

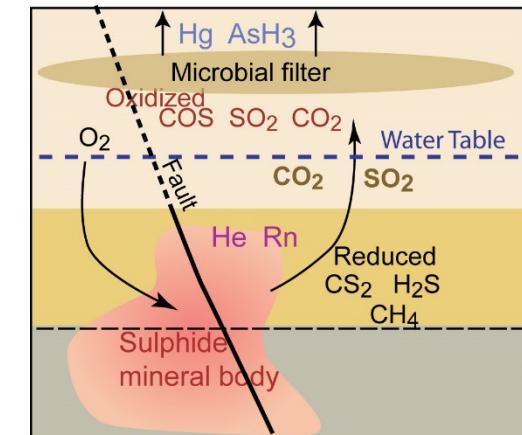
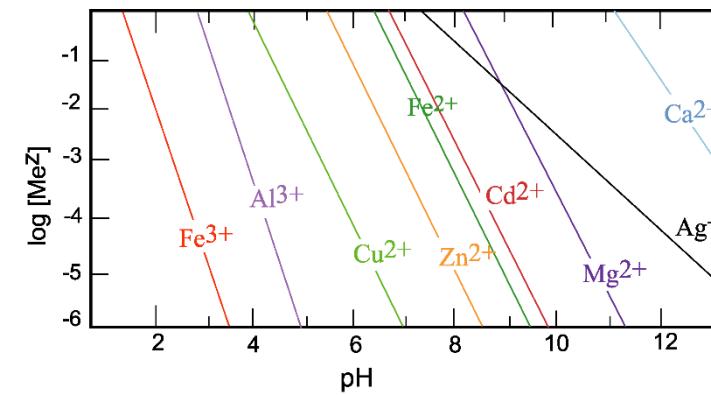
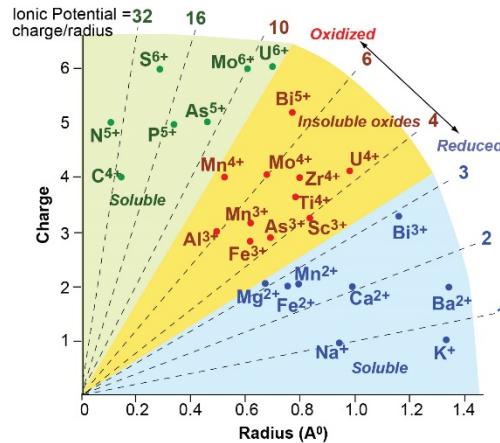
## Workshop for Northern Star Resources

