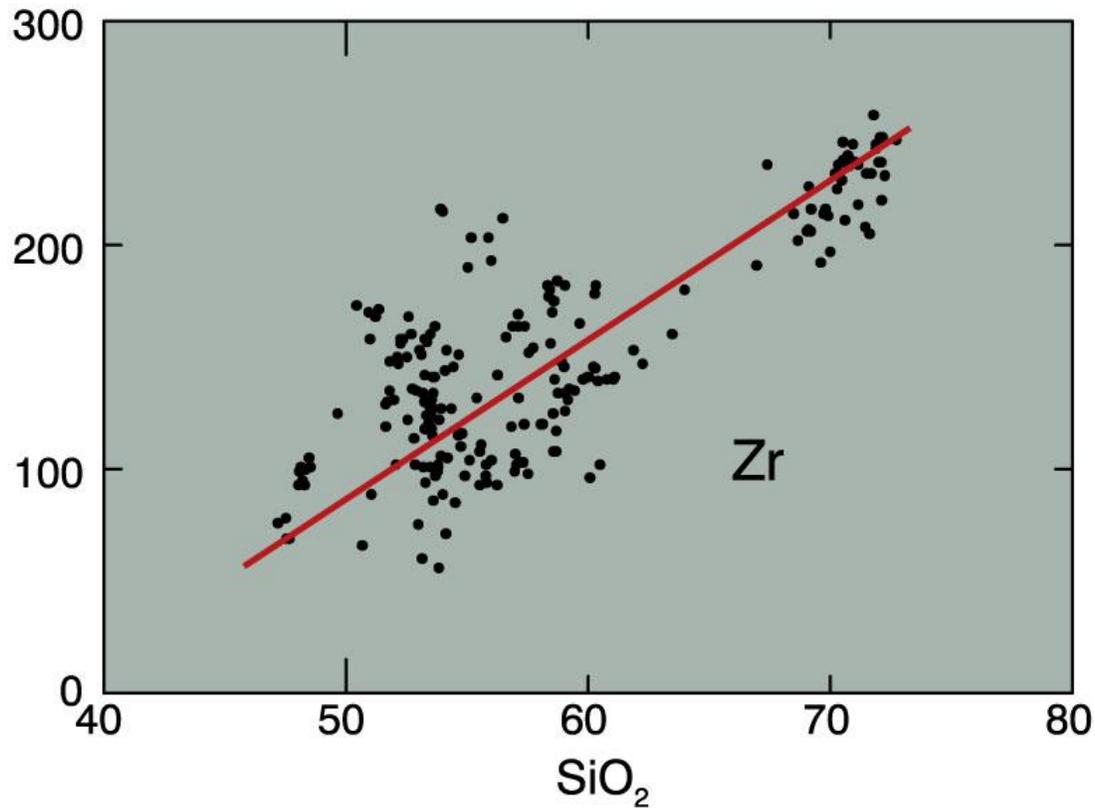
The example of Ni:



- Ni is highly compatible in Olivine
- With the increasing of Si content Ni will decrease.

# How geologists use chemistry – trace elements

The example of Zr:



- Zr is incompatible in most rock forming minerals
- With the increasing of Si content Zr will increase.

## $K_D$ and partial melting – the batch melting

During partial melting an initial composition ( $C_i^{tot}$ ) is progressively divided in a liquid phase, ( $C_{iL}$ ) and a solid phase ( $C_{iS}$ ) according to the degree of fusion of the rock (F):

$$C_i^{Total} = F * C_{iL} + (1 - F) * C_{iS}$$

And the  $K_D$  equation can be rearranged to give the **batch melting equation**:

$$C_{iL}/C_i^{Total} = 1 / [D_i * (1 - F) + F]$$

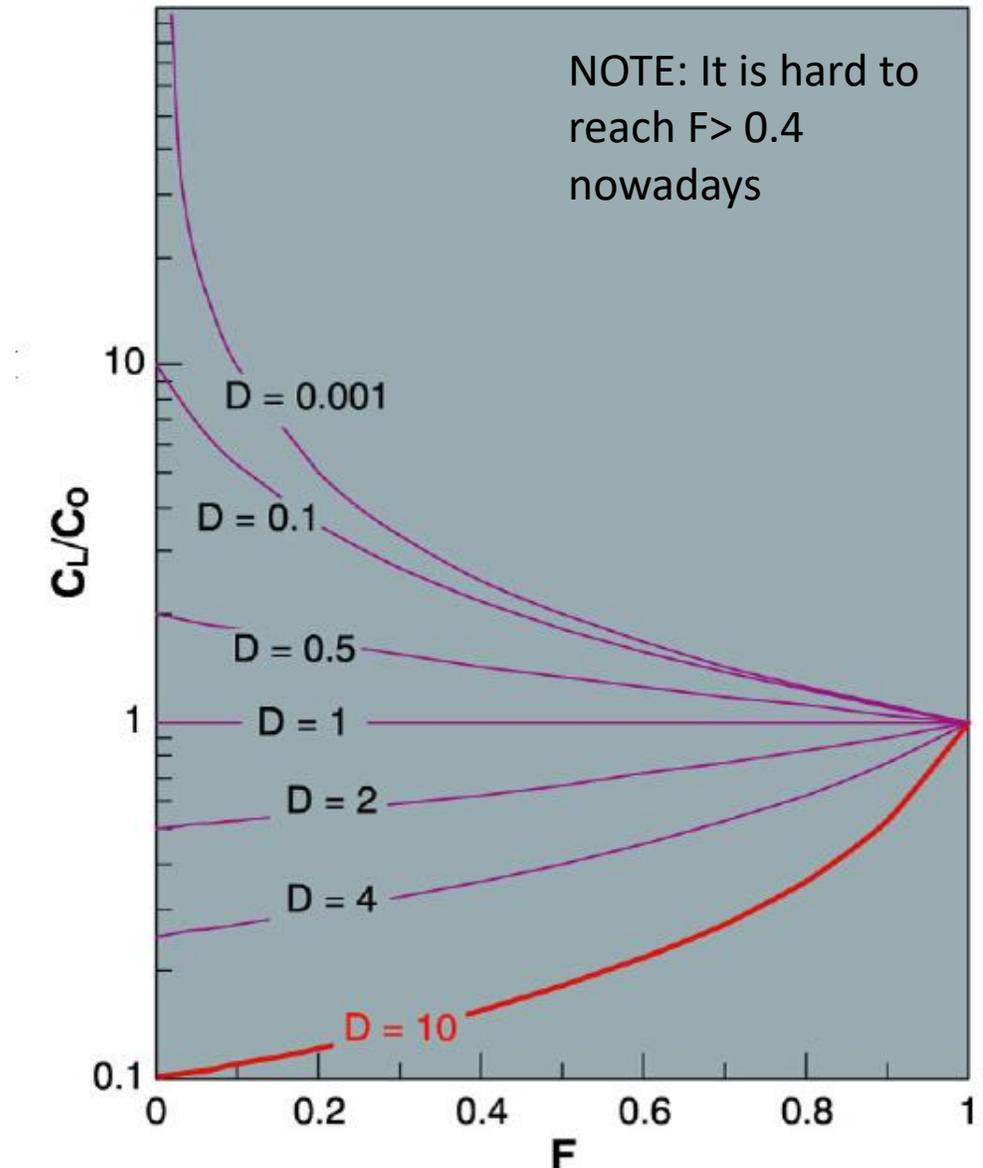
(Where  $D_i$  is the partition coefficient)

# How geologists use chemistry – trace elements

## $K_D$ and partial melting – the batch melting

If  $D \gg 1$  (compatible element):

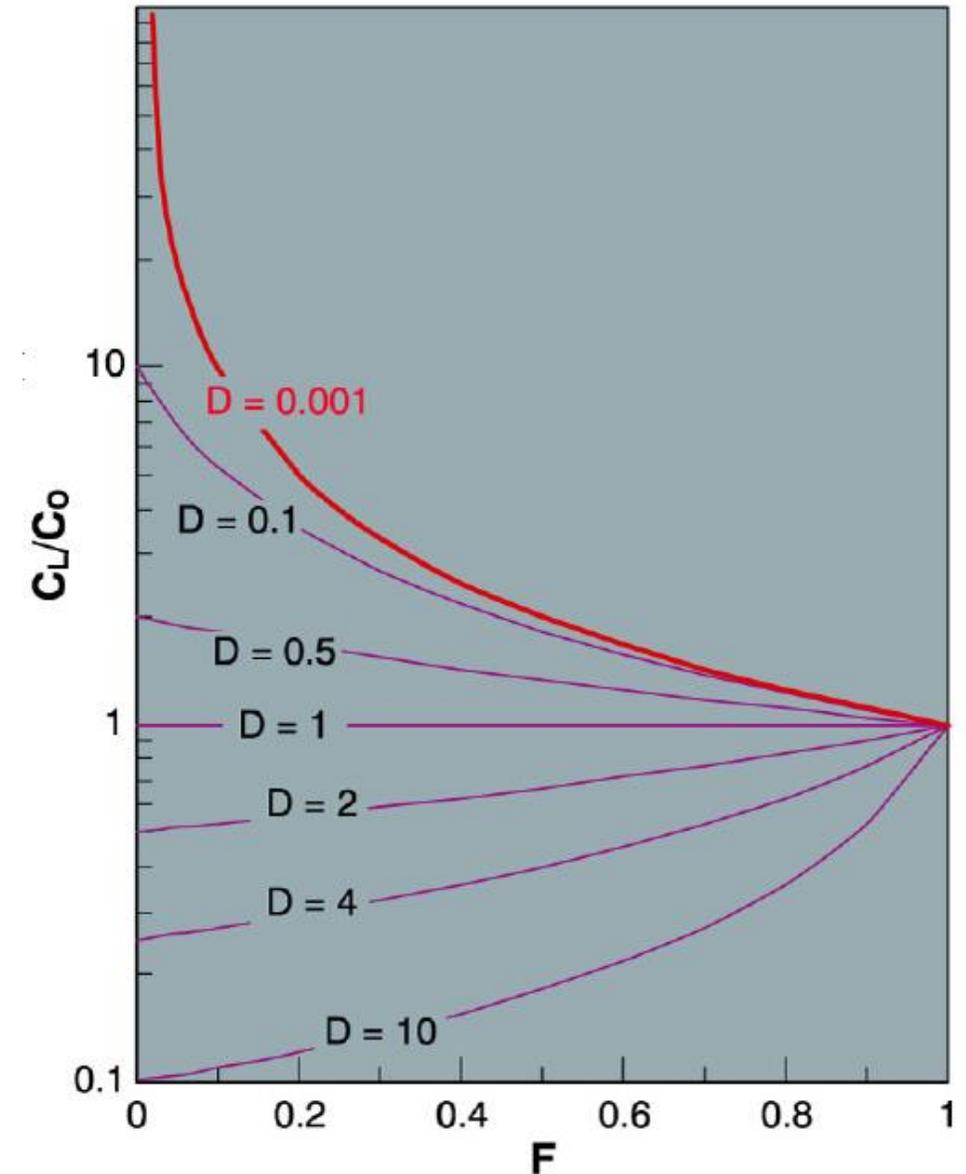
- Very **low concentration** of the element in the melt
- Relative concentration **increases** with increasing melt fraction



