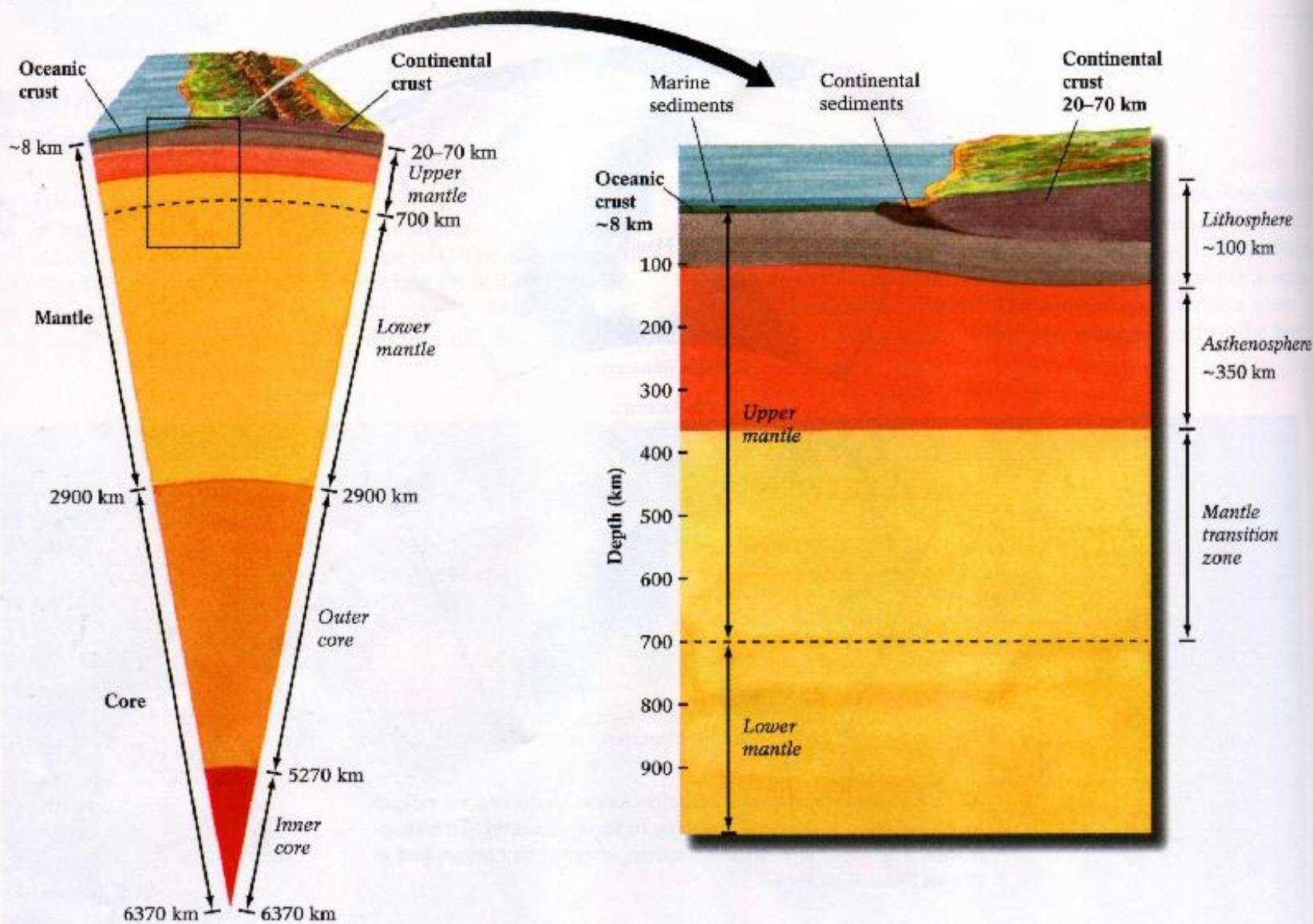


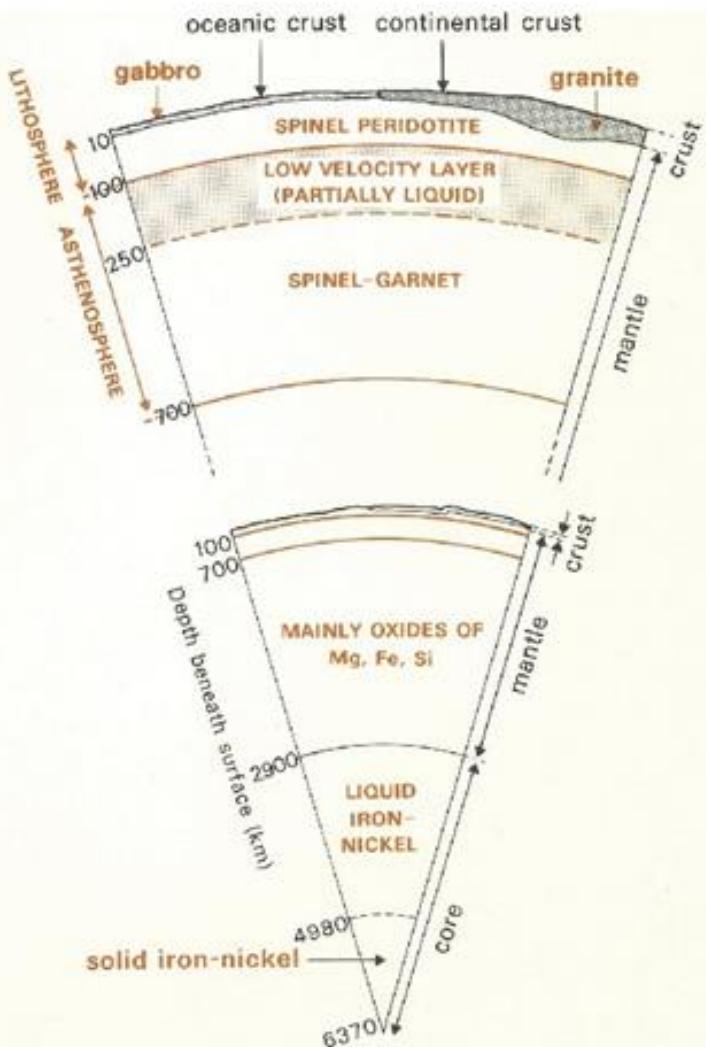
# Geochemical Classification of the Elements

Earth 281

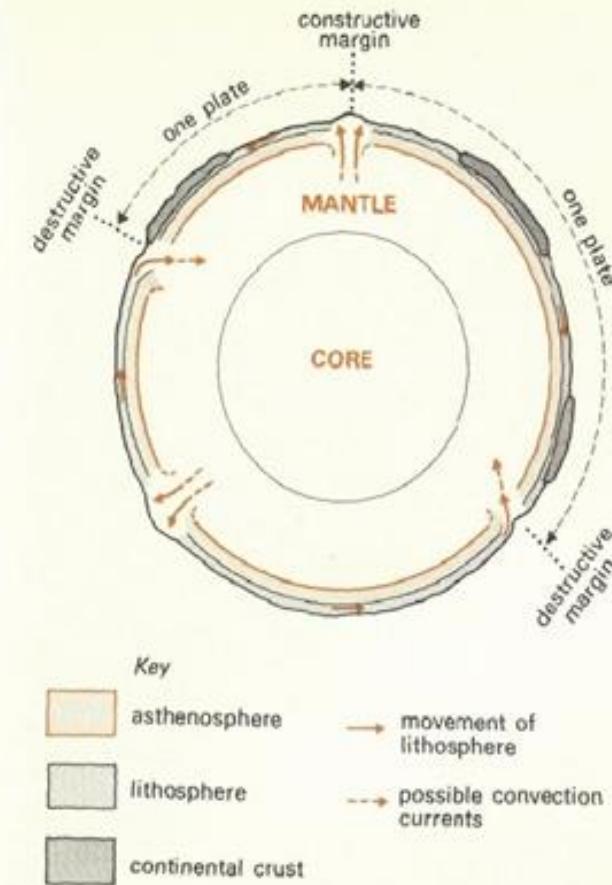
- In Chemistry you are taught a great deal about the periodic table.
- For example, various tables – atomic theory, numbers of protons, electrons, valence, etc.
- BUT geologists must think of elements as they function in the Earth, Atmosphere, Water, etc. around us.



**Figure 11-3** As well as delineating the three major components (crust, mantle, and core) of the Earth, seismological studies provide details about the different natures of the layers. For example, the studies reveal that continental crust is significantly thicker and less dense than oceanic crust. These studies also show the rugged topography of the Earth's core-mantle boundary.



**Figure 3.8** Generalised segment of the Earth at two scales to show the main layers beneath the surface.



**Figure 3.13** A schematic section illustrating the mechanism envisaged by plate tectonics. Rising currents within the mantle create lithospheric material at a constructive margin. Lithospheric plates move away from constructive margins, sliding over the underlying asthenosphere. Lithospheric material is destroyed at destructive margins, which lie above descending mantle currents.

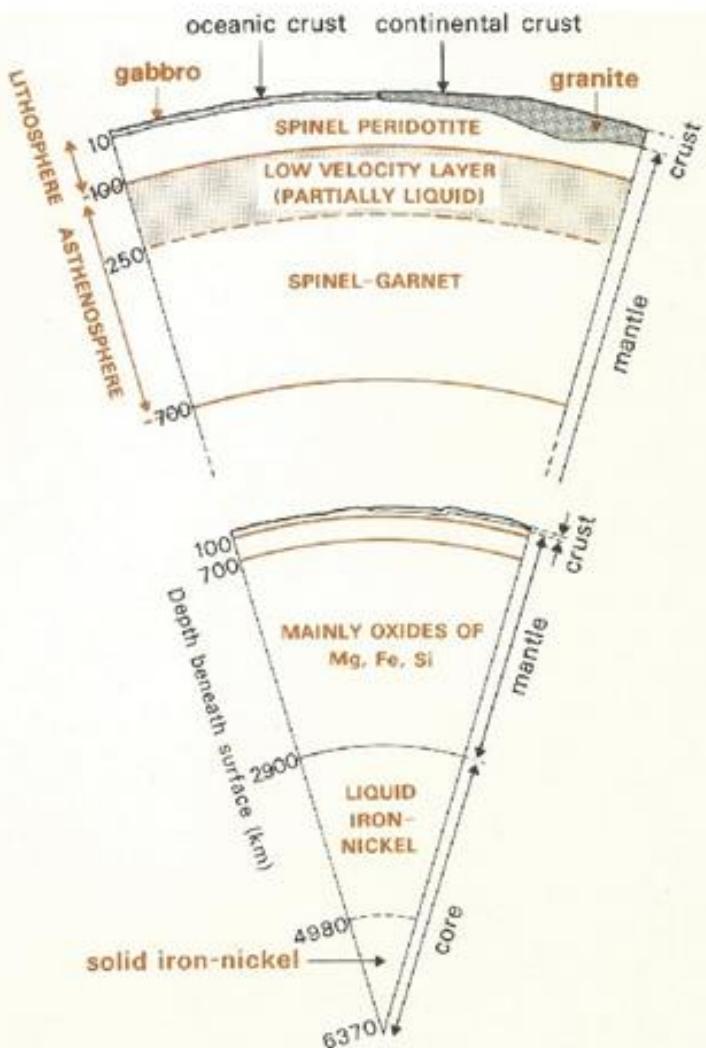
Thus Goldschmidt:

**TABLE I. Geochemical Classification of Elements (Selinus et al. 2005)**

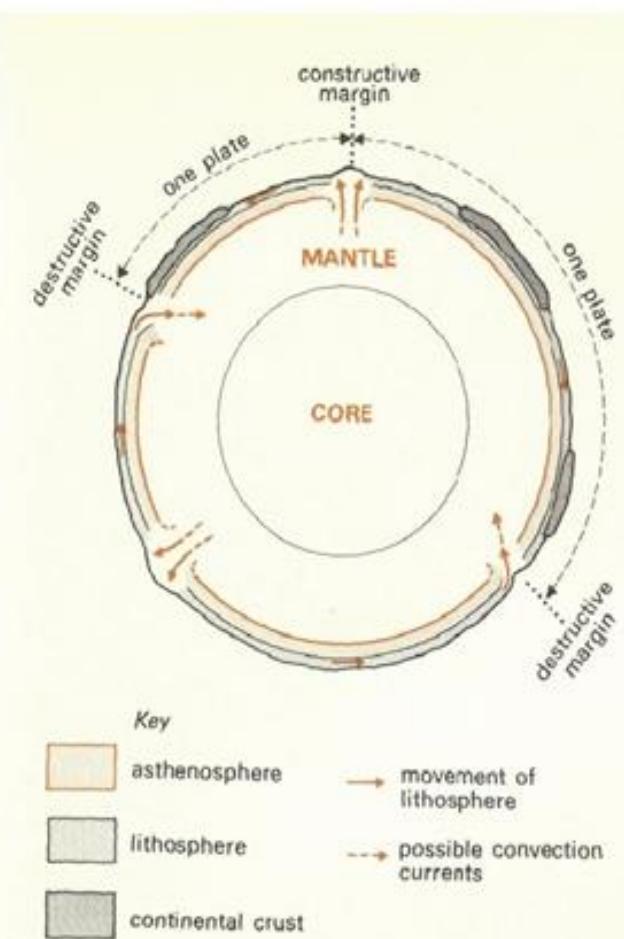
<b>Group</b>	<b>Elements</b>
<b>Siderophile</b>	<b>Fe, Co, Ni, Pt, Au, Mo, Ge, Sn, C, P</b>
<b>Atmophile</b>	<b>H, N, O</b>
<b>Chalcophile</b>	<b>Cu, Ag, Zn, Cd, Hg, Pb, As, S, T</b>
<b>Lithophile</b>	<b>Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba, Al, rare earths (REE)</b>

- Goldschmidt's geochemical classification has four families of elements (Table I).
- The siderophilic elements are associated with the Earth's core which is iron-nickel (Fe-Ni) based. These elements occur in other environments as well.
- For example, platinum and associated metals are rare in crustal rocks; but for, e.g. Sudbury Pt minerals in the Ni deposits are common due to deep mantle rocks brought near the surface due to "Impact"