# REGOLITH GEOCHEMISTRY DISPERSION MECHANISMS, METAL MOBILITY, AND GOLD!

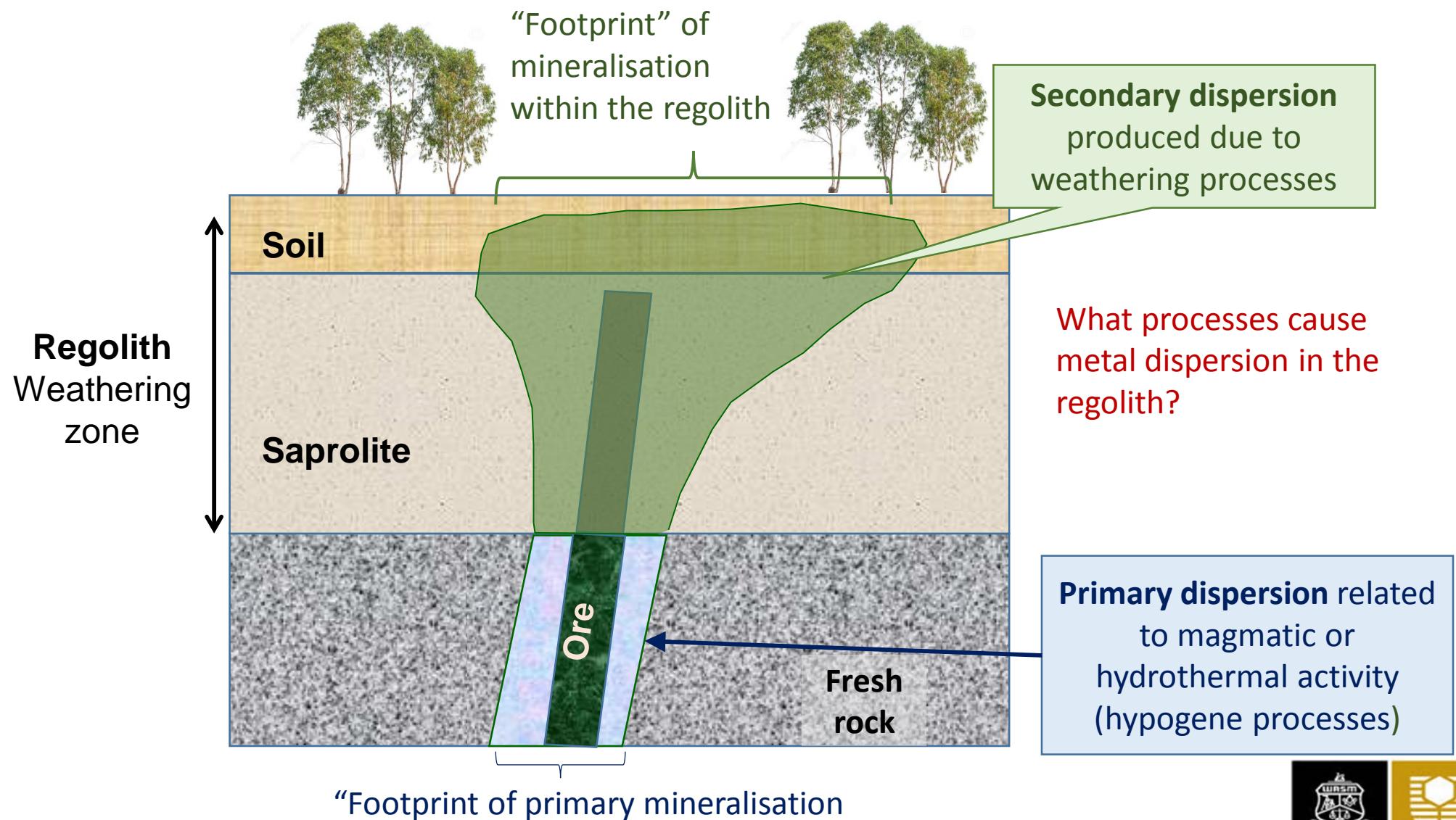
Mehrooz F Aspandiar

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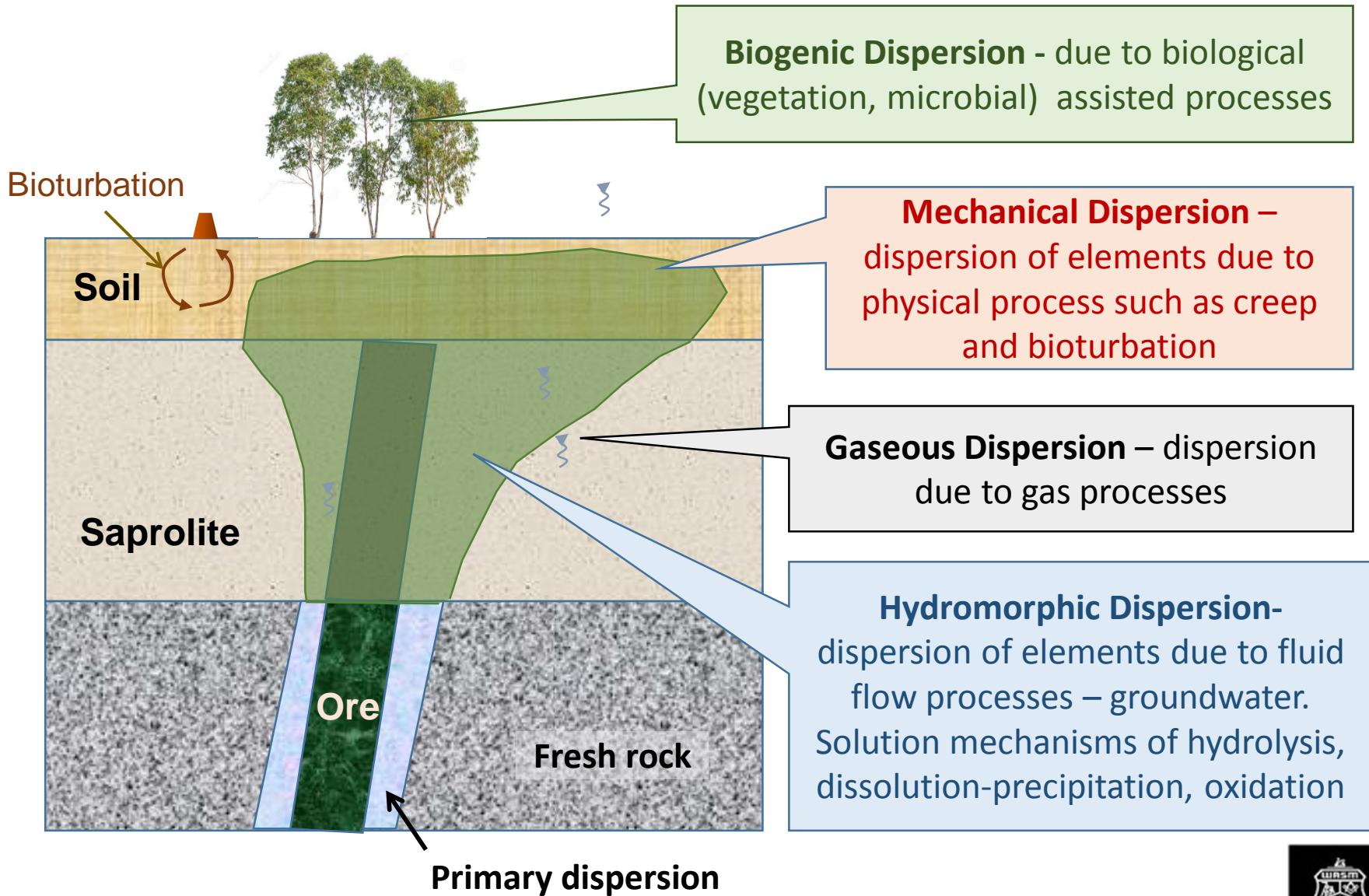
Western Australian School of Mines