## $K_D$ and partial melting – the batch melting

If  $D \ll 1$  (incompatible element):

- Very **high concentration** of the element in the melt (especially at low degrees of partial melting)
- Relative concentration decreases with increasing melt fraction (**dilution**)





# How geologists use chemistry – REEs

**Table 9-1.** Partition Coefficients ( $C_S/C_L$ ) for Some Commonly Used Trace Elements in Basaltic and Andesitic Rocks

|    | Olivine     | Opx   | Cpx   | Garnet | Plag            | Amph  | Magnetite |
|----|-------------|-------|-------|--------|-----------------|-------|-----------|
| Rb | 0.01        | 0.022 | 0.031 | 0.042  | 0.071           | 0.29  |           |
| Sr | 0.014       | 0.04  | 0.06  | 0.012  | 1.83            | 0.46  |           |
| Ba | 0.01        | 0.013 | 0.026 | 0.023  | 0.23            | 0.42  |           |
| Ni | <i>14.0</i> | 5.0   | 7.0   | 0.955  | <i>0.01</i>     | 6.8   | 29.       |
| Cr | 0.7         | 10.0  | 34.0  | 1.345  | <i>0.01</i>     | 2.0   | 7.4       |
| La | 0.007       | 0.03  | 0.056 | 0.001  | 0.148           | 0.544 | 2.        |
| Ce | 0.006       | 0.02  | 0.092 | 0.007  | 0.082           | 0.843 | 2.        |
| Nd | 0.006       | 0.03  | 0.23  | 0.026  | 0.055           | 1.34  | 2.        |
| Sm | 0.007       | 0.05  | 0.445 | 0.102  | 0.039           | 1.804 | 1.        |
| Eu | 0.007       | 0.05  | 0.474 | 0.243  | <i>0.1/1.5*</i> | 1.557 | 1.        |
| Dy | 0.013       | 0.15  | 0.582 | 3.17   | 0.023           | 2.024 | 1.        |
| Er | 0.026       | 0.23  | 0.583 | 6.56   | 0.02            | 1.74  | 1.5       |
| Yb | 0.049       | 0.34  | 0.542 | 11.5   | 0.023           | 1.642 | 1.4       |
| Lu | 0.045       | 0.42  | 0.506 | 11.9   | 0.019           | 1.563 |           |

Data from Rollinson (1993).

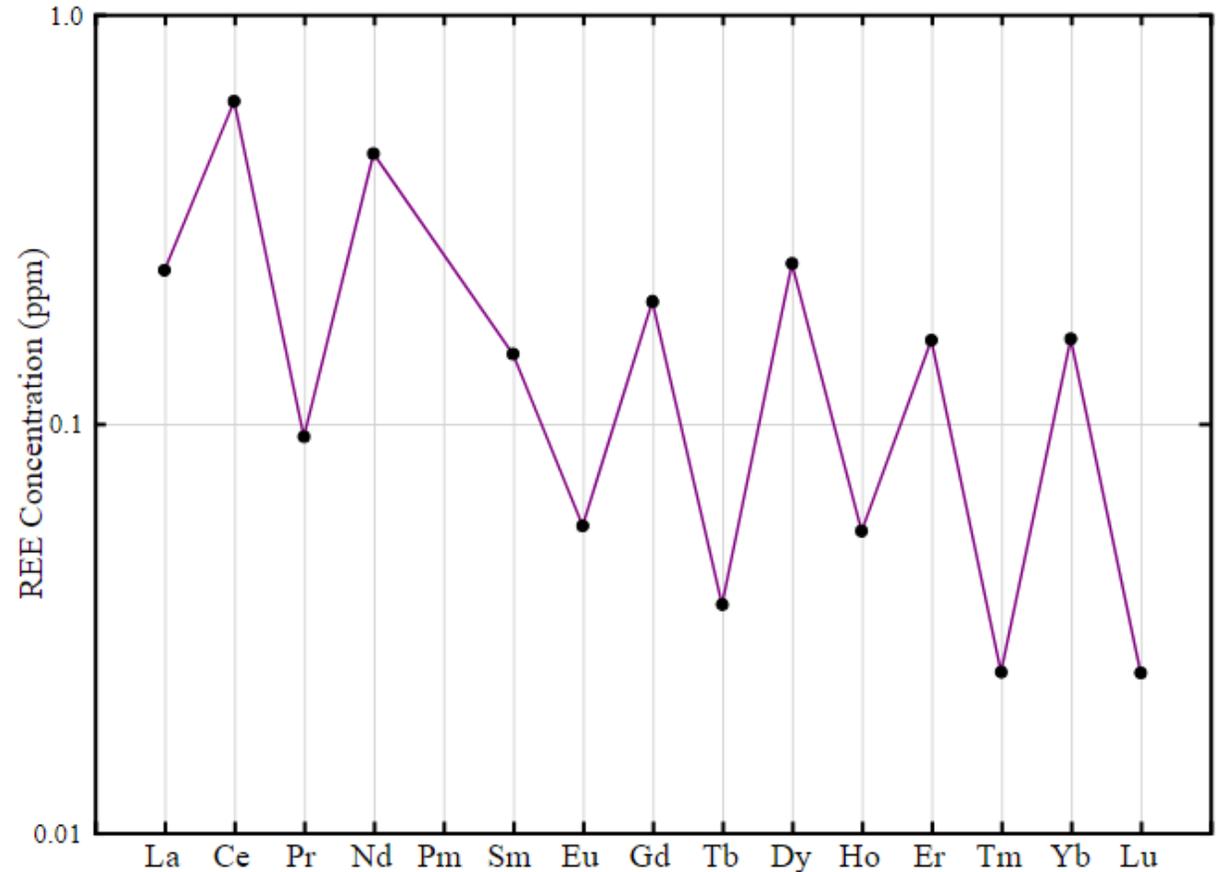
\*  $\text{Eu}^{3+}/\text{Eu}^{2+}$  *Italics* are estimated