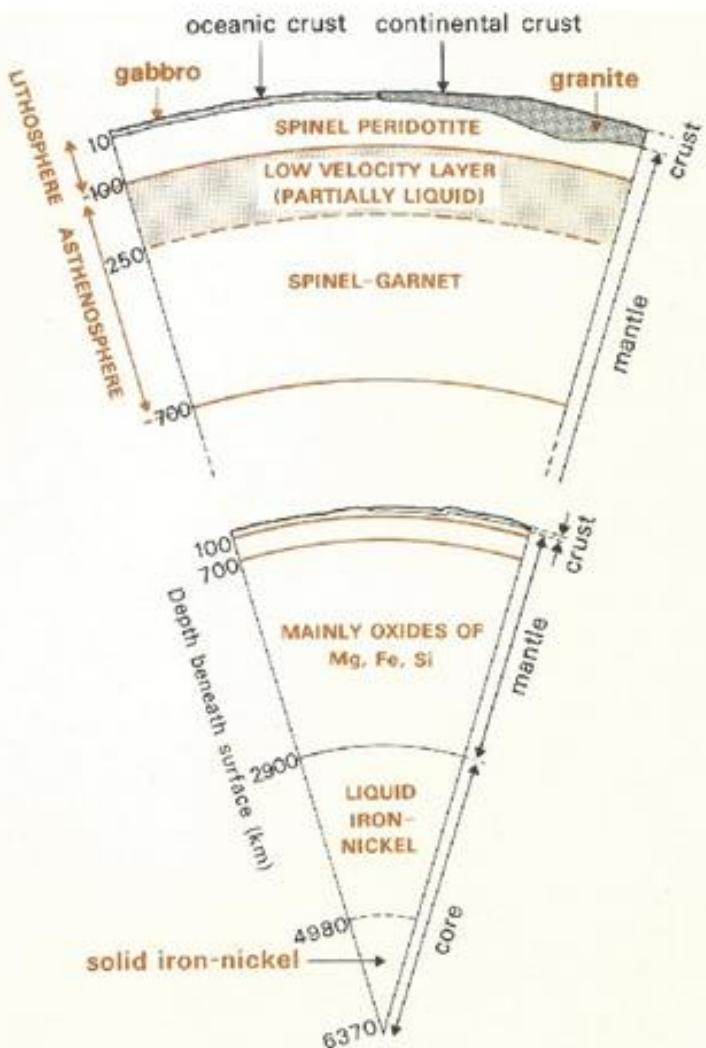


**Figure 3.8** Generalised segment of the Earth at two scales to show the main layers beneath the surface.

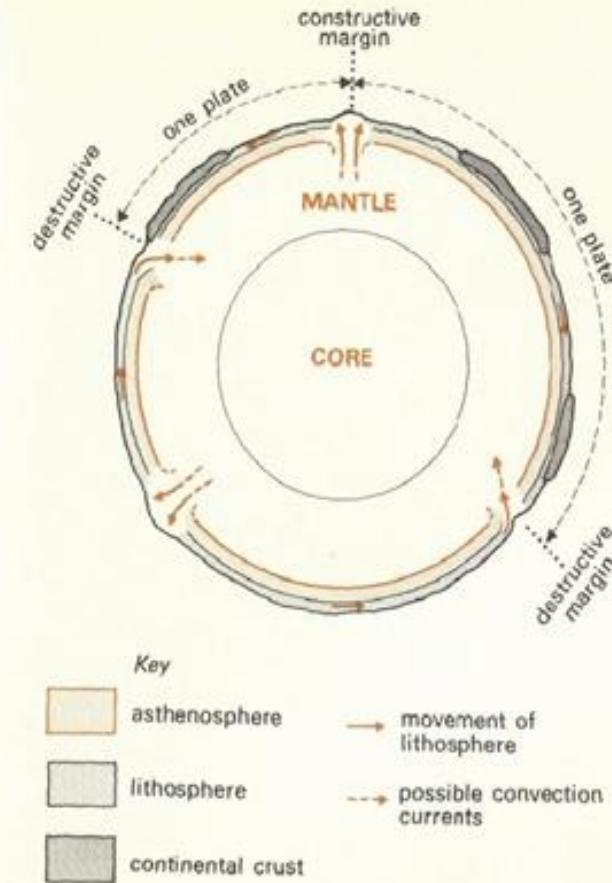


**Figure 3.13** A schematic section illustrating the mechanism envisaged by plate tectonics. Rising currents within the mantle create lithospheric material at a constructive margin. Lithospheric plates move away from constructive margins, sliding over the underlying asthenosphere. Lithospheric material is destroyed at destructive margins, which lie above descending mantle currents.

- A unique aspect of these mantle/core rocks coming to the surface is that many elemental components are rare in crustal rocks.
- For instance, Alvarez et al (1980) used the wide spread occurrence of the element Iridium (Ir) on the K/T (Cretaceous/Tertiary Age) boundary to correlate the mass extinction of species at that time with a major asteroid impact that fractured the crust so deeply that Ir rich mantle rocks were vaporized to dust and spread worldwide as a distinctive layer.

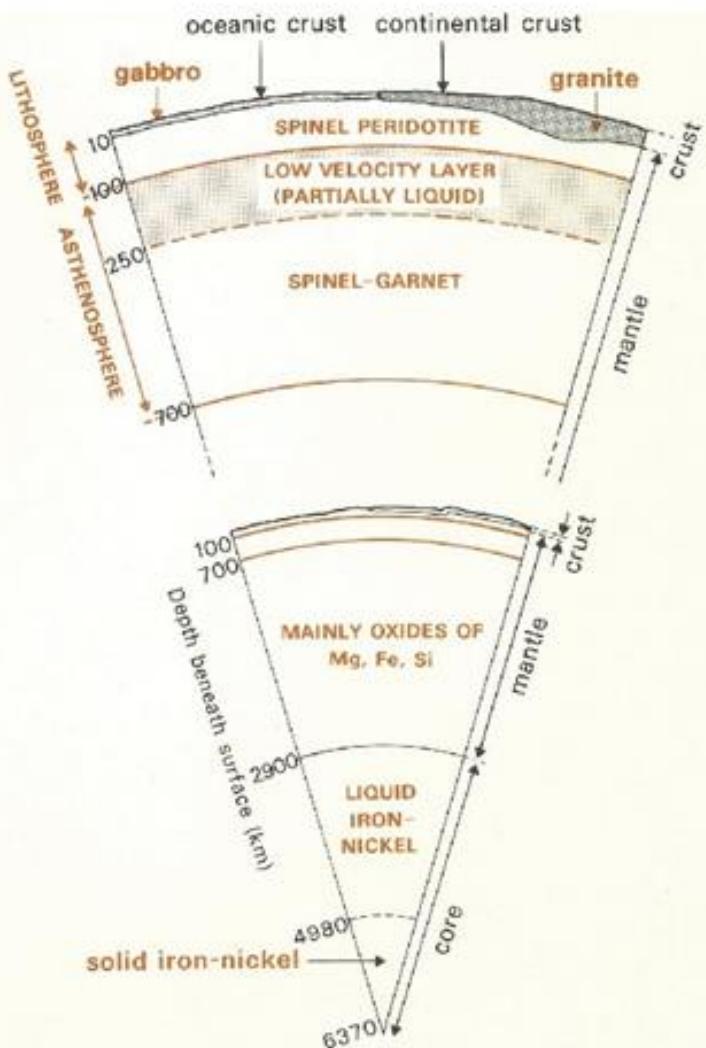


**Figure 3.8** Generalised segment of the Earth at two scales to show the main layers beneath the surface.

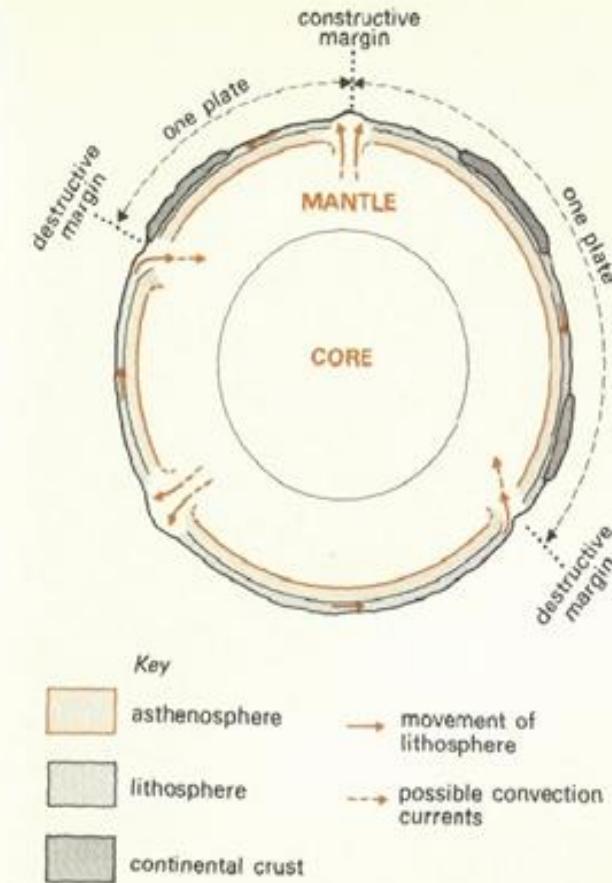


**Figure 3.13** A schematic section illustrating the mechanism envisaged by plate tectonics. Rising currents within the mantle create lithospheric material at a constructive margin. Lithospheric plates move away from constructive margins, sliding over the underlying asthenosphere. Lithospheric material is destroyed at destructive margins, which lie above descending mantle currents.

- Goldschmidt's classification continues with *atmophile or atmophilic* elements that are represented by those most commonly found in air and gases.
- Elements most commonly found in Crustal rocks, nearer the Earth's surface, or composed of silicate rich continental type rocks are called *lithophile or lithophilic*. As you might expect many of these trace and major elements are the critical building blocks for life. (Why?)

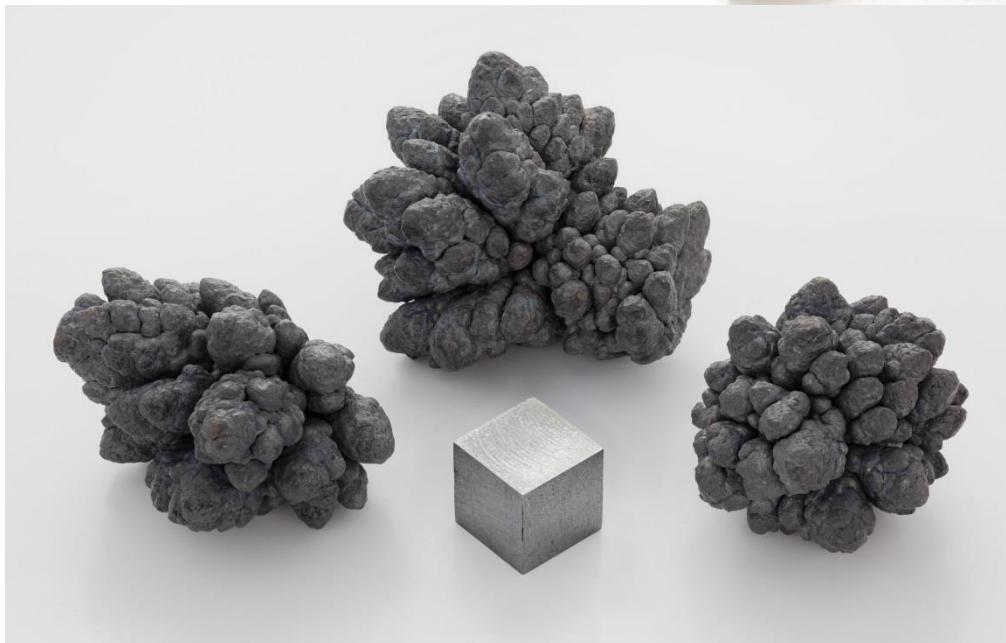


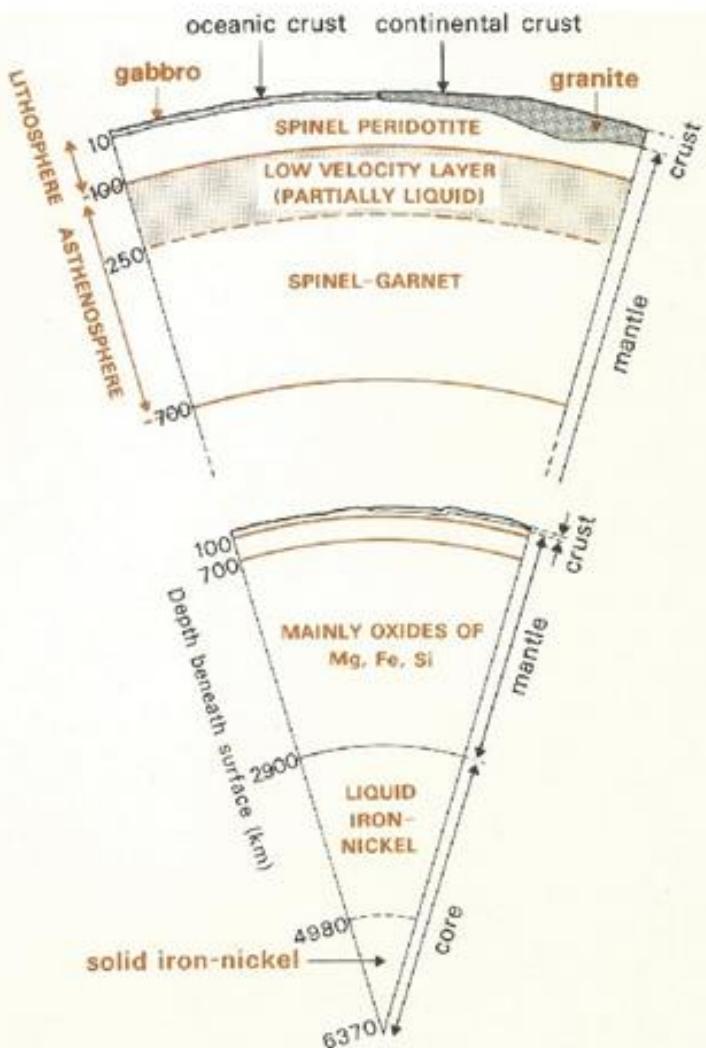
**Figure 3.8** Generalised segment of the Earth at two scales to show the main layers beneath the surface.



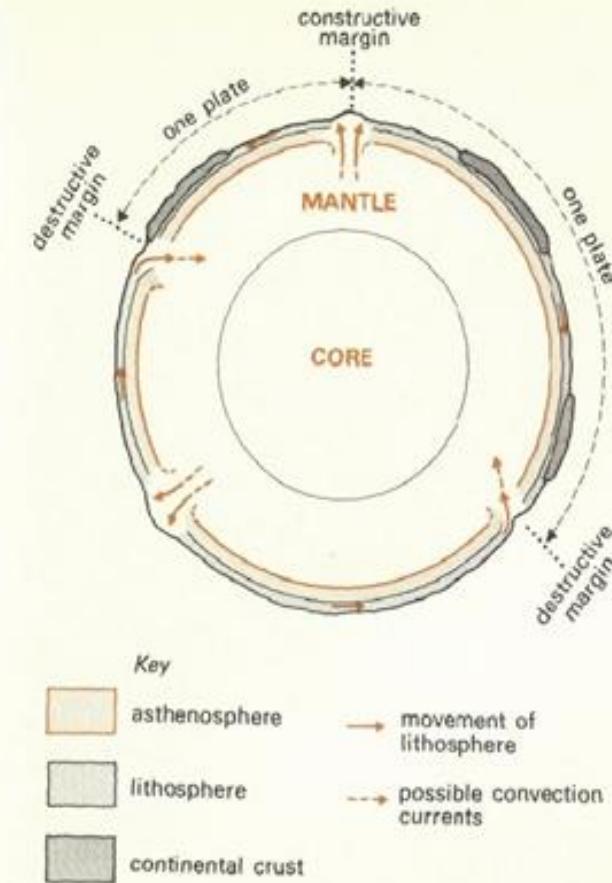
**Figure 3.13** A schematic section illustrating the mechanism envisaged by plate tectonics. Rising currents within the mantle create lithospheric material at a constructive margin. Lithospheric plates move away from constructive margins, sliding over the underlying asthenosphere. Lithospheric material is destroyed at destructive margins, which lie above descending mantle currents.

- Goldschmidt's final grouping is the *chalcophiles*.
- The trace metals or sometimes known as transition elements are the major family found in this group. Most are found in the middle of the Periodic Table. Many of these metals are associated with and form sulphur compounds.
- Thus chalcophile or “copper” elements could be represented by the mineral chalcopyrite  $\text{CuFeS}_2$  sometimes called ‘fool’s’ gold.
- These elements often concentrate in both magmatic hydrothermal and hydrogeologic related processes to form ore deposits.
- They are among the most toxic of elements (e.g. lead, mercury, cadmium and arsenic).