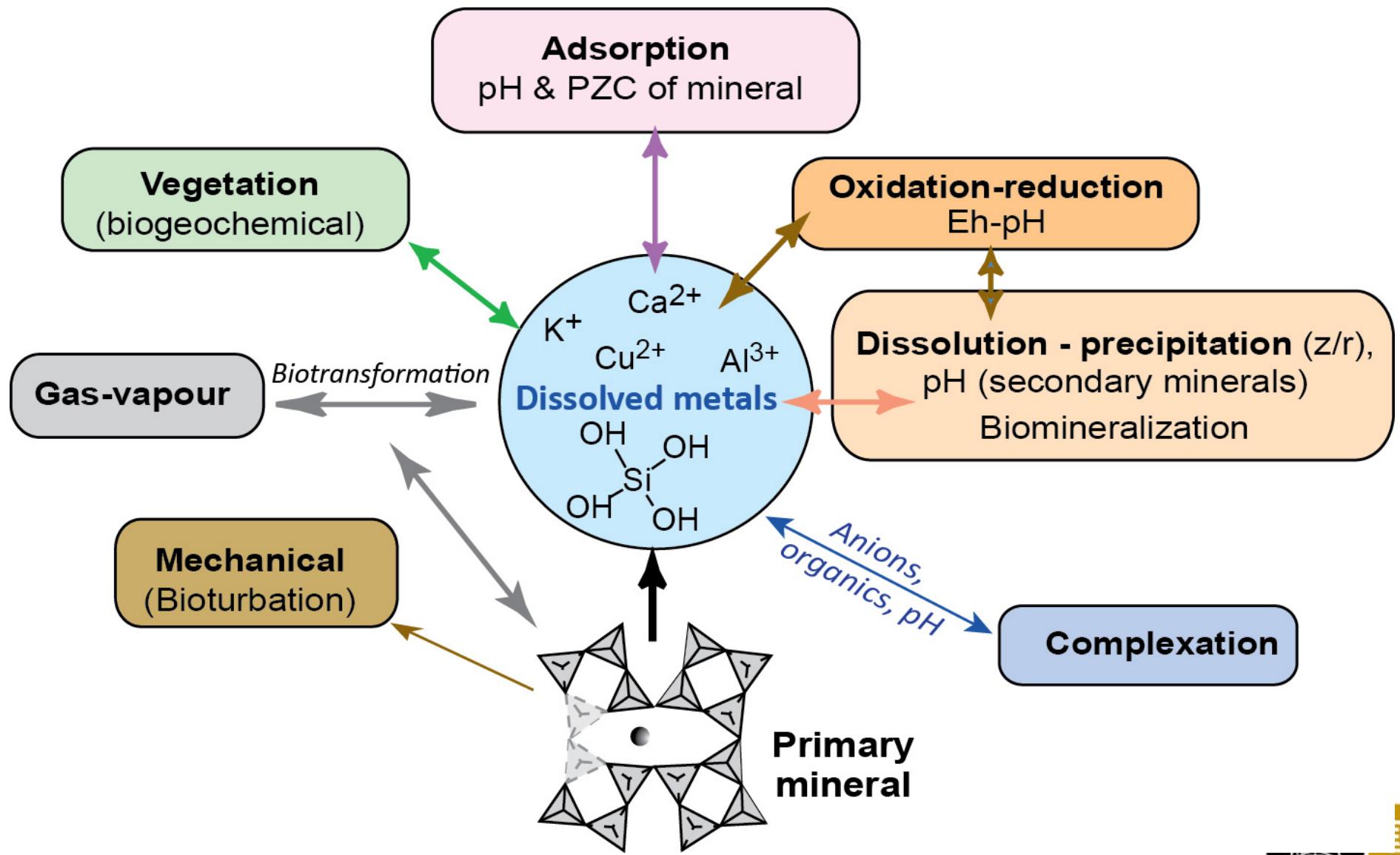
# Types of Dispersion



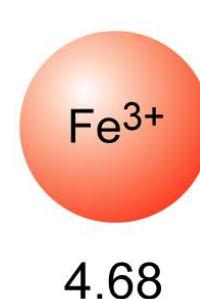
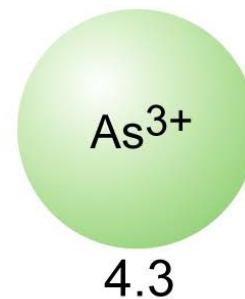
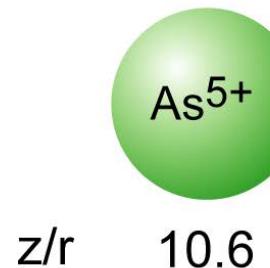
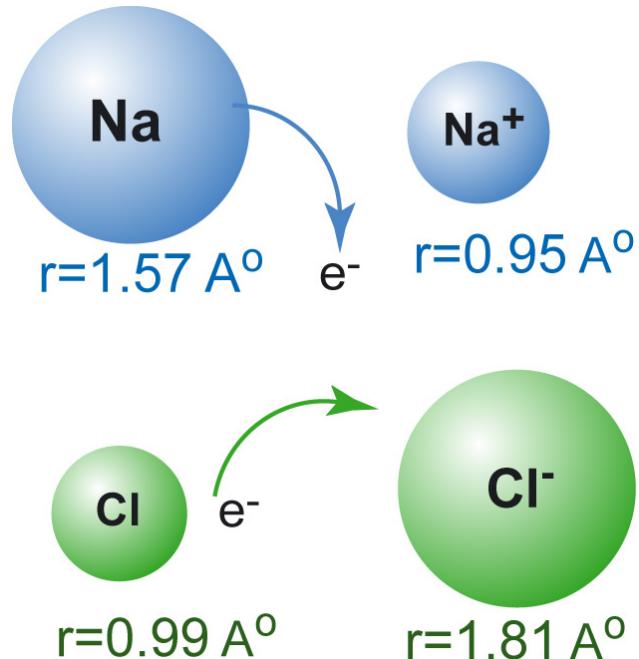
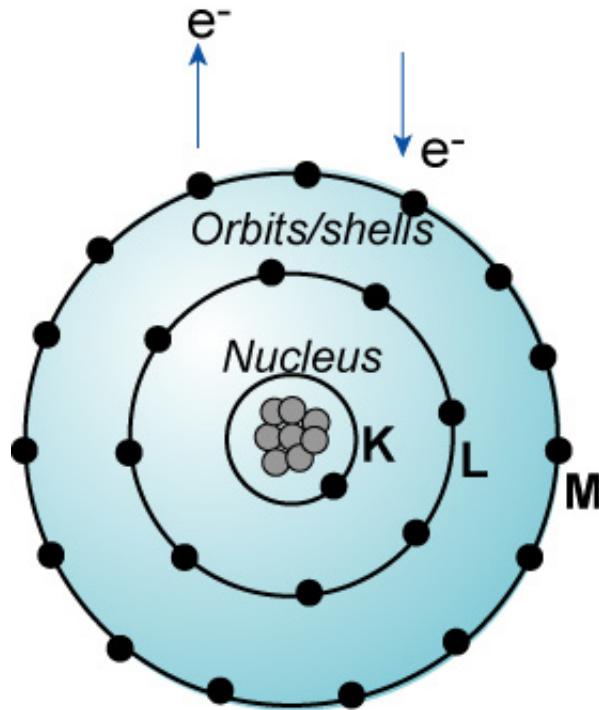
# Surficial Dispersion Processes