- Generally, REEs are **incompatible** but,
- Incompatibility decreases with increasing Z (from La to Lu)
- HREE are even **compatible** in Garnet
- And Eu is **compatible** in Plagioclase

# How geologists use chemistry – REEs

The REEs distribution in a **chondrite** is affected by the Oddo-Harkins effect:

The chondrite represents the «**primordial**» element abundances and it is taken as reference for igneous rocks to remove the «even vs odd» effect in order to reveal more interesting patterns

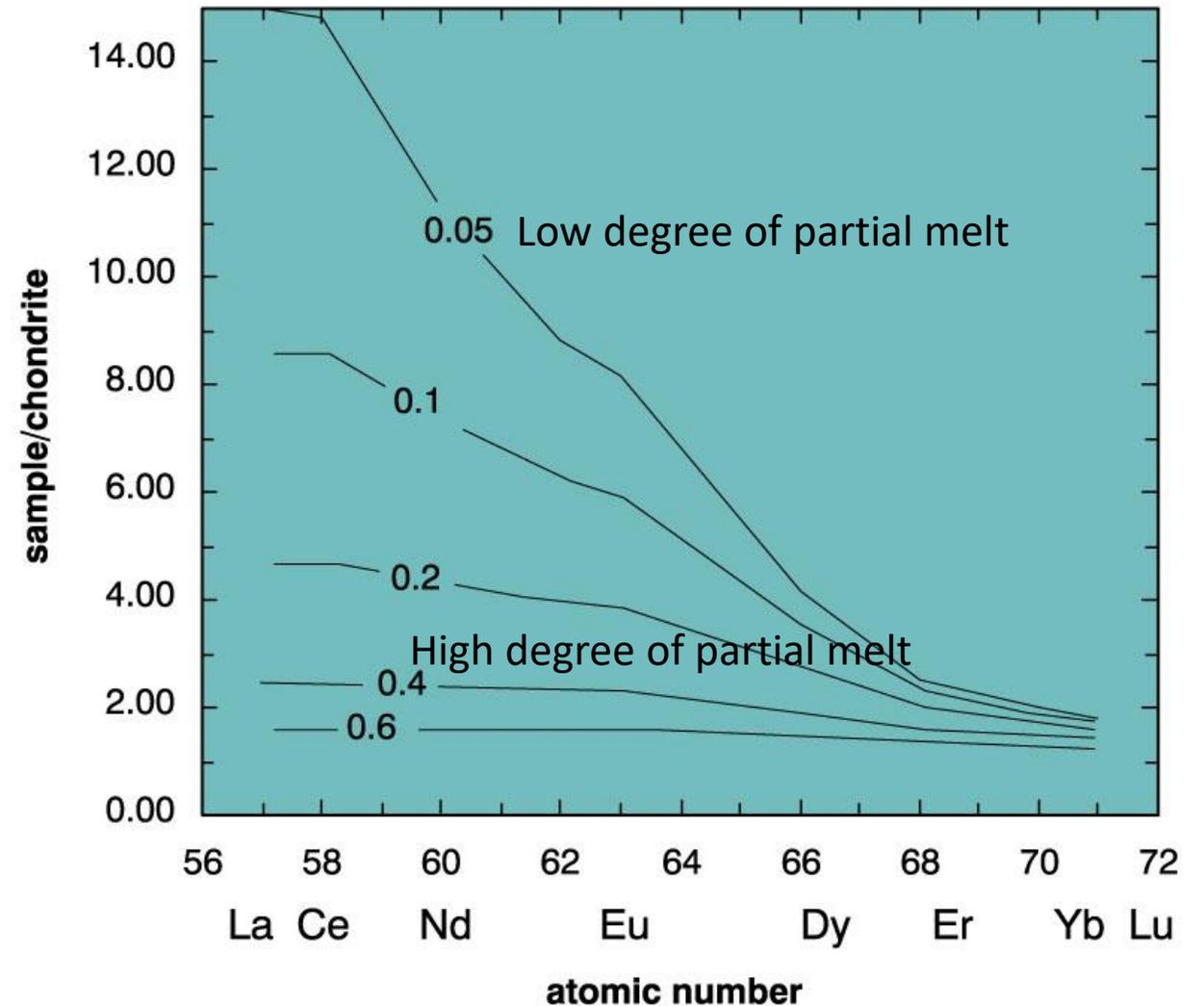