**Figure 3.8** Generalised segment of the Earth at two scales to show the main layers beneath the surface.

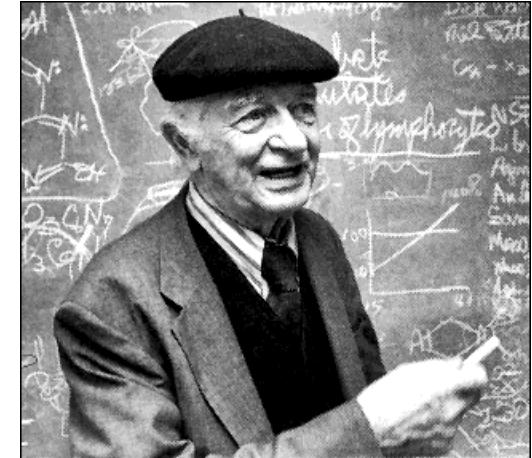


**Figure 3.13** A schematic section illustrating the mechanism envisaged by plate tectonics. Rising currents within the mantle create lithospheric material at a constructive margin. Lithospheric plates move away from constructive margins, sliding over the underlying asthenosphere. Lithospheric material is destroyed at destructive margins, which lie above descending mantle currents.

- At the same time their ability to readily change valence state (e.g. sulphide to sulphate) not only makes them major controllers of redox (oxidation-reduction) processes; but also major controllers of enzymic processes (e.g. SH groups, soft bases and acids etc.).
- The very origin of life, our present atmosphere etc. was and is highly dependent on the chalcophile elements to govern redox processes  
–More on this Biochemistry and The Earth



# Goldschmidt and Pauling:

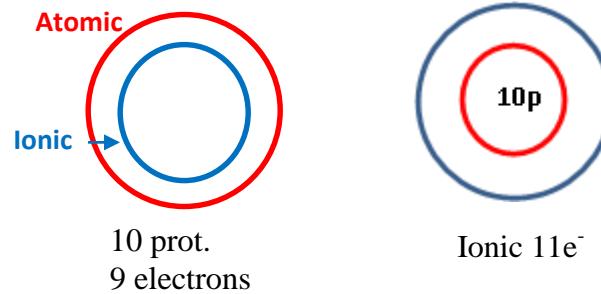


- Goldschmidt's rules of ionic substitution and later Pauling and others refining of these rules is important to the concept of mineral formation/stability and geochemical stability of compounds.
- Why are some compounds easily broken into elemental form and readily available for use (good or bad) in biological processes?
- Whereas other compounds and their elements can be highly resistive to separation and tend to be very stable over long periods of time.

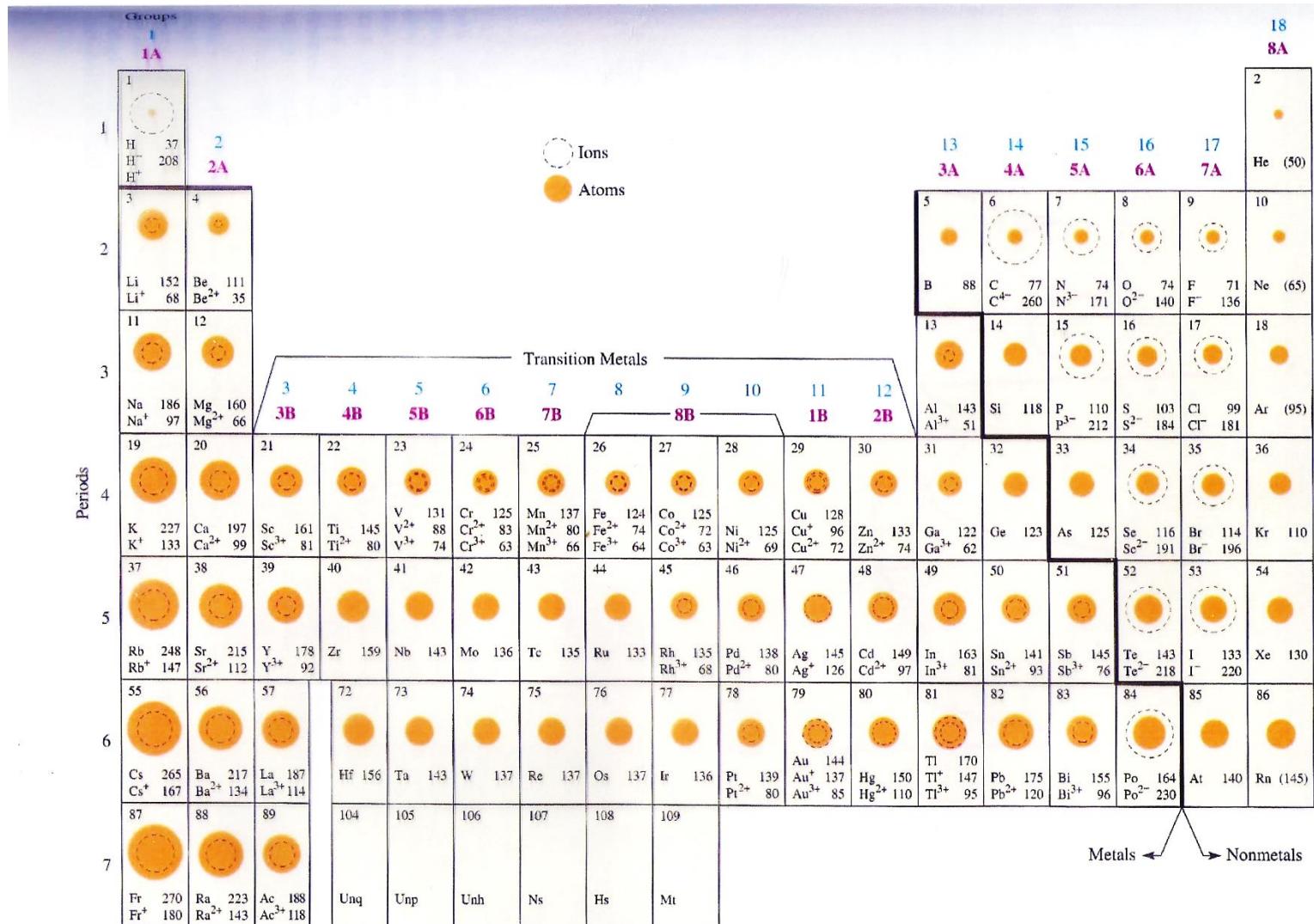
# Goldschmidt's Rules of Substitution

(Selinus *et al* 2005 – with comments by S. Frape)

1. “*The ions of one element can replace another in ionic crystals if their radii differ by less than 15%*”
  - a) Ionic Radius: Non-neutral: + or – charged
  - b) Atomic Radius: Neutral    Protons = Electrons
  - c) Positive Ions: Ionic radius smaller than Atomic
  - d) Negative Ions: Ionic radius larger



# Atomic and Ionic Radii



**Figure 8.9**

Atomic and ionic radii, with values in picometers ( $1 \text{ m} = 10^{12} \text{ pm}$ ). (The values in parentheses are estimated.) With some exceptions, radii increase from top to bottom within a group and decrease from left to right across a period. Positive ions are always smaller than their parent atoms, and negative ions are always larger.

# Atomic and Ionic Radii

Petrucci *et al.* 2011

<b>Li</b>	<b>Be</b>						<b>B</b>	<b>C</b>	<b>N</b>	<b>O</b>	<b>F</b>
152	111						88	77	75	73	71
$\text{Li}^+$	$\text{Be}^{2+}$						$\text{N}^{3-}$	$\text{O}^{2-}$	$\text{F}^-$		
59	27						171	140	133		
<b>Na</b>	<b>Mg</b>						<b>Al</b>	<b>Si</b>	<b>P</b>	<b>S</b>	<b>Cl</b>
186	160						143	117	110	104	99
$\text{Na}^+$	$\text{Mg}^{2+}$						$\text{Al}^{3+}$	$\text{P}^{3-}$	$\text{S}^{2-}$	$\text{Cl}^-$	
99	72						53	212	184	181	
<b>K</b>	<b>Ca</b>	<b>Sc</b>	<b>Ti</b>	<b>V</b>	<b>Cr</b>	<b>Mn</b>	<b>Fe</b>	<b>Co</b>	<b>Ni</b>	<b>Cu</b>	<b>Zn</b>
227	197	161	145	132	125	124	124	125	125	128	133
$\text{K}^+$	$\text{Ca}^{2+}$	$\text{Sc}^{3+}$	$\text{Ti}^{2+}$	$\text{V}^{2+}$	$\text{Cr}^{2+}$	$\text{Mn}^{2+}$	$\text{Fe}^{2+}$	$\text{Co}^{2+}$	$\text{Ni}^{2+}$	$\text{Cu}^+$	$\text{Zn}^{2+}$
138	100	75	86	79	82	83	77	75	70	96	75
$\text{V}^{3+}$	$\text{Cr}^{3+}$	$\text{Mn}^{2+}$	$\text{Fe}^{3+}$	$\text{Co}^{3+}$	$\text{Ni}^{2+}$	$\text{Cu}^{2+}$	$\text{Zn}^{2+}$	$\text{Ga}^{3+}$			
<b>Rb</b>	<b>Sr</b>						<b>Ag</b>	<b>Cd</b>	<b>In</b>	<b>Sn</b>	<b>Sb</b>
248	215						144	149	163	141	140
$\text{Rb}^+$	$\text{Sr}^{2+}$						$\text{Ag}^+$	$\text{Cd}^{2+}$	$\text{In}^{3+}$	$\text{Sn}^{2+}$	$\text{Sb}^{3+}$
149	113						115	95	79	93	76
<b>Te</b>	<b>I</b>						<b>Te</b>	<b>I</b>			
							198	196			

# Goldschmidt's Rules of Substitution

2. “*Ions whose charges differ by one unit can substitute provided electrical neutrality of the crystal is maintained.*”
- For example: NaCl (salt – the mineral halite)
  - → CaCl<sub>2</sub> · 6H<sub>2</sub>O (the mineral antarcticite)

What determines the Charge – go to (point 1): electrons

# Atomic and Ionic Radii

Petrucci *et al.* 2011

<b>Li</b>	<b>Be</b>						<b>B</b>	<b>C</b>	<b>N</b>	<b>O</b>	<b>F</b>
152	111						88	77	75	73	71
$\text{Li}^+$	$\text{Be}^{2+}$						$\text{N}^{3-}$	$\text{O}^{2-}$	$\text{F}^-$		
59	27						171	140	133		
<b>Na</b>	<b>Mg</b>						<b>Al</b>	<b>Si</b>	<b>P</b>	<b>S</b>	<b>Cl</b>
186	160						143	117	110	104	99
$\text{Na}^+$	$\text{Mg}^{2+}$						$\text{Al}^{3+}$	$\text{P}^{3-}$	$\text{S}^{2-}$	$\text{Cl}^-$	
99	72						53	212	184	181	
<b>K</b>	<b>Ca</b>	<b>Sc</b>	<b>Ti</b>	<b>V</b>	<b>Cr</b>	<b>Mn</b>	<b>Fe</b>	<b>Co</b>	<b>Ni</b>	<b>Cu</b>	<b>Zn</b>
227	197	161	145	132	125	124	124	125	125	128	133
$\text{K}^+$	$\text{Ca}^{2+}$	$\text{Sc}^{3+}$	$\text{Ti}^{2+}$	$\text{V}^{2+}$	$\text{Cr}^{2+}$	$\text{Mn}^{2+}$	$\text{Fe}^{2+}$	$\text{Co}^{2+}$	$\text{Ni}^{2+}$	$\text{Cu}^+$	$\text{Zn}^{2+}$
138	100	75	86	79	82	83	77	75	70	96	75
$\text{V}^{3+}$	$\text{Cr}^{3+}$	$\text{Mn}^{2+}$	$\text{Fe}^{3+}$	$\text{Co}^{3+}$	$\text{Ni}^{2+}$	$\text{Cu}^{2+}$	$\text{Zn}^{2+}$	$\text{Ga}^{3+}$			
<b>Rb</b>	<b>Sr</b>						<b>Ag</b>	<b>Cd</b>	<b>In</b>	<b>Sn</b>	<b>Sb</b>
248	215						144	149	163	141	140
$\text{Rb}^+$	$\text{Sr}^{2+}$						$\text{Ag}^+$	$\text{Cd}^{2+}$	$\text{In}^{3+}$	$\text{Sn}^{2+}$	$\text{Sb}^{3+}$
149	113						115	95	79	93	76
<b>Te</b>	<b>I</b>						<b>Te</b>	<b>I</b>			
							198	196			

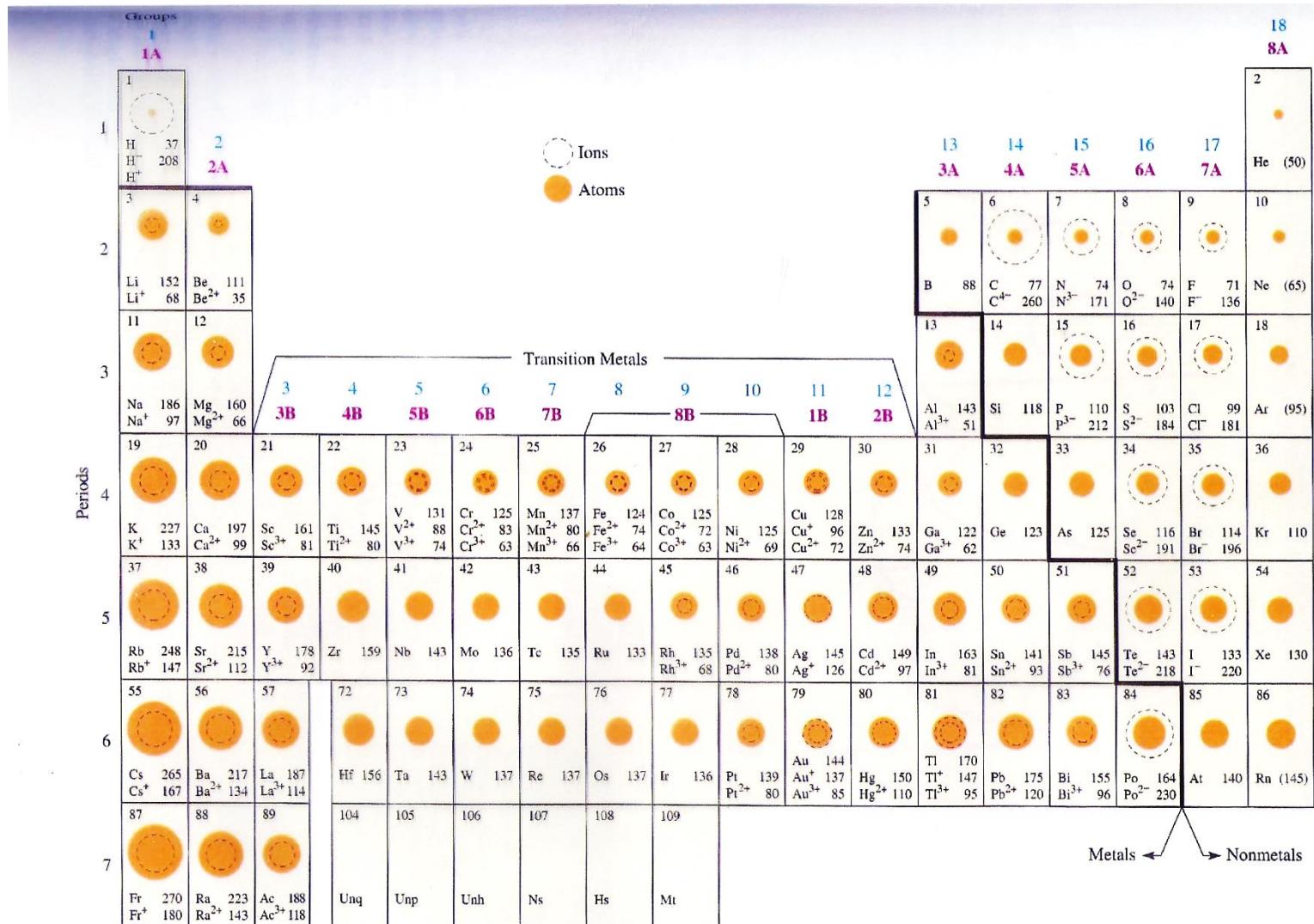
# Goldschmidt's Rules of Substitution

(Selinus et al 2005 – with comments by S. Frape)

3. “*For two competing ions in substitutions, the one with the higher ionic potential (charge/radius) is preferred.*” (Which radius? → Ionic)

e.g.       $\text{Na}^+$  vs  $\text{K}^+$    *in this case  $\text{Na}^+$  is preferred*  
              1/97 vs 1/133 *over  $\text{K}^+$  for substitution*  
              (*So more likely to get Na cpds*)

# Atomic and Ionic Radii



**Figure 8.9**

Atomic and ionic radii, with values in picometers ( $1 \text{ m} = 10^{12} \text{ pm}$ ). (The values in parentheses are estimated.) With some exceptions, radii increase from top to bottom within a group and decrease from left to right across a period. Positive ions are always smaller than their parent atoms, and negative ions are always larger.