# Factors affecting ionic mobility once ion is free from primary mineral



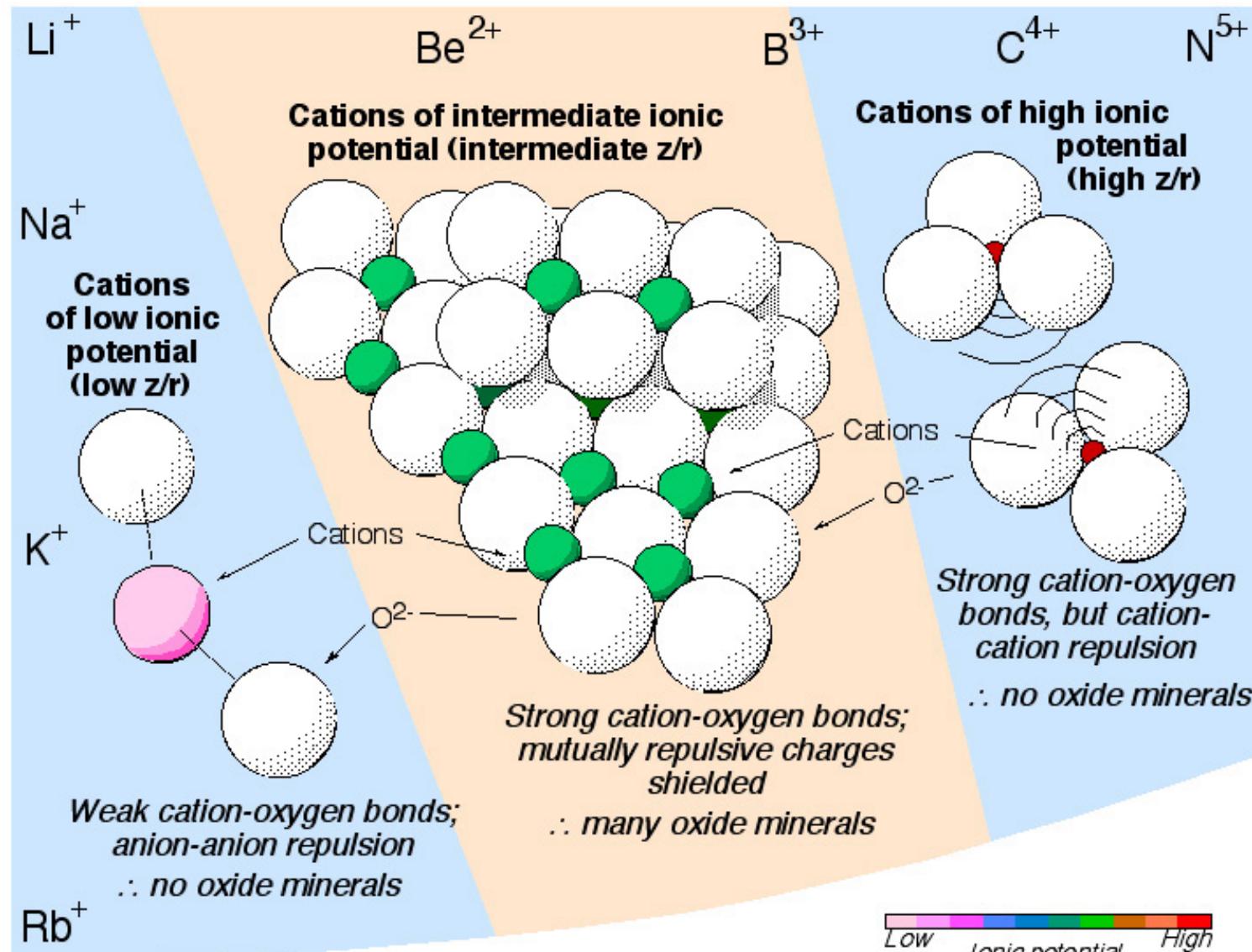
# Ionic principles – charge and radius



# Element properties critical to low temperature geochemistry

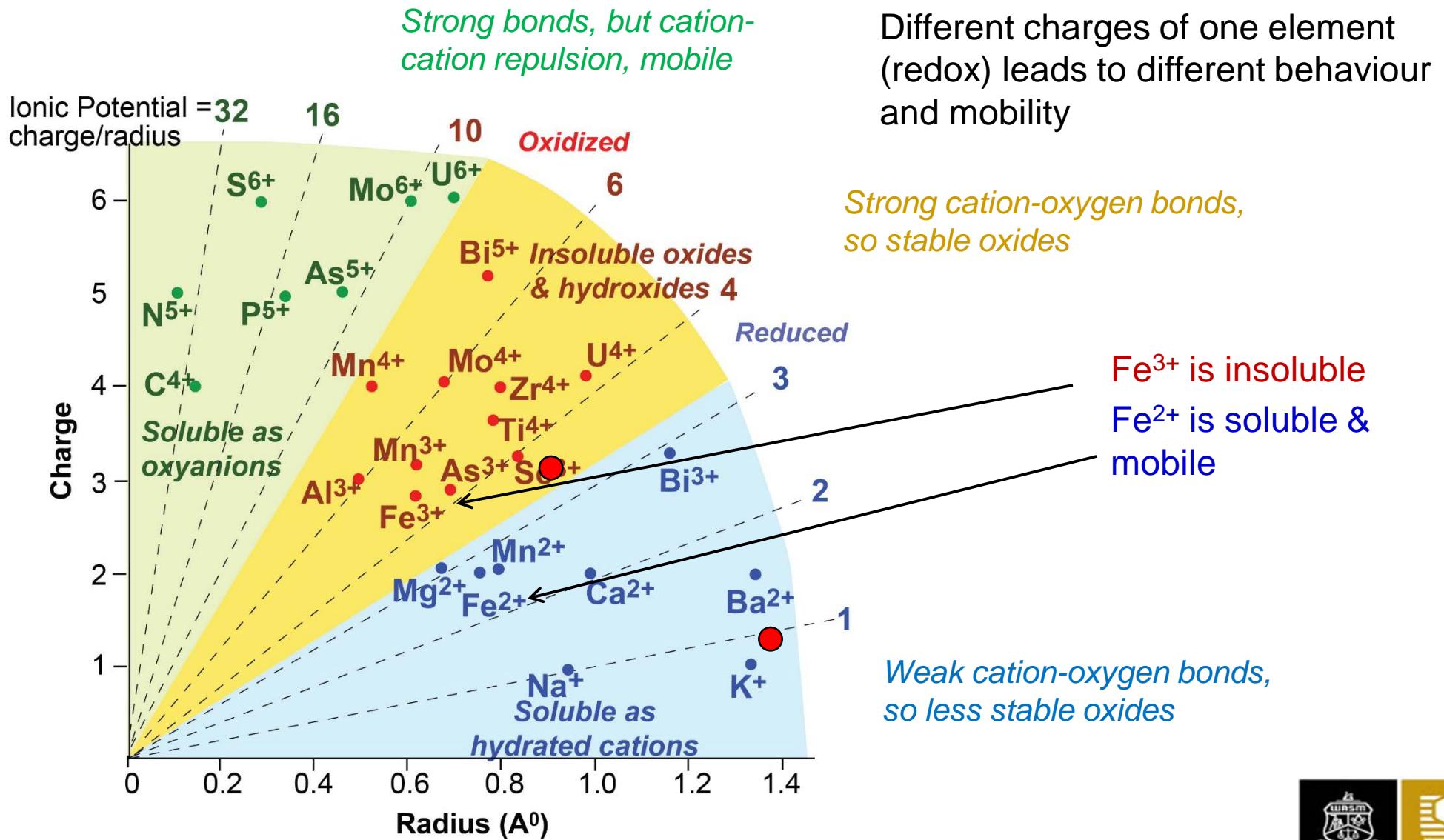
- **Ionic Potential:** ratio of ionic charge to ionic radius  $z/r$
- Different charges or redox states within natural conditions
- Cations (+ve charge) but smaller radii, and anions (-ve), larger
- Hard cations (no outer-shell electrons):  $\text{Na}^+$ ,  $\text{K}^+$   $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Si}^{4+}$  etc;  
Soft cation (some electrons in outer shell):  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{3+}$ ,  $\text{V}^{4+}$  etc;
- Anions: Simple:  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{S}^{2-}$ ,  $\text{Br}^-$ ,  $\text{O}^{2-}$ ,  $\text{I}^-$
- Oxyanions: metal ion that combines with oxygen to from anionic species:  $\text{NO}_3^-$   $\text{SO}_4^{2-}$   $\text{PO}_4^{3-}$   $\text{MoO}_4^{2-}$   $\text{AsHO}_4^{2-}$   $\text{SeO}_4^{3-}$