# How geologists use chemistry – REEs

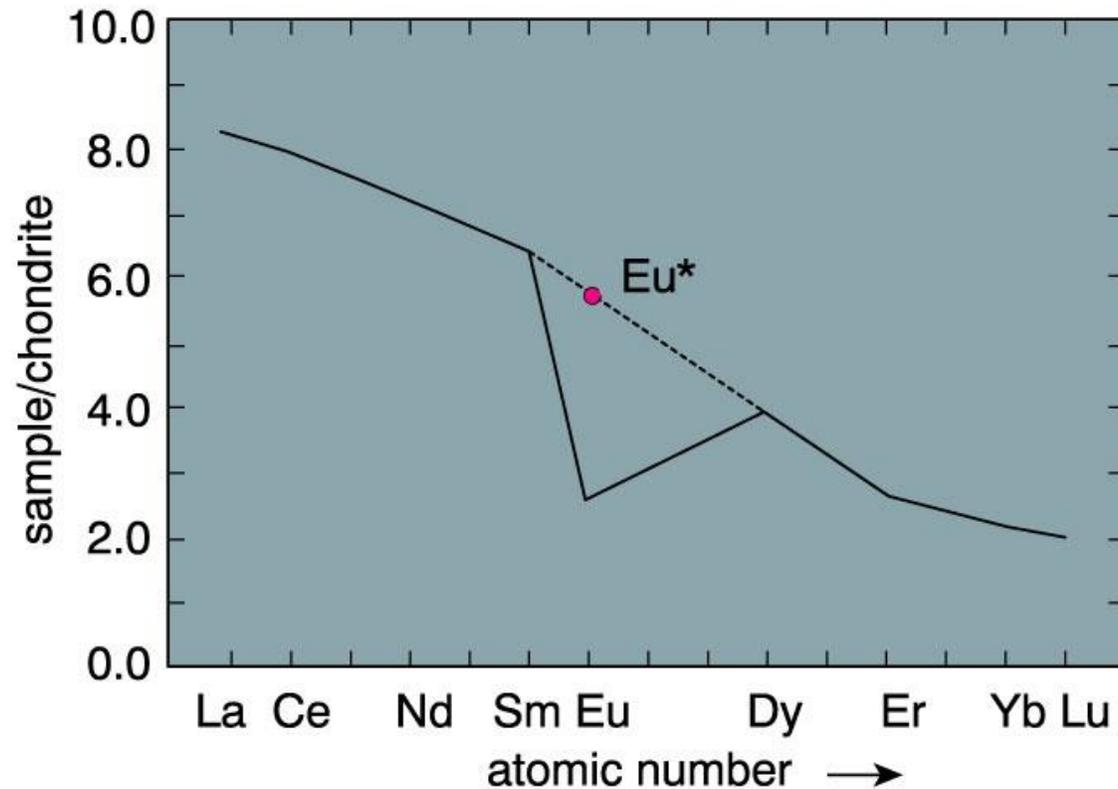
During partial melting of a garnet lherzolite (fertile mantle):

Slopes of REE patterns are **sensitive to mantle melting:**

- LREE are more abundant in low degree of melting
- They dilute with increasing fusion rate



## The «Europium anomaly»



Crystallisation of residual Plagioclase can lead to incorporate  $Eu^{2+}$  in its crystal lattice, causing a **negative anomaly** in the extracted melt.

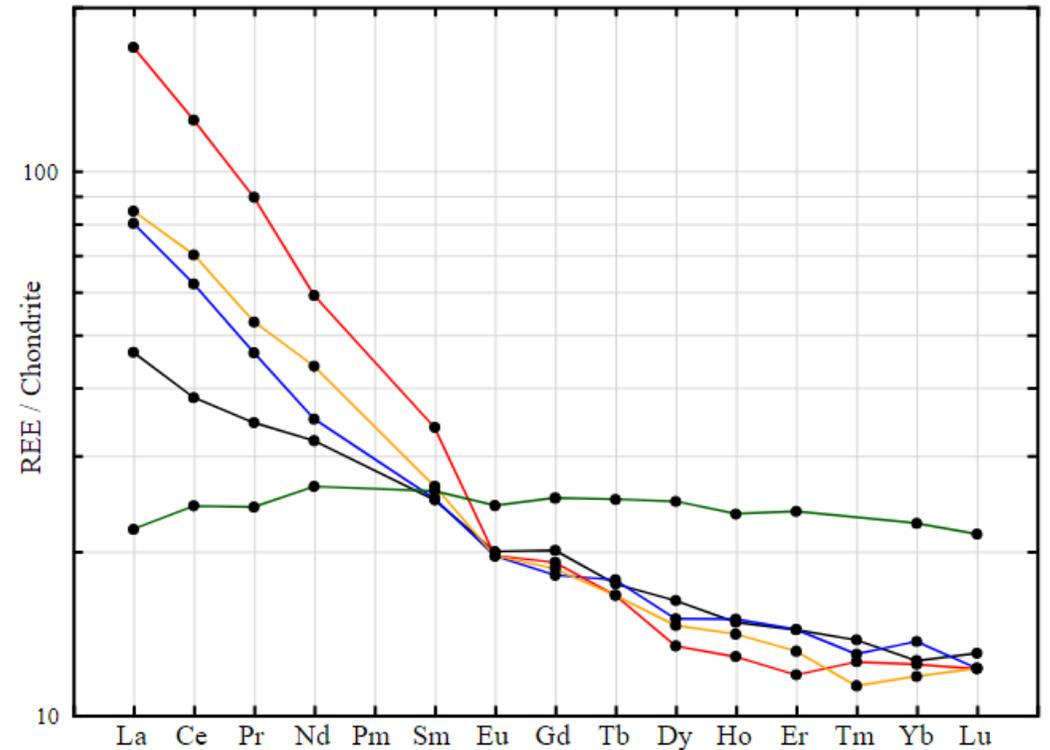
...so, REE useful to constrain:

- **source rock** or minerals involved during partial melting...
- **fractionating minerals** during magma ascent...

# How geologists use chemistry – REEs

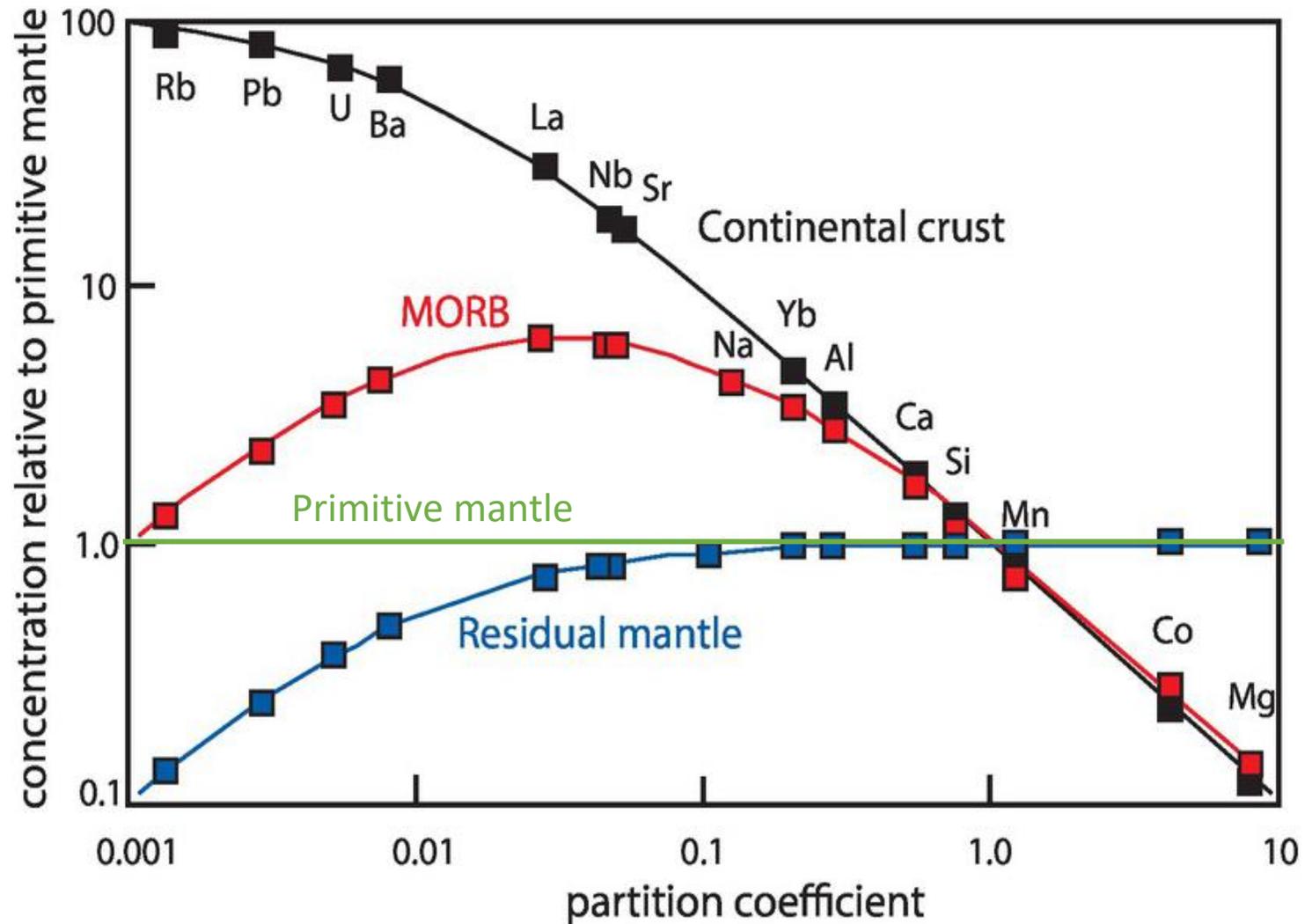
The different patterns show different rock sources:

- **Average granite:** clearly enriched in LREE relative to the HREE
- **MORB** is slightly depleted in the LREE relative to the HREE



# How geologists use chemistry – REEs

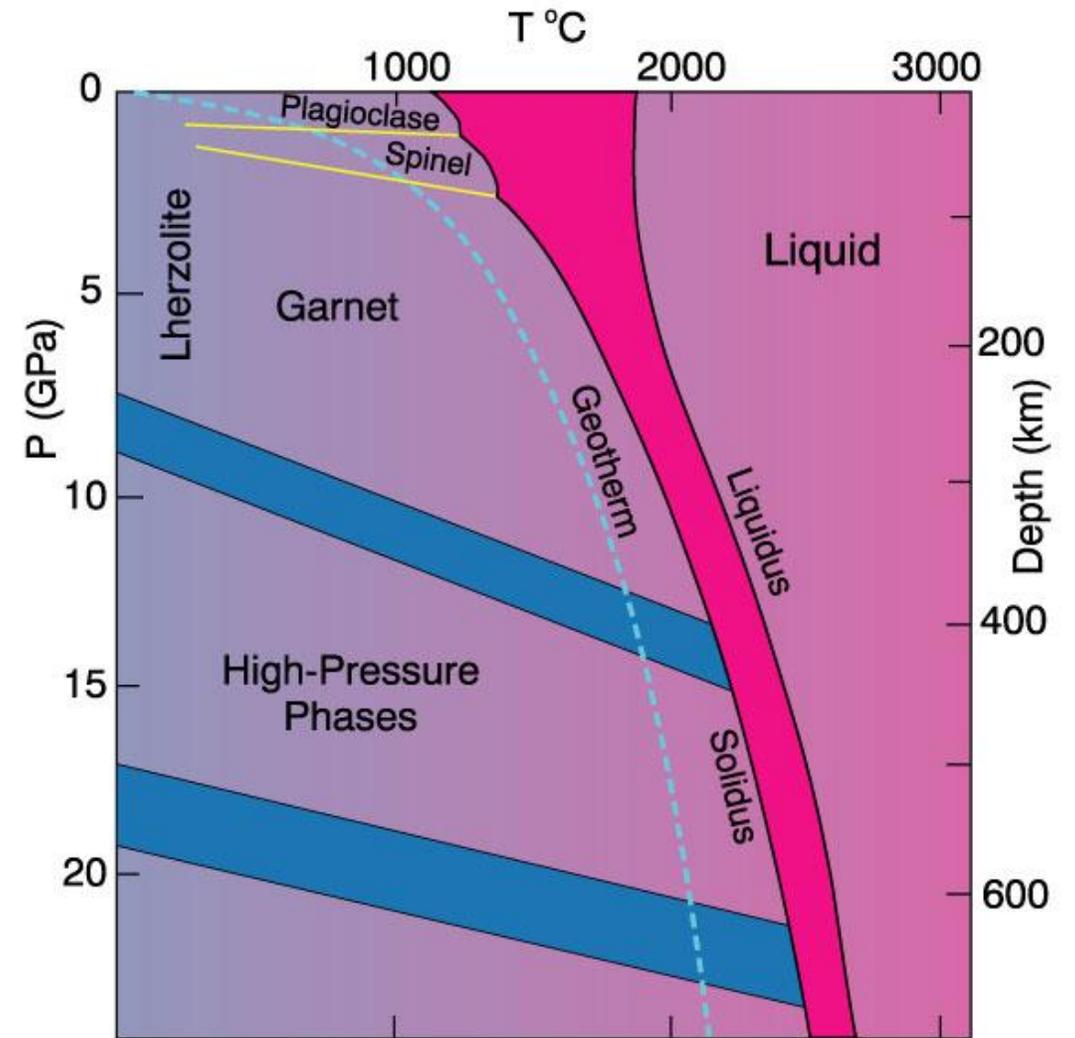
Using a multielement diagram makes it clearer:



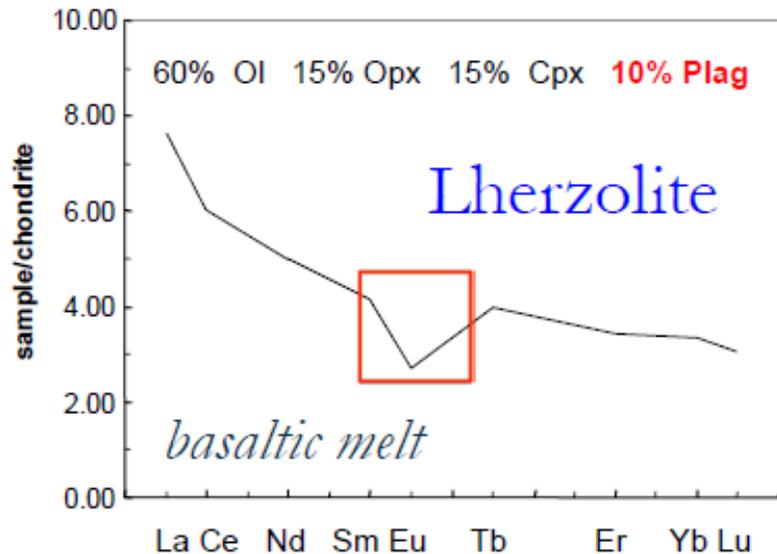
# How geologists use chemistry – REEs

## An example:

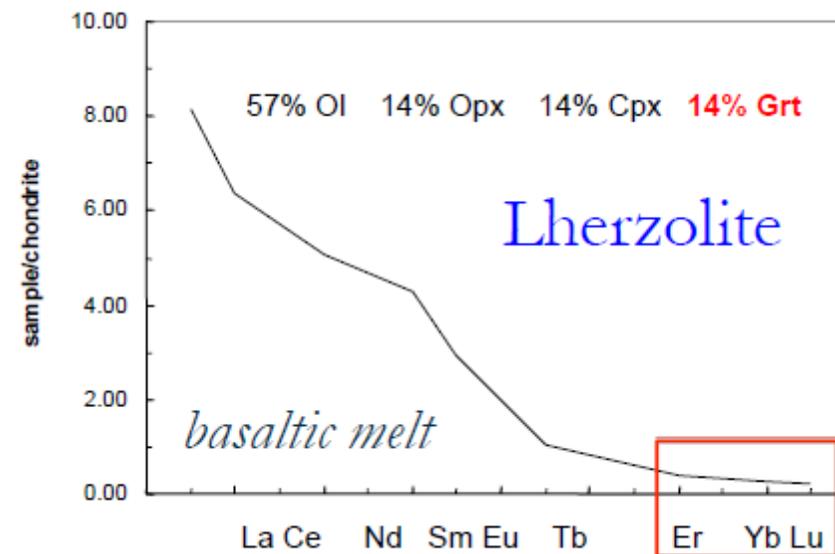
distinguish between high-P and low-P sources of mantle-derived magmas (residual plagioclase versus garnet)...



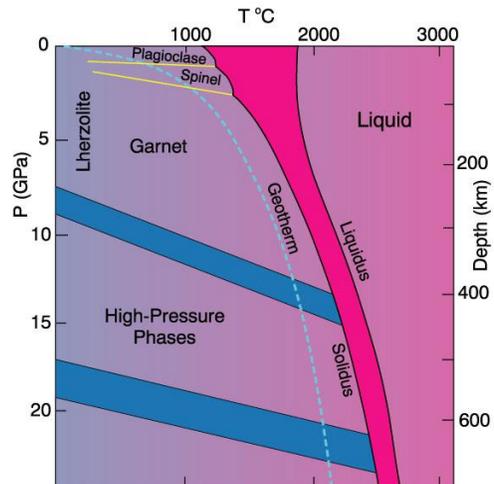
# How geologists use chemistry - example



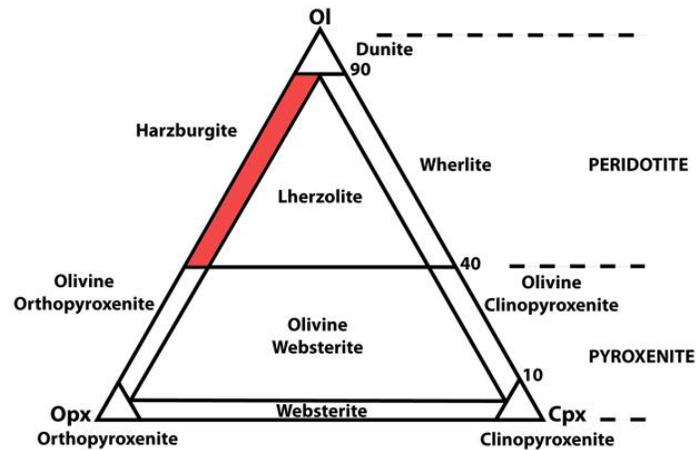
with plagioclase but NO garnet:  
mantle source rock <50 km deep



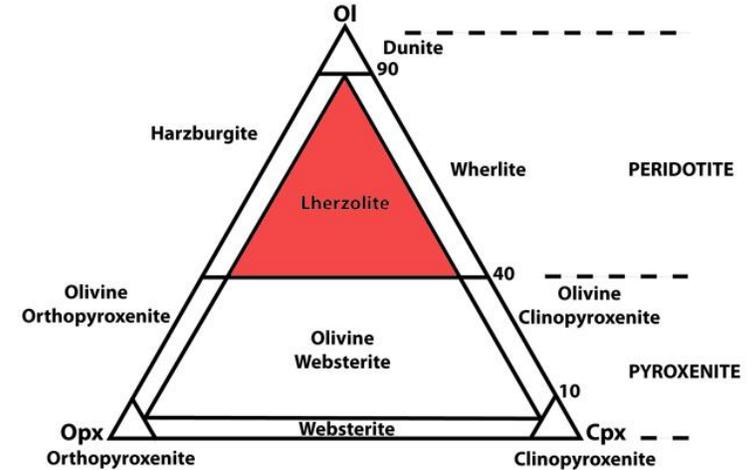
with garnet – NO plagioclase:  
mantle source rock >80 km deep



# Lithosphere vs Asthenosphere



The composition of the lithosphere is generally a **dry, chemically depleted peridotite** with local influence of different geodynamics settings (not homogeneous). Visible with REEs patterns.



The composition of the asthenosphere is generally more homogeneous than the lithospheric mantle. It is indicated as a **hydrated fertile peridotite**.

BUT: it also depends on the PT conditions and in the definition that you use

# References

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