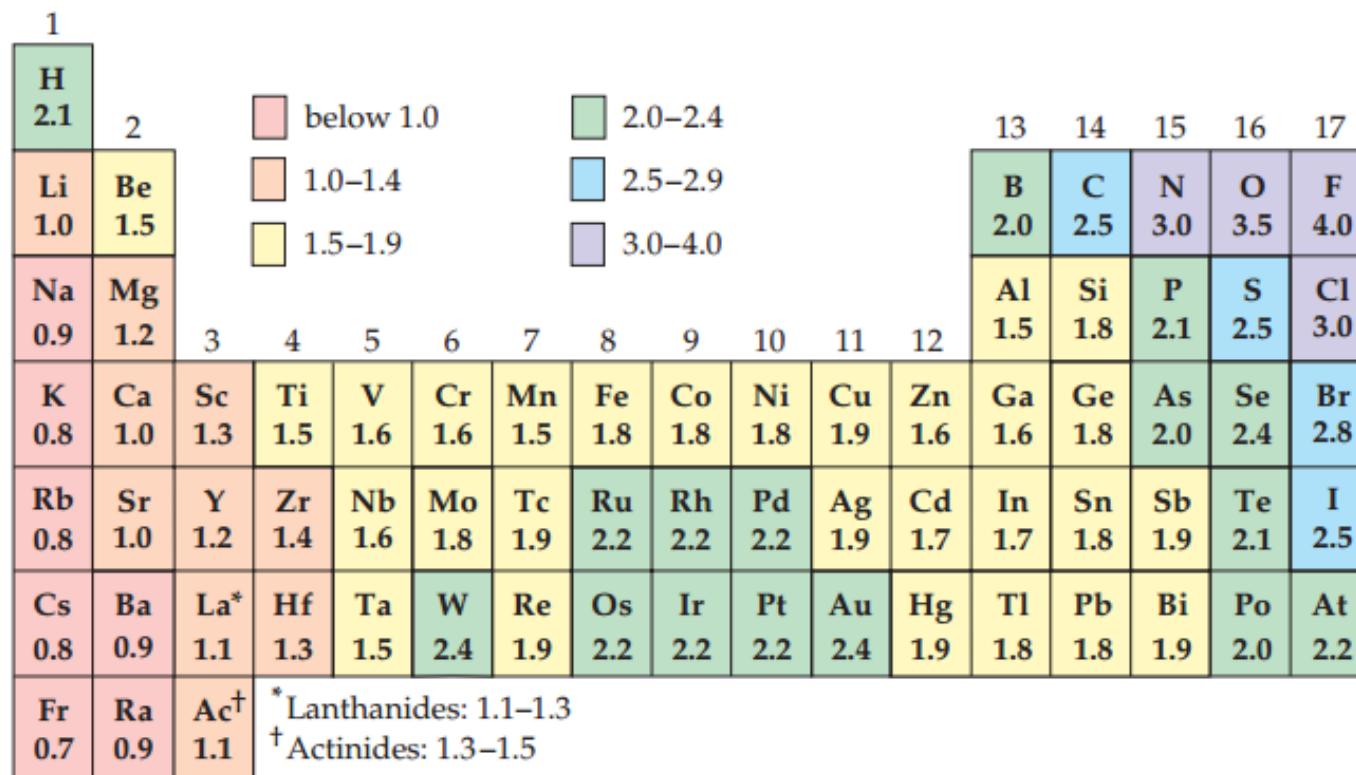
# Goldschmidt's Rules of Substitution

(Selinus et al 2005 – with comments by S. Frape)

4. *“Substitution is limited when competing ions differ in electronegativity and form bonds of different ionic character.”*
  - Usually difference in electronegativity between two atoms is what defines what kind of bond these atoms will form.
  - Therefore, when substituting a cation (e.g.  $\text{Ca}^{2+}$ ) with another one;  $2+$  is usually substituted with cations that have similar electronegativity (e.g.  $\text{Mg}^{2+}$ ) and hence the bond type stays the same and does not change in the crystal compound structure.

# Electronegativity

Petrucci *et al.* 2011

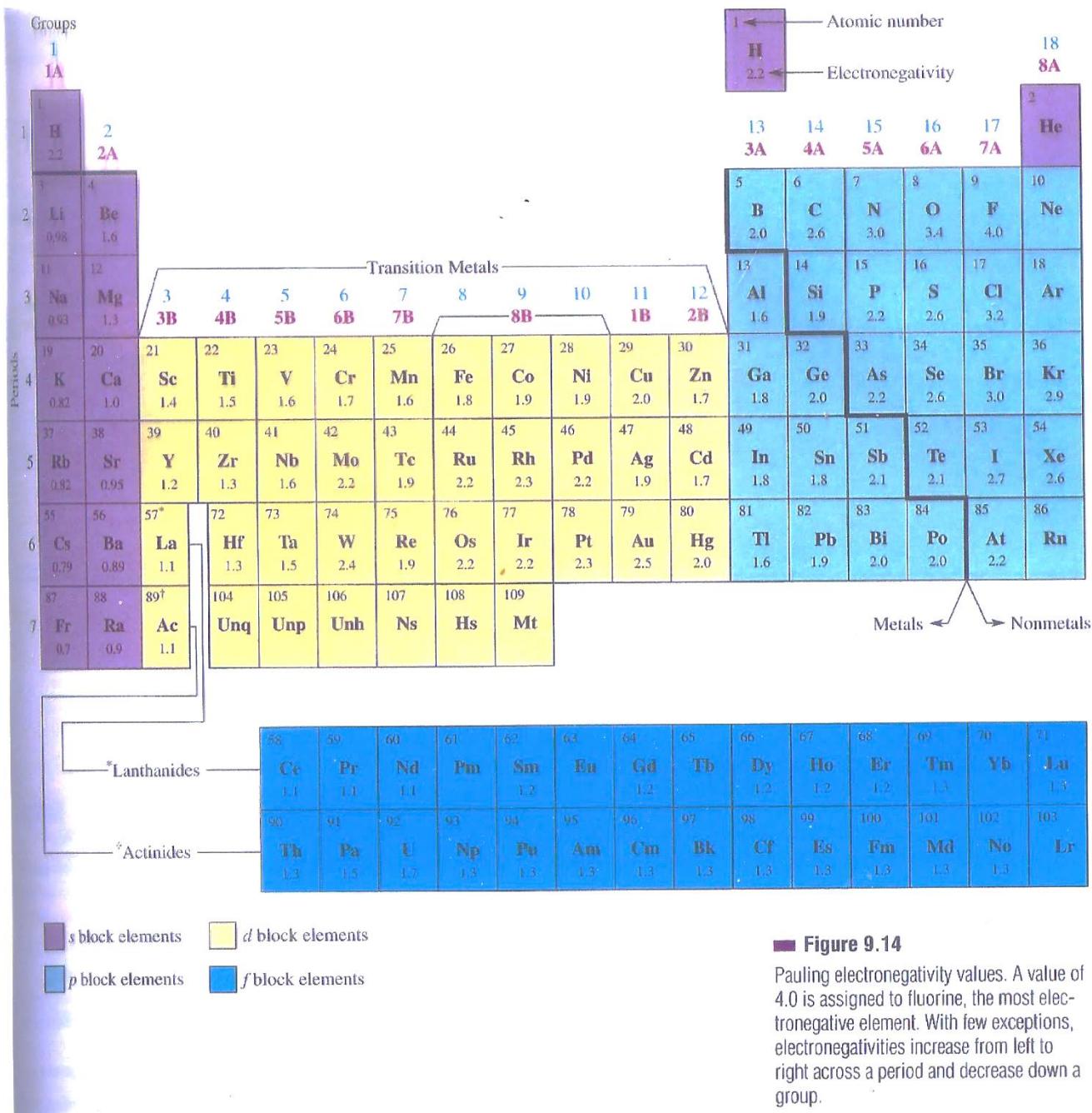


▲ FIGURE 10-6

## Electronegativities of the elements

As a general rule, electronegativities *decrease from top to bottom* in a group and *increase from left to right* in a period of elements. The values are from L. Pauling, *The Nature of the Chemical Bond*, 3rd ed, Cornell University, Ithaca, NY, 1960, page 93. Values may be somewhat different when based on other electronegativity scales.





**Figure 9.14**

Pauling electronegativity values. A value of 4.0 is assigned to fluorine, the most electronegative element. With few exceptions, electronegativities increase from left to right across a period and decrease down a group.

- If a cation is substituted with one that has totally different electronegativity then the electronegativity between the anion and the new cation changes dramatically which would change the bond type and this is not favoured.
- For example, in NaCl the electronegativity difference between Na and Cl is  $3.2 - 0.93 = 2.27$  and since it is larger than 1.7 then it is an ionic bond.
- Therefore  $\text{Na}^+$  can be replaced by K, Li, Rb, Cs and that difference does not change that much and it stays greater than 1.7.
- However, substituting  $\text{Na}^+$  with say, Zn, Fe, Be or any cation with an electronegativity greater than 1.5 would result in a difference between the new cation and  $\text{Cl}^-$  that is less than 1.7 which results in polar covalent or covalent bonding instead of the original ionic bond.

# High Electronegativity

Highly reactive because of their strong tendency to capture electrons.

Periodic Table of the Elements

Highly reactive because they yield electrons easily.

Low Ionization Energy

I	II	Transition Metals												VIIA	VIIIB	VA	VI	VII	0
H <sup>1</sup>																			He <sup>10</sup>
Li <sup>3</sup>	Be <sup>4</sup>													B <sup>5</sup>	C <sup>6</sup>	N <sup>7</sup>	O <sup>8</sup>	F <sup>9</sup>	Ne <sup>10</sup>
Na <sup>11</sup>	Mg <sup>12</sup>	IIIIB	IVB	VIB	VIB	VIIIB	VIIIB	IB	IB					Al <sup>13</sup>	Si <sup>14</sup>	P <sup>15</sup>	S <sup>16</sup>	Cl <sup>17</sup>	Ar <sup>18</sup>
K <sup>19</sup>	Ca <sup>20</sup>	Sc <sup>21</sup>	Ti <sup>22</sup>	V <sup>23</sup>	Cr <sup>24</sup>	Mn <sup>25</sup>	Fe <sup>26</sup>	Co <sup>27</sup>	Ni <sup>28</sup>	Cu <sup>29</sup>	Zn <sup>30</sup>	Ga <sup>31</sup>	Ge <sup>32</sup>	As <sup>33</sup>	Se <sup>34</sup>	Br <sup>35</sup>	Kr <sup>36</sup>		
Rb <sup>37</sup>	Sr <sup>38</sup>	Y <sup>39</sup>	Zr <sup>40</sup>	Nb <sup>41</sup>	Mo <sup>42</sup>	Tc <sup>43</sup>	Ru <sup>44</sup>	Rh <sup>45</sup>	Pd <sup>46</sup>	Ag <sup>47</sup>	Cd <sup>48</sup>	In <sup>49</sup>	Sn <sup>50</sup>	Sb <sup>51</sup>	Te <sup>52</sup>	I <sup>53</sup>	Xe <sup>54</sup>		
Cs <sup>55</sup>	Ba <sup>56</sup>	Hf <sup>57</sup>	Ta <sup>58</sup>	W <sup>59</sup>	Re <sup>60</sup>	Os <sup>61</sup>	Ir <sup>62</sup>	Pt <sup>63</sup>	Au <sup>64</sup>	Hg <sup>65</sup>	Tl <sup>66</sup>	Pb <sup>67</sup>	Bi <sup>68</sup>	Po <sup>69</sup>	At <sup>70</sup>	Rn <sup>71</sup>			
Fr <sup>87</sup>	Ra <sup>88</sup>	Rf <sup>89</sup>	Ha <sup>90</sup>																
Lanthanides																			
Actinides																			
		La <sup>57</sup>	Ce <sup>58</sup>	Pr <sup>59</sup>	Nd <sup>60</sup>	Pm <sup>61</sup>	Sm <sup>62</sup>	Eu <sup>63</sup>	Gd <sup>64</sup>	Tb <sup>65</sup>	Dy <sup>66</sup>	Ho <sup>67</sup>	Er <sup>68</sup>	Tm <sup>69</sup>	Yb <sup>70</sup>	Lu <sup>71</sup>			
		Ac <sup>92</sup>	Th <sup>93</sup>	Pa <sup>94</sup>	U <sup>95</sup>	Np <sup>96</sup>	Pu <sup>97</sup>	Am <sup>98</sup>	Cm <sup>99</sup>	Bk <sup>100</sup>	Cf <sup>101</sup>	Es <sup>102</sup>	Fm <sup>103</sup>	Md <sup>104</sup>	No <sup>105</sup>	Lr <sup>106</sup>			

■ Metal      ■ Metalloid      ■ Nonmetal

The highly reactive corners of the Periodic Table

- See the Extra Material on Bonds for further reading, “If you are Interested”, from Notes made for Earth 281 by Dr. Orfan Shouakar-Stash.

# **Elements – Distribution in Natural Environment**

**CHAPTER 2**  
*Selinus et al. 2005*

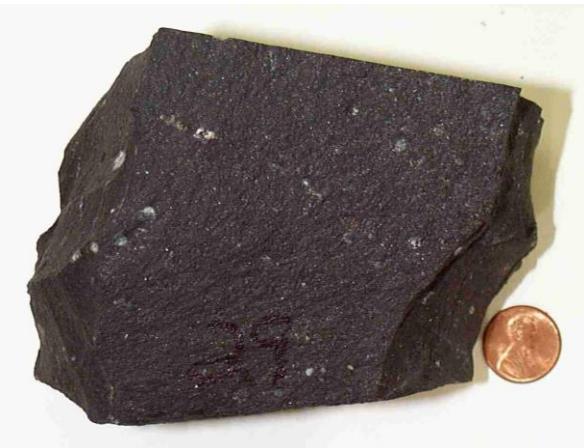
# 1. Different geological environments: Different Rock Chemistry (Table II)

**Table 3.2** Common geochemical associations

Group	Associations
Generally associated elements	K-Rb                    Ca-Sr Al-Ga                    Si-Ge Zr-Hf                    Nb-Ta Rare earths (REEs), La, Y Pt-Ru-Rh-Pd-Os-Ir      Au-Ag
Plutonic rocks	
Generally associated elements	Si-Al-Fe-Mg-Ca-Na-K-Ti-Mn-Cr-V Zr-Hf-REEs-Th-U-Sr-Ba-P B-Be-Li-Sn-Ga-Nb-Ta-W-Halides
Specific associations	
Felsic igneous rocks	Si-K-Na
Alkaline igneous rocks	Al-Na-Zr-Ti-Nb-Ta-F-P-Ba-Sr- REEs
Mafic igneous rocks	Fe-Mg-Ti-V
Ultramafic igneous rocks	Mg-Fe-Cr-Ni-Co
Some pegmatites	Li-Be-B-Rb-Cs-REEs-Nb-Ta-U-Th
Some contact metasomatic deposits	Mo-W-Sn
Potassium feldspars	K-Rb-Ba-Pb
Many other potassium-rich minerals	K-Na-Rb-Cs-Tl
Ferromagnesian minerals	Fe-Mg-Mn-Ni-Co-Cu-Zn
Sedimentary rocks	
Fe-oxide rich	Fe-As-Co-Ni-Se
Mn-oxide rich	Mn-As-Ba-Co-Mo-Ni-V-Zn
Phosphatic limestones	P-F-U-Cd-Ag-Pb-Mo
Black shales	Al-As-Sb-Se-Mo-Zn-Cd-Ag-U-Au- Ni-V

After Rose et al. (1979)

# 1. Different geological environments: Different Rock Chemistry (Table II)



<http://itc.gsw.edu/>



<http://www.geologyclass.org/>

Plutonic rocks	
Generally associated elements	Si-Al-Fe-Mg-Ca-Na-K-Ti-Mn-Cr-V Zr-Hf-REEs-Th-U-Sr-Ba-P B-Be-Li-Sn-Ga-Nb-Ta-W-Halides
Specific associations	
Felsic igneous rocks	Si-K-Na
Alkaline igneous rocks	Al-Na-Zr-Ti-Nb-Ta-F-P-Ba-Sr- REEs
Mafic igneous rocks	Fe-Mg-Ti-V
Ultramafic igneous rocks	Mg-Fe-Cr-Ni-Co
Some pegmatites	Li-Be-B-Rb-Cs-REEs-Nb-Ta-U-Th
Some contact metasomatic deposits	Mo-W-Sn
Potassium feldspars	K-Rb-Ba-Pb
Many other potassium-rich minerals	K-Na-Rb-Cs-Tl
Ferromagnesian minerals	Fe-Mg-Mn-Ni-Co-Cu-Zn
Sedimentary rocks	
Fe-oxide rich	Fe-As-Co-Ni-Se
Mn-oxide rich	Mn-As-Ba-Co-Mo-Ni-V-Zn
Phosphatic limestones	P-F-U-Cd-Ag-Pb-Mo
Black shales	Al-As-Sb-Se-Mo-Zn-Cd-Ag-U-Au-Ni-V

After Rose et al. (1979)

# 1. Different geological environments:

- Add to this different earth processes, e.g. (a) glaciation and (b) desert processes.