# Ionic potential – prediction of solubility once element in solution



Source: Bruce Railsback

# Qualitative estimate of element mobility – $z/r$



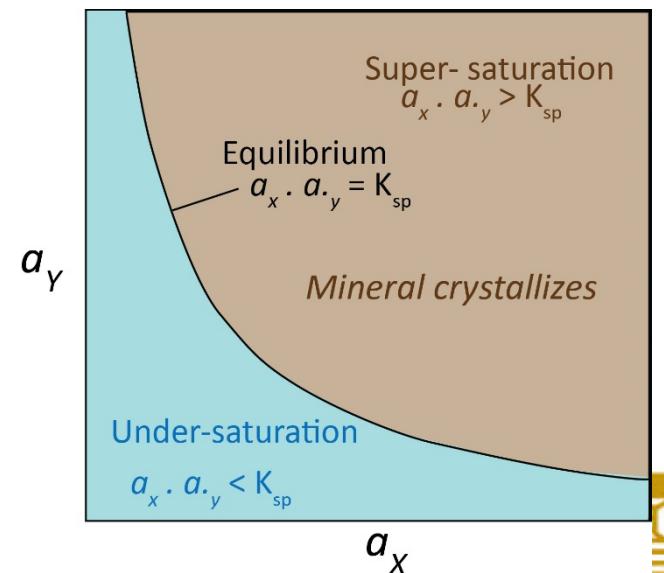
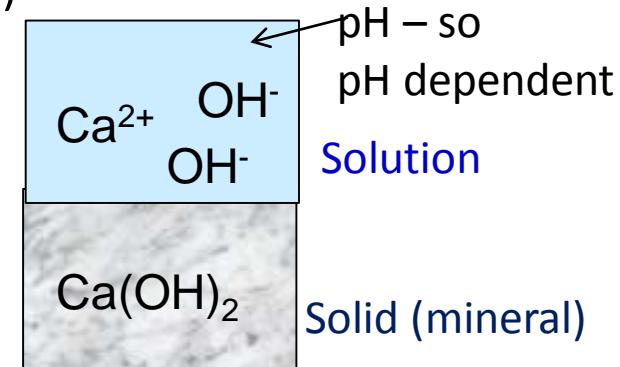
# Solubility Product (SP)

- The *hydroxide* is the **least soluble** salt of the metal (others are *carbonates, phosphates*)
- Example:  $\text{Ca}(\text{OH})_2 \leftrightarrow \text{Ca}^{2+} + 2(\text{OH})^-$  ( $\text{Ca}(\text{OH})_2 + 2\text{H}^+ = \text{Ca}^{2+} + 2\text{H}_2\text{O}$ )
- Reported as **Solubility Product (SP) –  $K_{sp}$**
- $K_{sp} = [\text{M}^{2+}][\text{OH}^-]^2$  (moles/l)<sup>3</sup> or  $K_{sp} = [\text{Ca}^{2+}][\text{OH}^-]^2$