Photo courtesy Emily Henkemans



# 1. Different geological environments: Different Rock Chemistry (Table II)

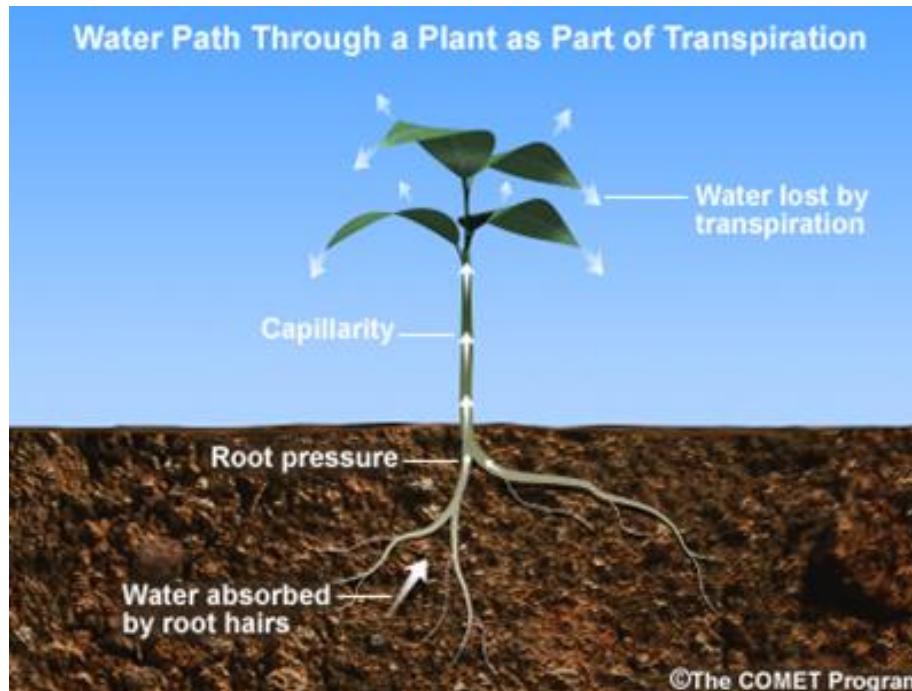
- This leads to different surficial materials (soils) and different ecosystems.

The profile on the right is a typical temperate forest Podzol-Podsoil



# 1. Different geological environments: Different Rock Chemistry (Table II)

- = all impact the chemistry of the environment.
- Soil = plant nutrition = input to the ecosystem



# **Soil Age**

- decades vs. 100 millions of years
- time necessary to break those bonds
- weathering – removal or enrichment of elements

# **Process**

- can determine size of material, heterogeneity (sorting), maturity of the soil material (good vs. bad, i.e. what elements are concentrated)
- resistates (Zr, Al) vs. nutrients (C, N, P)
- wet vs. dry → hot vs. frozen

2. All the background processes, etc. can lead to what elements in the periodic table become dominant and available in some geological and soil environments.

e.g. Rich volcanic soils (shown on slide)

VS.

Australian outback

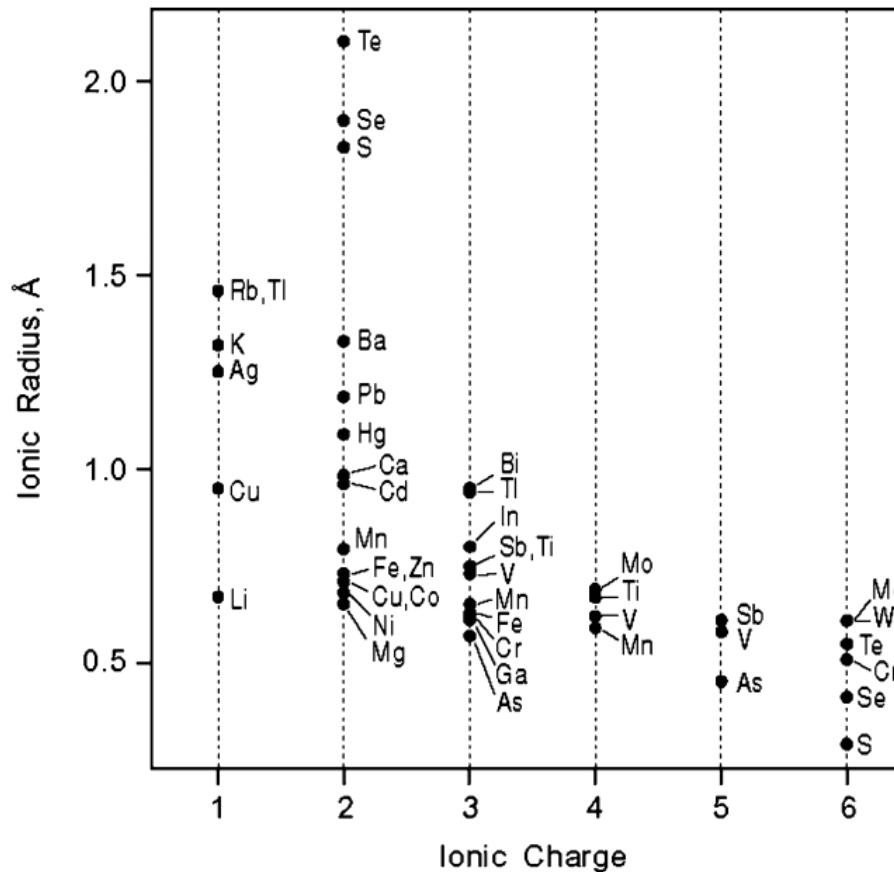


2. All the background processes, etc. can lead to what elements in the periodic table become dominant and available in some geological and soil environments.
- Plants adapt – in Australia fertilizer can kill many native plants.



# Minerals and Chemistry

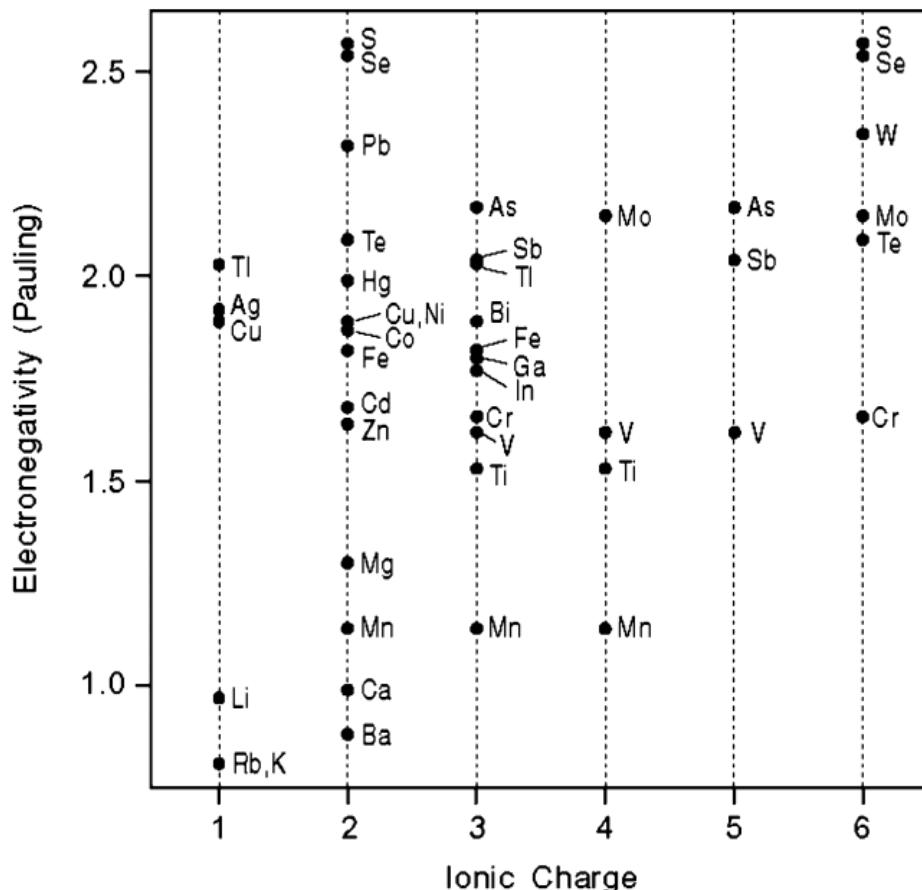
- Substitutions: Figure 8 and 9 → ionic radius and electronegativity



**Fig. 3.8** The relationship of ionic radius to ionic charge (valence) for major and trace elements of mineralogical and geochemical interest

# Minerals and Chemistry

- Substitutions: Figure 8 and 9 → ionic radius and electronegativity



**Fig. 3.9** The relationship of electronegativity to ionic charge (valence) for major and trace elements of mineralogical and geochemical interest

# Minerals and Chemistry

- Olivine:  $(\text{Mg}, \text{Fe})_2 \text{SiO}_4$
- Fe, Mg ionic radius 0.74 and 0.66 $\text{\AA}$
- Other 2 $^+$  ions Ni 0.69A°, Cu 0.72A° Co .72A°  
Zn 0.74A° and Mn 0.8A°
- In some cases Ca 0.99A° → Mg 0.66A° series

- Return to Table I, page 26...

**Table 3.1** Classification of elements as lithophile, chalcophile, siderophile, or atmophile

Lithophile	Chalcophile	Siderophile	Atmophile
C, O, P, H, F, Cl, Br, I, Si, Al, Fe, Mg, Ca, Na, K, Ti, Sc, Cr, V, Mn, Th, U, Nb, Ta, Sn, W, Be, Li, Rb, Cs, Ba, Sr, B, Y, Zr, Hf, rare earths (REEs), Ga, (Cd), (Zn), (Pb), (Cu), (Ni), (Co), (Mo), (Tl)	S, Se, Te, As, Sb, Bi, Ag, In, Ge, Tl, Hg, Cd, Zn, Pb, Cu, Ni, Co, Mo, Re, (Fe), (Sn), (Au)	Pt, Ir, Os, Ru, Rh, Pd, Au, (Fe)	N, O, C (as CO <sub>2</sub> ), H, He, Rn, and other noble gases, (S as oxides), (Hg)

- Return to Table I, page 26...

e.g. Hg as an Atmophile – long range transport of Hg as a gas

## Chalcophile

---

S, Se, Te, As, Sb, Bi, Ag, In,  
Ge, Tl, Hg, Cd, Zn, Pb, Cu,  
Ni, Co, Mo, Re, (Fe), (Sn),  
(Au)

## Atmophile

---

N, O, C (as CO<sub>2</sub>), H, He, Rn,  
and other noble gases, (S as  
oxides), (Hg)

- Return to Table I, page 26...
  - Table I: Let's look at what these groups are

- What elements have natural associations as a result of Goldschmidt/Pauling rules of substitution?

## Lithophile

C, O, P, H, F, Cl, Br, I, Si, Al, Fe, Mg, Ca, Na, K, Ti, Sc, Cr, V, Mn, Th, U, Nb, Ta, Sn, W, Be, Li, Rb, Cs, Ba, Sr, B, Y, Zr, Hf, rare earths (REEs), Ga, (Cd), (Zn), (Pb), (Cu), (Ni), (Co), (Mo), (Tl)

# Rocks: types and chemistry (Table III).

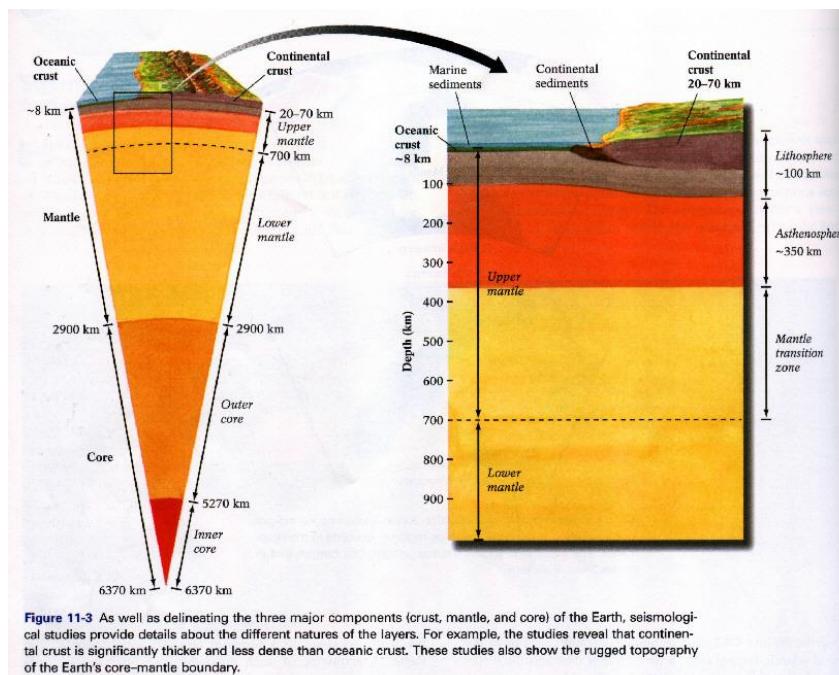
**Table 3.3** Compilation of average geochemical background data for the earth's crust and selected rock types

	Hg ( $\mu\text{g kg}^{-1}$ )	Pb ( $\text{mg kg}^{-1}$ )	Cd ( $\text{mg kg}^{-1}$ )	Cr ( $\text{mg kg}^{-1}$ )	Ni ( $\text{mg kg}^{-1}$ )	As ( $\text{mg kg}^{-1}$ )	Cu ( $\text{mg kg}^{-1}$ )	Zn ( $\text{mg kg}^{-1}$ )	Ref.
<b>Earth's crust</b>									
	80	13	0.2	100	75	2	55	70	Taylor (1964)
	90	12	0.2	110	89	2	63	94	Lee and Yao (1970)
<b>Upper continental crust</b>									
		20	0.1	35	20	1.5	25	71	McLennan (1992)
		80	13	0.2	77	61	1.7	50	Lee and Yao (1970)
<b>Igneous rocks</b>									
Ultramafic	4	1	0.1	1,600	2,000	1	10	50	Turekian and Wedepohl (1961)
Mafic	13	6	0.2	170	130	2	87	105	Turekian and Wedepohl (1961)
Intermediate	21	15	0.1	22	15	2	30	60	Turekian and Wedepohl (1961)
		10		55	30		60		McLennan (1992)
Felsic (4)	39	19	0.1	4	5	1	10	39	Turekian and Wedepohl (1961)
<b>Sedimentary rocks</b>									
Sandstone	57	14	0.02	120	3	1	15	16	Faust and Aly (1981)
Limestone	46	16	0.05	7	13	2	4	16	Faust and Aly (1981)
Shale	270	80	0.2	423	29	9	45	130	Faust and Aly (1981)
Black shale		15	4	18	68	22	50	189	Dunn (1990)
		100		700	300		200	1,500	Vine and Tourtelot (1970)

# Rocks: types and chemistry (Table III).

**Table 3.3** Compilation of average geochemical background data for the earth's crust and selected rock types

Hg ( $\mu\text{g kg}^{-1}$ )	Pb ( $\text{mg kg}^{-1}$ )	Cd ( $\text{mg kg}^{-1}$ )	Cr ( $\text{mg kg}^{-1}$ )	Ni ( $\text{mg kg}^{-1}$ )	As ( $\text{mg kg}^{-1}$ )	Cu ( $\text{mg kg}^{-1}$ )	Zn ( $\text{mg kg}^{-1}$ )	Ref.
<b>Earth's crust</b>								
80	13	0.2	100	75	2	55	70	Taylor (1964)
90	12	0.2	110	89	2	63	94	Lee and Yao (1970)
<b>Upper continental crust</b>								
20	0.1	35	20	1.5	25	71	McLennan (1992)	
80	13	0.2	77	61	1.7	50	81	Lee and Yao (1970)



# Rocks: types and chemistry (Table III).

**Table 3.3** Compilation of average geochemical background data for the earth's crust and selected rock types

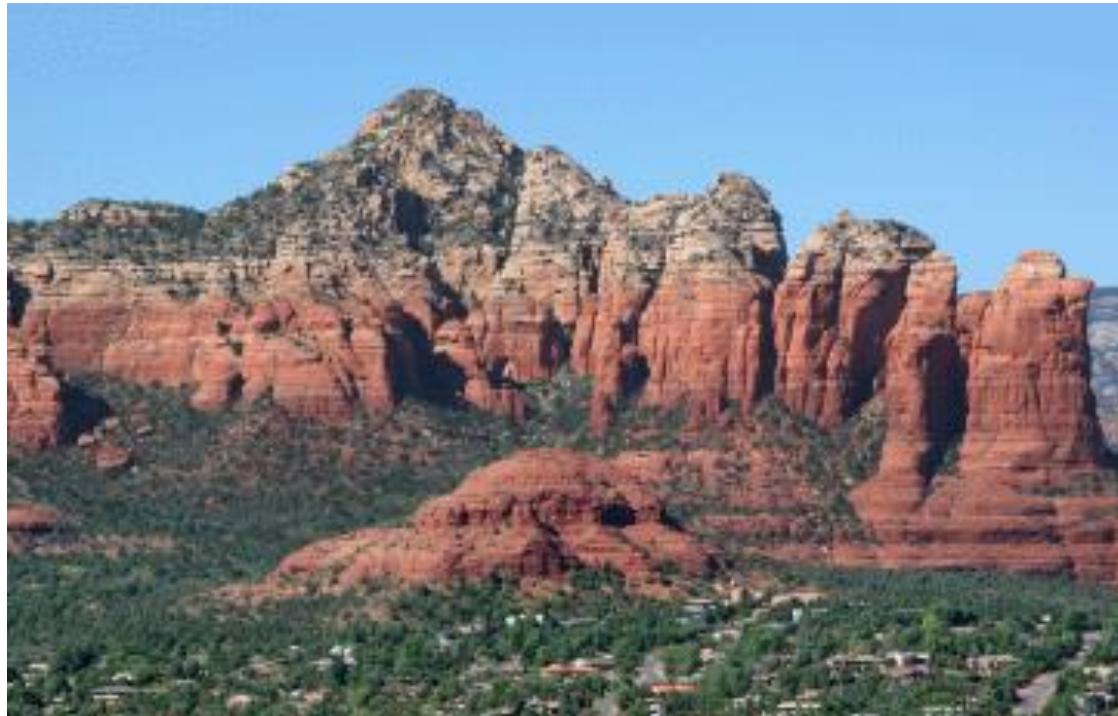
	Hg ( $\mu\text{g kg}^{-1}$ )	Pb ( $\text{mg kg}^{-1}$ )	Cd ( $\text{mg kg}^{-1}$ )	Cr ( $\text{mg kg}^{-1}$ )	Ni ( $\text{mg kg}^{-1}$ )	As ( $\text{mg kg}^{-1}$ )	Cu ( $\text{mg kg}^{-1}$ )	Zn ( $\text{mg kg}^{-1}$ )	Ref.
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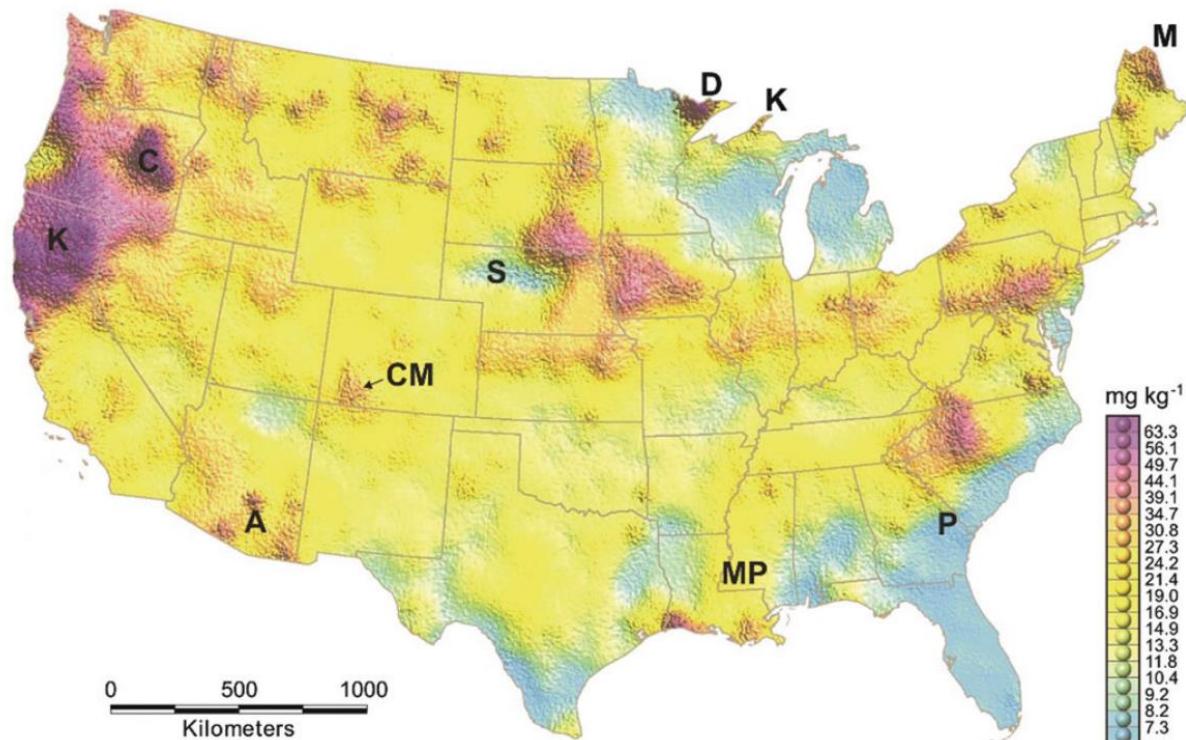


# Chemical Variability and Maps

1. Maps
  - (1) Geology and Elements
  - (2) Soils – Tills etc.
  - (3) Water – Surface (streams) and Groundwater

# Chemical Variability and Maps

- e.g. Figure 1 in book Cu in soil 7 to 63 mg/Kg
- a) Uncontaminated soils
  - b) High Cu associated with certain geological features
  - c) Highs (red) in NW basalt flows: lows SE - limestones

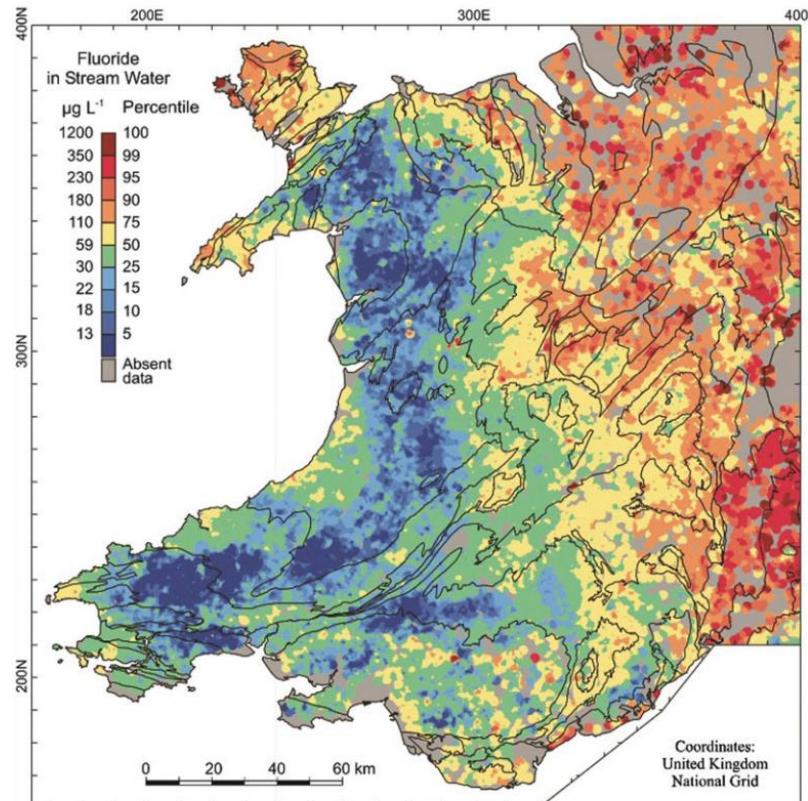


**Fig. 3.1** Copper content ( $\text{mg kg}^{-1}$ ) of soils in the conterminous United States (After Gustavsson et al. 2001 and Shacklette and Boerngen 1984. Reproduced with the permission of the United States Geological Survey)

# Chemical Variability and Maps

e.g. Figure 14 (Wales and England) Fluoride (F) in Streams

- a) High (red) Permo-Triassic paleo desert along seashore
- b) Low (blue) old Paleozoics
- c) Ability of the environment to retain F (will discuss later in the course)

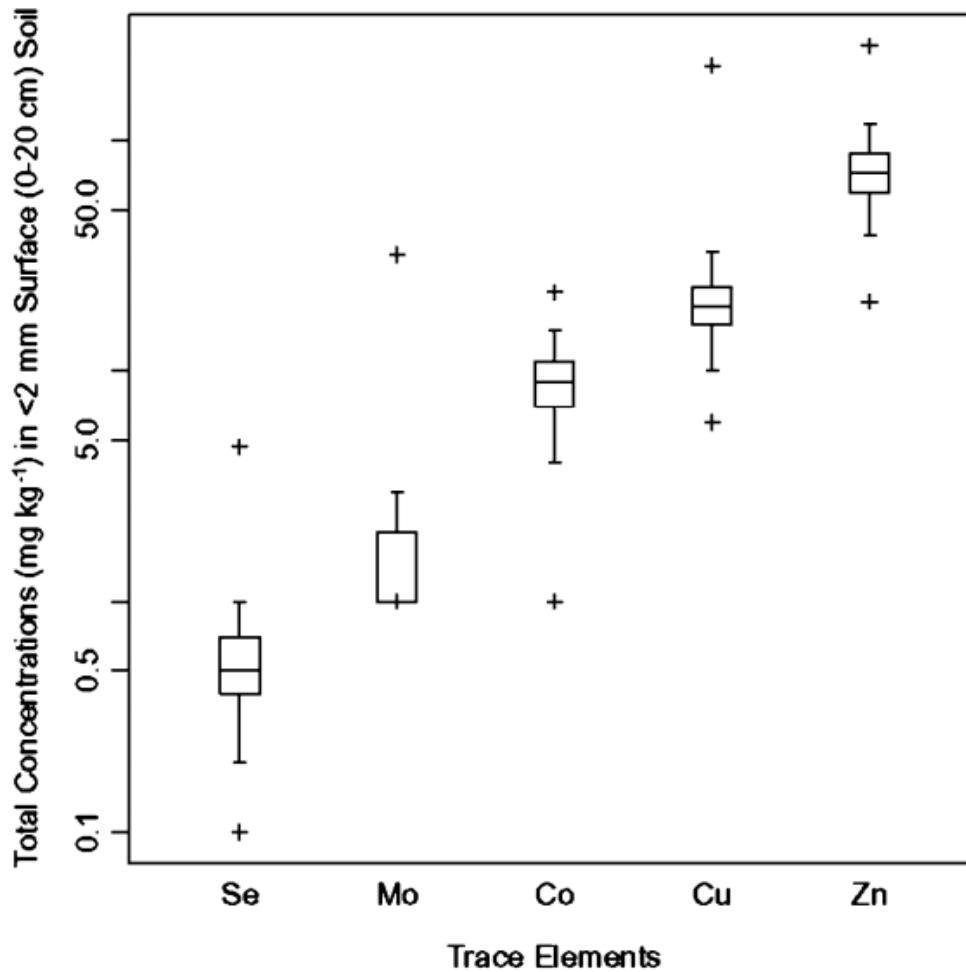


**Fig. 3.14** Fluoride ( $\mu\text{g/L}^{-1}$ ) in stream waters ( $N = 17,416$ ) from Wales and adjacent parts of England (Reproduced with the permission of the British Geological Survey and Pergamon Press)