$$K_{sp} \text{ calcium hydroxide} = a_{\text{Ca}^{2+}} \cdot a_{\text{OH}^-}$$

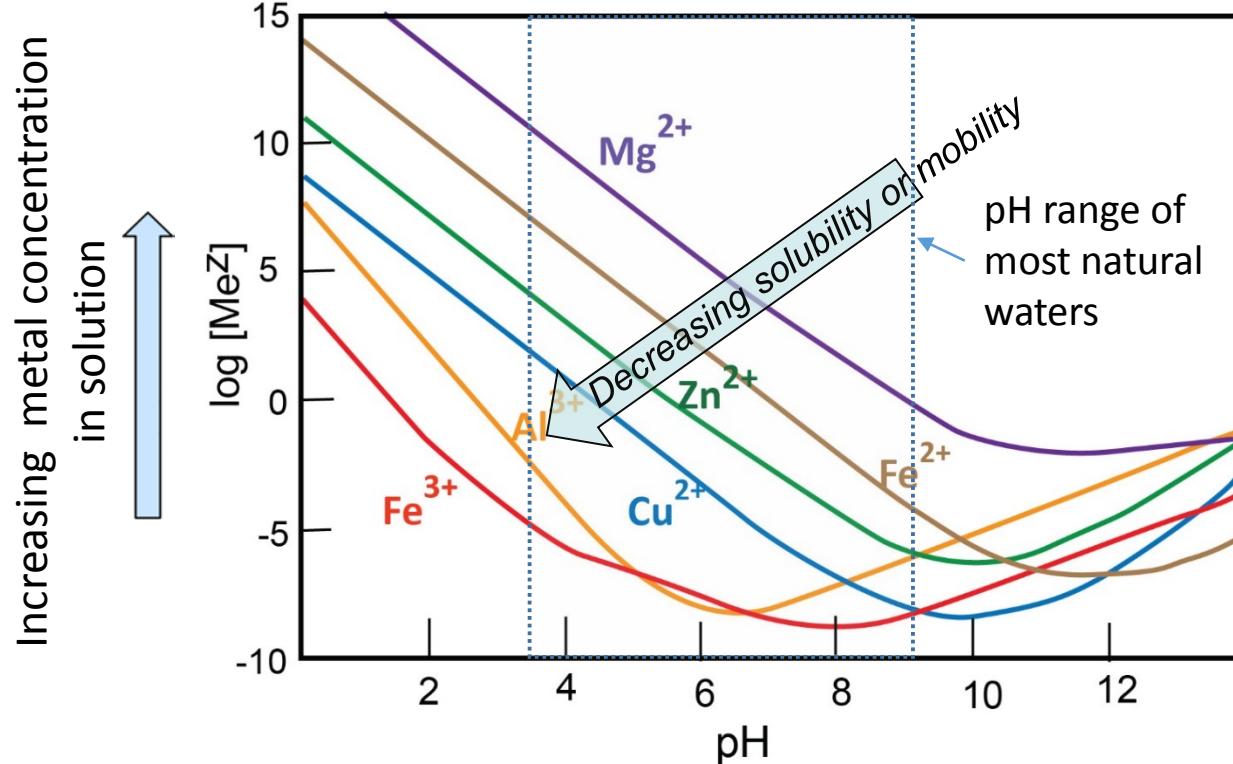
$K_{sp}$  = when  $\text{Ca}^{2+}$  concentration achieves *equilibrium* with  $\text{Ca}(\text{OH})_2$  (the mineral solid) = 5.2

- From experimentally determined  $K_{sp}$  of a reaction – concentration of metal in solution to maintain equilibrium with solid hydroxide can be calculated





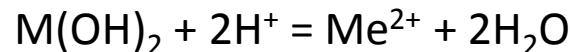
# Metal Hydrolysis



Ion	IP	SP hyd
$Na^+$	0.9	-2.9
$K^+$	0.7	-2.6
$Ca^{2+}$	1.9	5.3
$Mg^{2+}$	2.5	11.0
$Fe^{2+}$	2.3	15.1
$Al^{3+}$	4.9	32.5
$Fe^{3+}$	4.1	38.0
$Ti^{4+}$	5.8	40.0
$Zr^{4+}$	5.6	57

Solubility of metal hydroxides as a function of pH (source: Nordstrom & Alpers 1999)

Concentration of  $M^{2+}$  in solution is dependant on pH of solution (groundwater)



For many cations, concentration decreases in solution with increasing pH i.e metal mobility decreases with increase in pH

# Another way metal mobility is affected is via **Complexation**

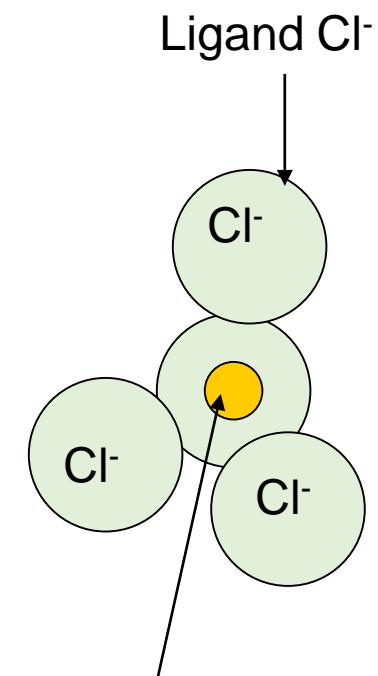
Besides  $\text{H}_2\text{O}$  – other complexes exist in water

**Central ion** (metal cation: Ca, Mg, Fe, Al, K) with  
**ligand** (anions: O, S, Cl, F, I, C)

- OH complexes:  $\text{FeOH}^+$ ,  $\text{Fe(OH)}_2^+$
- Halide ( $\text{Cl}^-$ ,  $\text{I}^-$ ):  $\text{CuCl}^-$ ,  $\text{PbCl}_3^-$ ,  $\text{AuCl}_4^-$
- Carbonate ( $\text{CO}_3^{2-}$ ):  $\text{CaCO}_3^0$ ,  $\text{MgCO}_3^0$
- Sulphate ( $\text{SO}_4^{2-}$ ):  $\text{CaSO}_4^{2-}$ ,
- Organic complexes: EDTA, oxalate