2. Exploration Geochemists: Like to use statistics and graphs to analyze large collections of data.

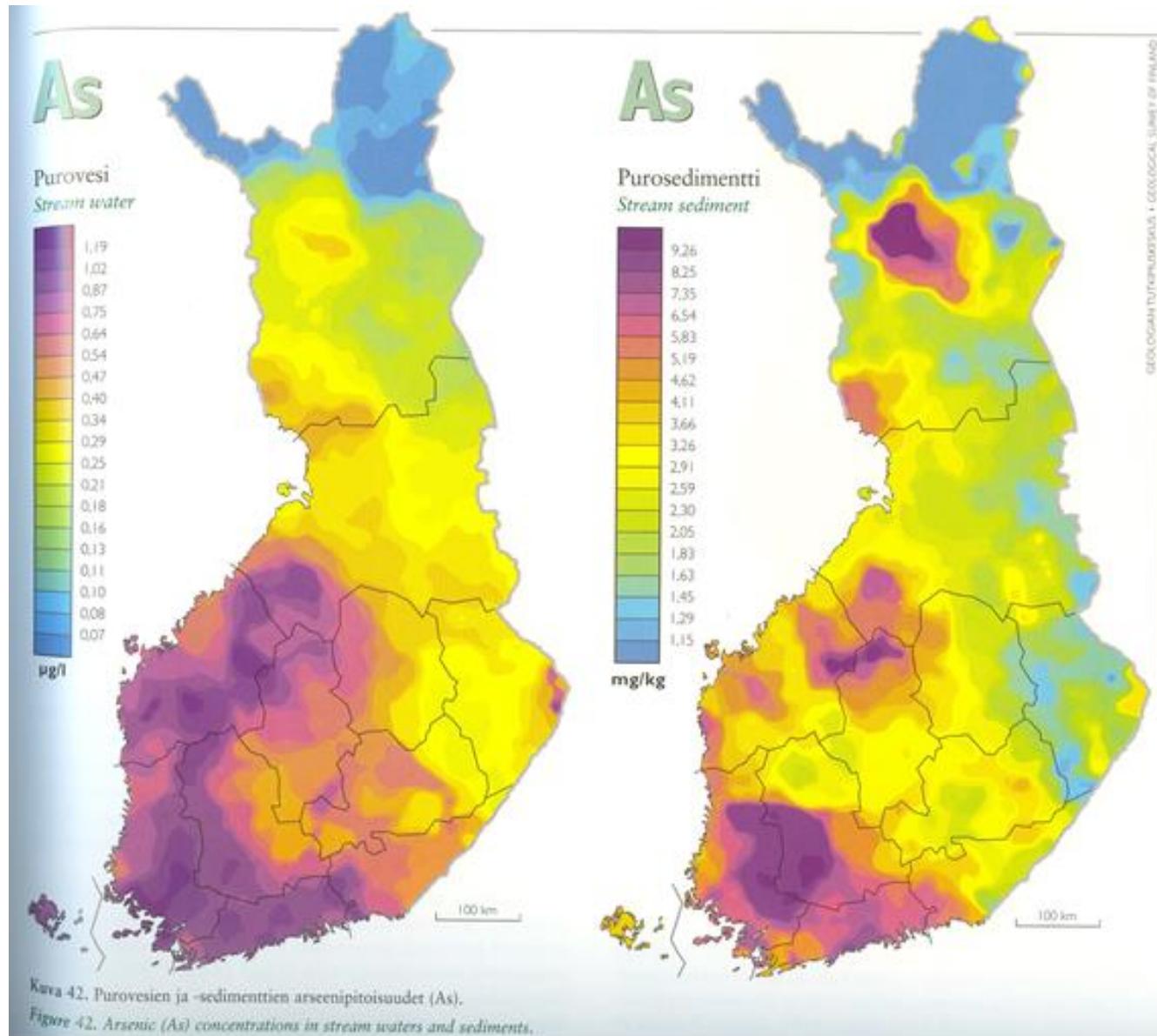
TERMS: Level – Relief (range)

- a) Level  $\cong$  mean, geometric mean, median; median less affected by abnormal values
- b) Relief  $\cong$  homogeneity or lack of
- c) High relief – noisy data; on local scale could be due to complex geology or multiple processes in one geological environment.  
e.g. mineral diversity, weathering, soil types, etc.
- d) So Figure 2... conc. vs. element



**Fig. 3.2** Selenium, molybdenum, cobalt, copper, and zinc contents ( $\text{mg kg}^{-1}$ ) of the <2 mm fraction of soils ( $N = 973$ ) from the Canadian Prairies. These were chosen because of biological importance (Note: Crosses indicate maximum and minimum values, ends of whiskers are the 5th and 95th percentiles, the box is bounded by the 1st and 3rd quartiles, and the bar indicates the median. If a notch is present rather than a bar, the notch indicates the 95% confidence bounds around the median, which is at the narrowest point)

# Finland – Geology - Water



# Finland – Geology

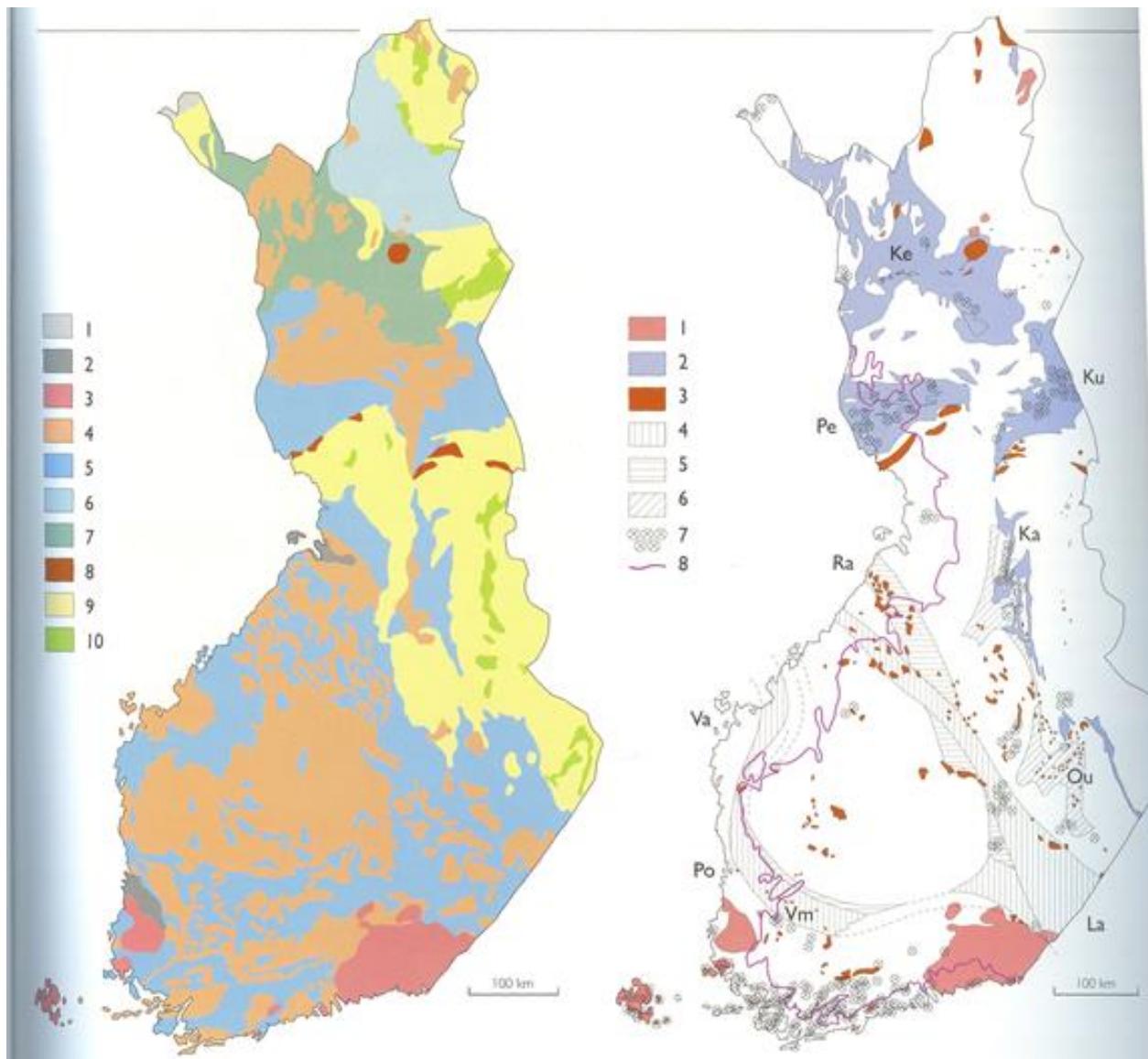


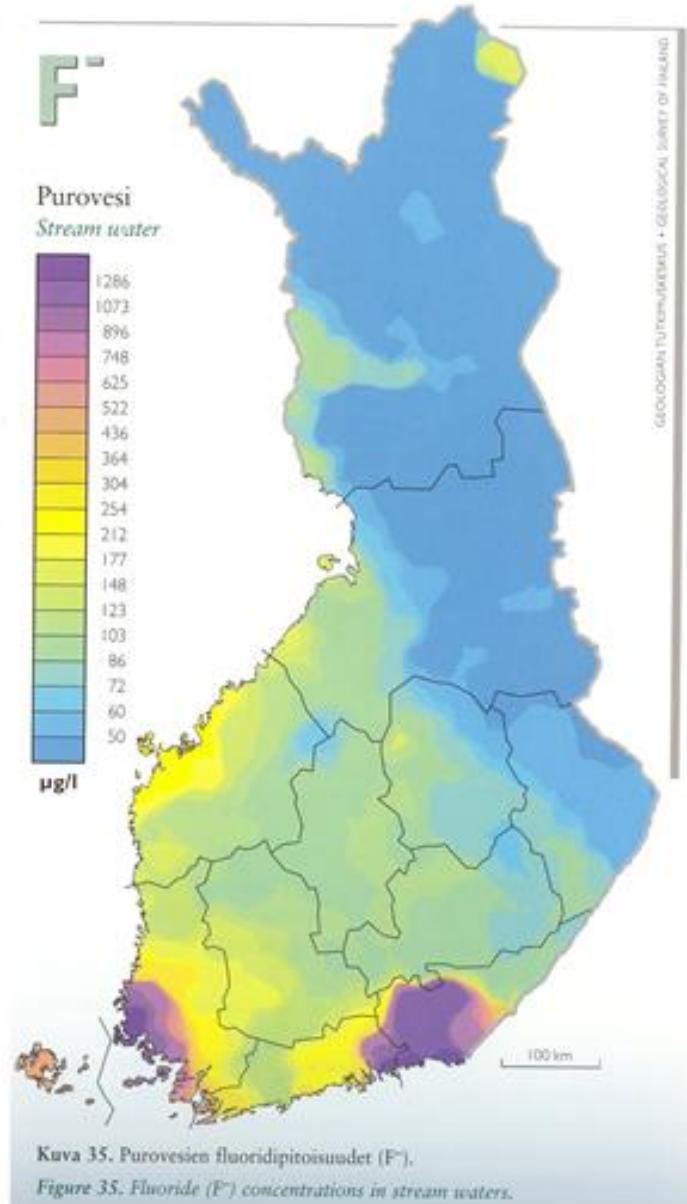
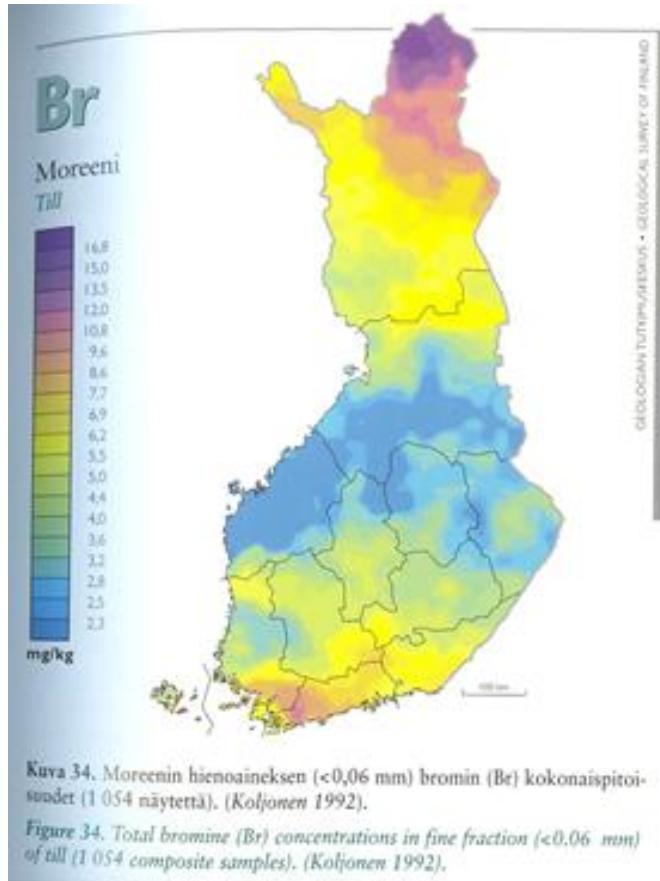
Figure 3. Bedrock of Finland.

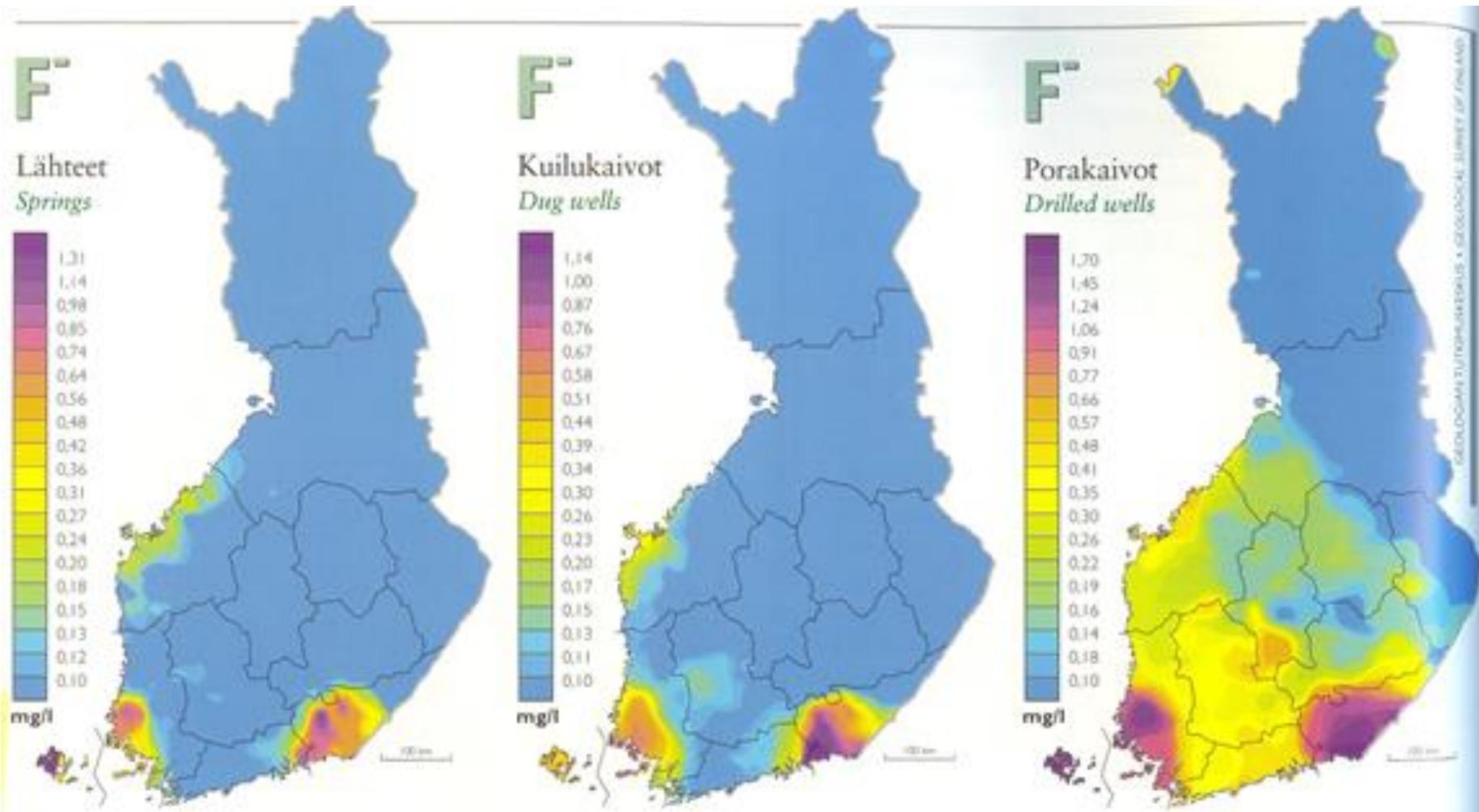
Paleozoic formations: 1. Caledonian allochthon.

Proterozoic formations: 2. Jotnian sedimentary sequences; 3. Rapakivi granite batholiths; 4. Plutonic Svecofennian intrusions; 5. Metamorphic schist and gneiss belts of Svecofennian and Karelian complexes; 6. Lapland granulite belt; 7. Central Lapland greenstone belt; 8. Mafic layered intrusions.

Archean formations: 9. Granitoids, migmatites and granulite gneisses; 10. Greenstone belts (Salkikoff et al. 1997, cf. Simonen 1980b).

# Finland – Br<sup>-</sup> & F<sup>-</sup>

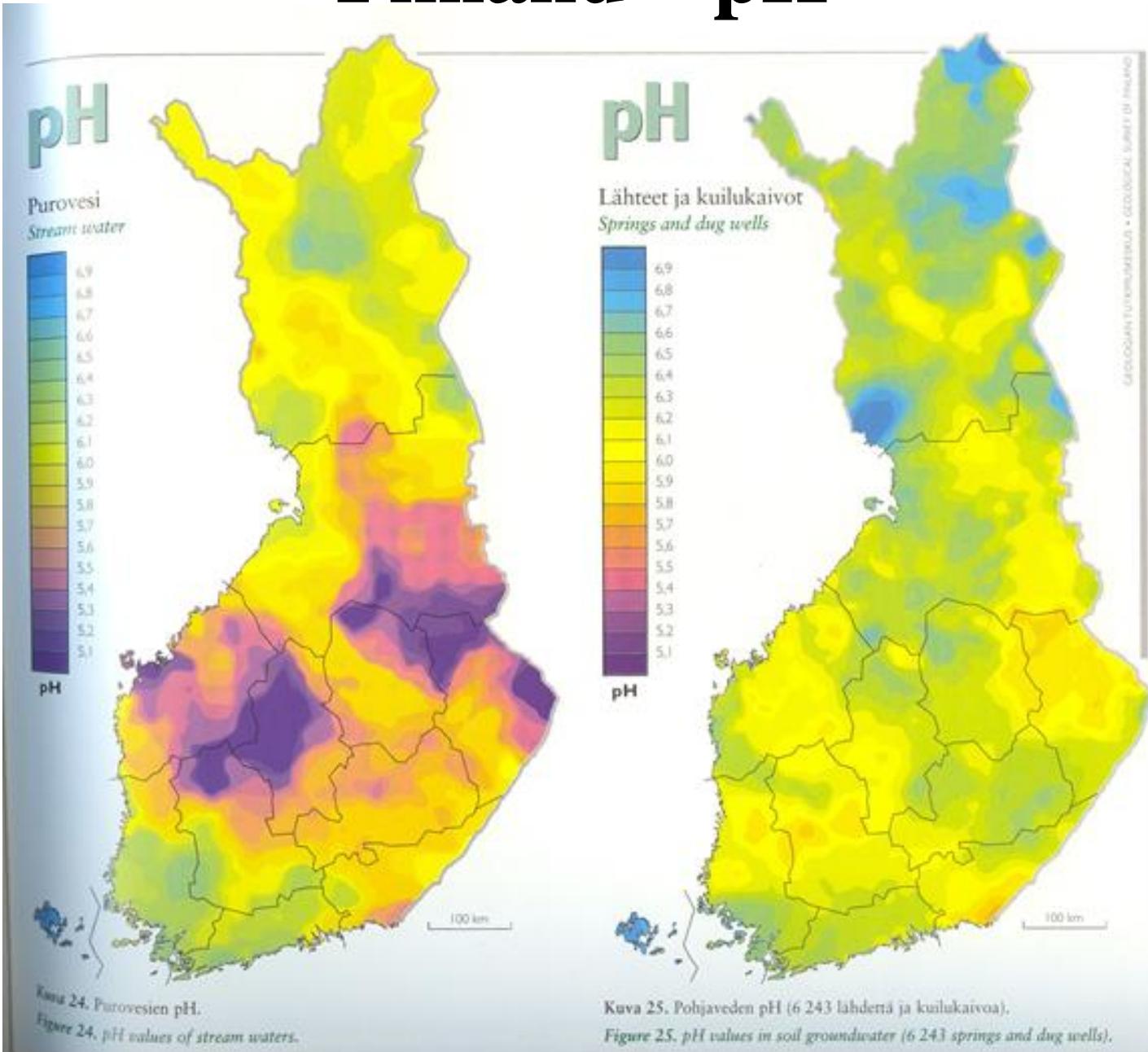




Kuva 36. Pohjavesien fluoridipitoisuudet (2 149 lähdeettä, 5 097 kuilukaivoa, 1 681 porakaivoa). (Laherimo 1990).

Figure 36. Fluoride concentrations in groundwater (2 149 springs, 5 097 wells in soil and 1 681 wells drilled into bedrock). (Laherimo 1990).

# Finland – pH



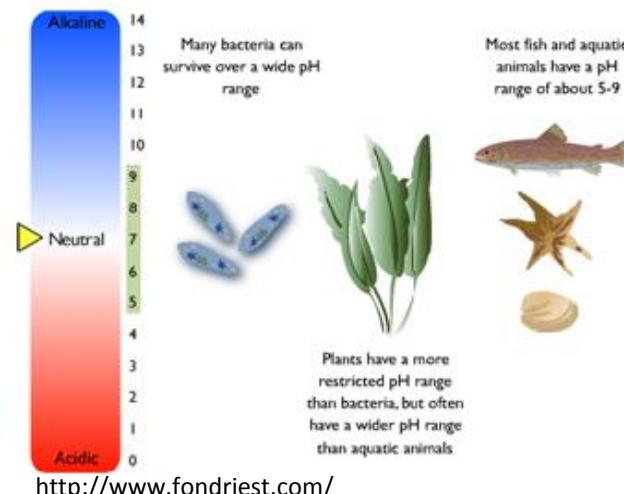
**Table 3.4** Mobility of elements in the surface environment

	Oxidizing (pH 5–8)	Oxidizing (pH < 4)	Reducing
Relative mobility			
Highly mobile	Cl, Br, I, S, Rn, He, C, N, Mo, B, Se, Te	Cl, Br, I, S, Rn, He, C, N, B	Cl, Br, I, Rn, He
Moderately mobile	Ca, Na, Mg, Li, F, Zn, Ag, U, V, As, Sb, Sr, Hg	Ca, Na, Mg, Sr, Li, F, Zn, Cd, Hg, Cu, Ag, Co, Ni, U, V, As, Mn, P	Ca, Na, Mg, Li, Sr, Ba, Ra, F, Mn
Slightly mobile	K, Rb, Ba, Mn, Si, Ge, P, Pb, Cu, Ni, Co, Cd, In, Ra, Be, W	K, Rb, Ba, Si, Ge, Ra	K, Rb, Si, P, Fe
Immobile	Fe, Al, Ga, Sc, Ti, Zr, Hf, Th, Sn, REEs, Pt metals, Au, Cr, Nb, Ta, Bi, Cs	Fe, Al, Ga, Sc, Ti, Zr, Hf, Th, Sn, REEs, Pt metals, Au, As, Mo, Se	Fe, Al, Ga, Sc, Ti, Zr, Hf, Th, Sn, Fe, REEs, Au, Cu, Pt metals, Ag, Pb, Zn, Cd, Hg, Ni, Co, As, Sb, Bi, U, V, Se, Te, Mo, In, Cr, Nb, Ta

After Rose et al. (1979)

## What is pH?

- pH describes the acidity or alkalinity of a solution.
- It is actually the measure of the amount of hydrogen ions in solution.
- $pH = -\log_{10}[H^+]$



## Oxidizing (pH 5–8)

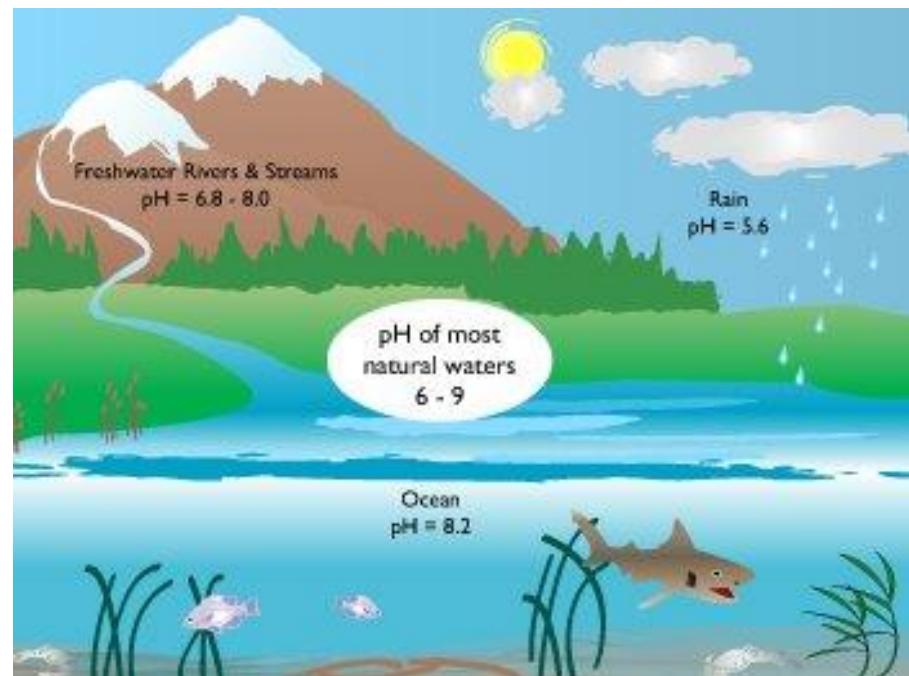
### Relative mobility

Highly mobile Cl, Br, I, S, Rn, He, C, N, Mo, B, Se, Te

Moderately mobile Ca, Na, Mg, Li, F, Zn, Ag, U, V, As, Sb, Sr, Hg

Slightly mobile K, Rb, Ba, Mn, Si, Ge, P, Pb, Cu, Ni, Co, Cd, In, Ra, Be, W

Immobile Fe, Al, Ga, Sc, Ti, Zr, Hf, Th, Sn, REEs, Pt metals, Au, Cr, Nb, Ta, Bi, Cs



## Oxidizing (pH < 4)

High Mobile

Cl, Br, I, S, Rn, He, C, N, B

Moderately Mobile

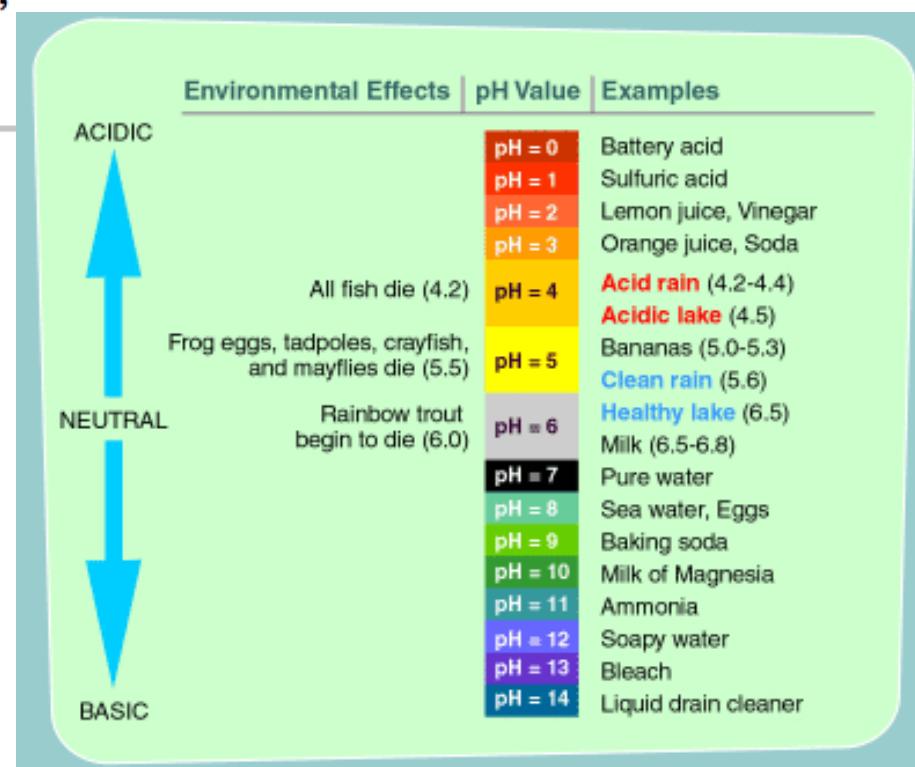
Ca, Na, Mg, Sr, Li, F, Zn, Cd, Hg, Cu, Ag, Co, Ni, U, V, As, Mn, P

Slightly Mobile

K, Rb, Ba, Si, Ge, Ra

Immobile

Fe, Al, Ga, Sc, Ti, Zr, Hf, Th, Sn, REEs, Pt metals, Au, As, Mo, Se



---

**Reducing**

---

High Mobile

**Cl, Br, I, Rn, He**

---

Moderately Mobile

**Ca, Na, Mg, Li, Sr, Ba, Ra, F, Mn**

---

Slightly Mobile

**K, Rb, Si, P, Fe**

---

Immobile

**Fe, Al, Ga, Sc, Ti, Zr, Hf, Th, Sn, Fe, REEs, Au, Cu, Pt metals, Ag, Pb, Zn, Cd, Hg, Ni, Co, As, Sb, Bi, U, V, Se, Te, Mo, In, Cr, Nb, Ta**

---

**Table 3.4** Mobility of elements in the surface environment

	Oxidizing (pH 5–8)	Oxidizing (pH < 4)	Reducing
Relative mobility			
Highly mobile	Cl, Br, I, S, Rn, He, C, N, Mo, B, Se, Te	Cl, Br, I, S, Rn, He, C, N, B	Cl, Br, I, Rn, He
Moderately mobile	Ca, Na, Mg, Li, F, Zn, Ag, U, V, As, Sb, Sr, Hg	Ca, Na, Mg, Sr, Li, F, Zn, Cd, Hg, Cu, Ag, Co, Ni, U, V, As, Mn, P	Ca, Na, Mg, Li, Sr, Ba, Ra, F, Mn
Slightly mobile	K, Rb, Ba, Mn, Si, Ge, P, Pb, Cu, Ni, Co, Cd, In, Ra, Be, W	K, Rb, Ba, Si, Ge, Ra	K, Rb, Si, P, Fe
Immobile	Fe, Al, Ga, Sc, Ti, Zr, Hf, Th, Sn, REEs, Pt metals, Au, Cr, Nb, Ta, Bi, Cs	Fe, Al, Ga, Sc, Ti, Zr, Hf, Th, Sn, REEs, Pt metals, Au, As, Mo, Se	Fe, Al, Ga, Sc, Ti, Zr, Hf, Th, Sn, Fe, REEs, Au, Cu, Pt metals, Ag, Pb, Zn, Cd, Hg, Ni, Co, As, Sb, Bi, U, V, Se, Te, Mo, In, Cr, Nb, Ta

After Rose et al. (1979)

# **Public Health: A Few Other Issues**

As, Cd, Hg

Many examples: Usually as a result of our disturbing the environment:

1. Zn mining and the release of Cd - bone disease, kidney failure
2. Sewage sludge – we tend to excrete heavy metals – sludge spreading = Cd and others (only on non-root crops in our area)
3. Coal (peat) – reducing therefore favours the accumulation of chalcophile elements. For example, pyrite  $\text{FeS}_2$  (contains As, Th, Se, Ni, Pb, Co) – incinerate coal release the metals.

## Element Interactions:

1. Elements tend to group together.
2. Elements can be:
  - (a) synergistic,
  - (b) antagonistic

a) Cadmium – can be high around black shales or mining contamination

- Several studies where Cd blamed for ill health, but when large population studied many were taking Se supplements and Cd effect minimal. (Se valence is important like S<sup>-</sup>) CdS vs Cd Selenite.
- Rice and Cd – Cd accumulation – NO! It was Fe, Zn, Ca deficiency in the rice that led to Cd retention

## b) Cu-Mo

- English example – Mo excess in pasture land not found until 1940's. Cure was to add Cu sulphate to the feed and inhibit Mo uptake. (Mo was in black shales). In some cases the two together can cause problems.
- 
- c) Mapping – Geochemical and Biogeochemical surveys. (Lahermo, P. *et al.* 1996)