Each metal complex has **stability constant** –  
dependant on

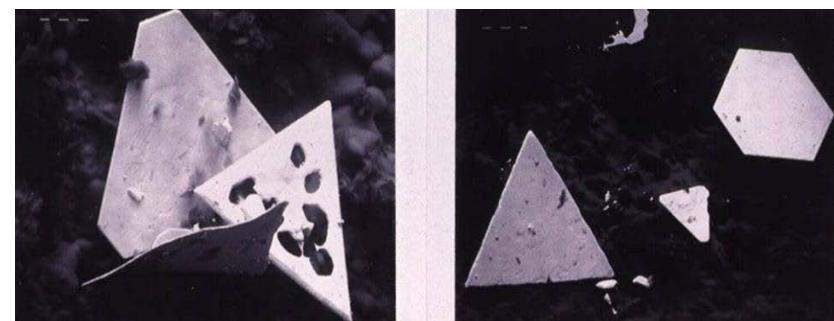
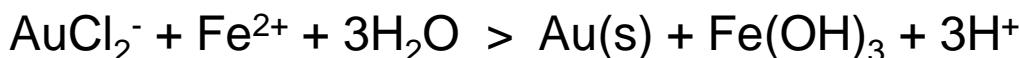
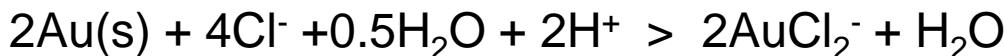
- pH
- concentration (activity) of metal & ligand





# Aqueous Gold Species

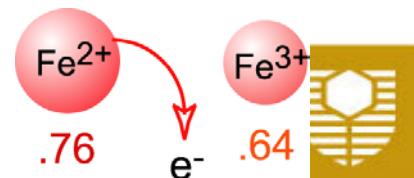
Species	Solubility conditions	Product
$\text{AuCl}^-$ , $\text{AuCl}_4^-$	Oxidized, saline, acid	High fineness Au
$\text{Au(CN)}_2^-$	Presence of cyanide, oxidizing	Low fineness
$\text{Au(I}_2\text{)}^-$	Iodide from organics, oxidizing	High fineness
$\text{Au(S}_2\text{O}_3)_2^{3-}$	Alkaline to weakly acid	Medium fineness
Au-organics	Organic environments, oxidizing	High fineness



# Another element property & surrounding conditions that affects its mobility is Oxidation – Reduction (redox)

- Many elements in the regolith exist in two or more oxidation states (e.g.  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ )
- Elements affected by the **oxidation-reduction** potential (redox) of the specific part of regolith
- **Redox potential** – ability of the specific environment to bring about oxidation or reduction

<i>Process</i>	<i>Change in electrons</i>	<i>Examples</i>	<i>Sources or sinks</i>
Oxidation	Loss of electrons	$\text{Fe}^{2+}$ to $\text{Fe}^{3+}$ ; $\text{S}^{2-}$ to $\text{S}^0$ to $\text{S}^{4+}$ to $\text{S}^{6+}$ ;	$\text{O}_2$ ;
Reduction	Gain of electrons	$\text{Fe}^{3+}$ to $\text{Fe}^{2+}$ ;	C in $\text{CH}_2$ ;



# Some redox elements – pathfinders and target

**Fe<sup>2+</sup> > Fe<sup>3+</sup> (FeOOH)**

**Mn<sup>2+</sup> > Mn<sup>3+</sup> > Mn<sup>4+</sup> (MnO<sub>2</sub>)**

**As<sup>3+</sup> > As<sup>5+</sup> (AsO<sub>4</sub><sup>3-</sup>)**

**Bi<sup>3+</sup> > Bi<sup>5+</sup>**

**Mo<sup>4+</sup> > Mo<sup>6+</sup> (MoO<sub>4</sub><sup>2-</sup>)**

**S<sup>2-</sup> > S<sup>2+</sup> > S<sup>4+</sup> > S<sup>6+</sup> (SO<sub>4</sub>)<sup>2-</sup>**

**Au<sup>0</sup> > Au<sup>+</sup> > Au<sup>3+</sup>**

**Sb<sup>+3</sup> > Sb<sup>+5</sup> (SbO<sub>3</sub><sup>-</sup>)**

**W<sup>4+</sup> > W<sup>6+</sup>**

**Ce<sup>2+</sup> > Ce<sup>3+</sup>**

**Cr<sup>3+</sup> > Cr<sup>6+</sup> (HCrO<sub>4</sub><sup>-</sup>, CrO<sub>4</sub><sup>2-</sup>)**

Fe<sup>2+</sup> more soluble than Fe<sup>3+</sup>

As<sup>5+</sup> more mobile (oxyanion) and toxic than As<sup>3+</sup>

Sb<sup>5+</sup> is more mobile (oxyanion) than Sb<sup>3+</sup>

Se<sup>6+</sup> more soluble but less toxic than Se<sup>4+</sup>

Cr<sup>6+</sup> more mobile and toxic than Cr<sup>3+</sup>

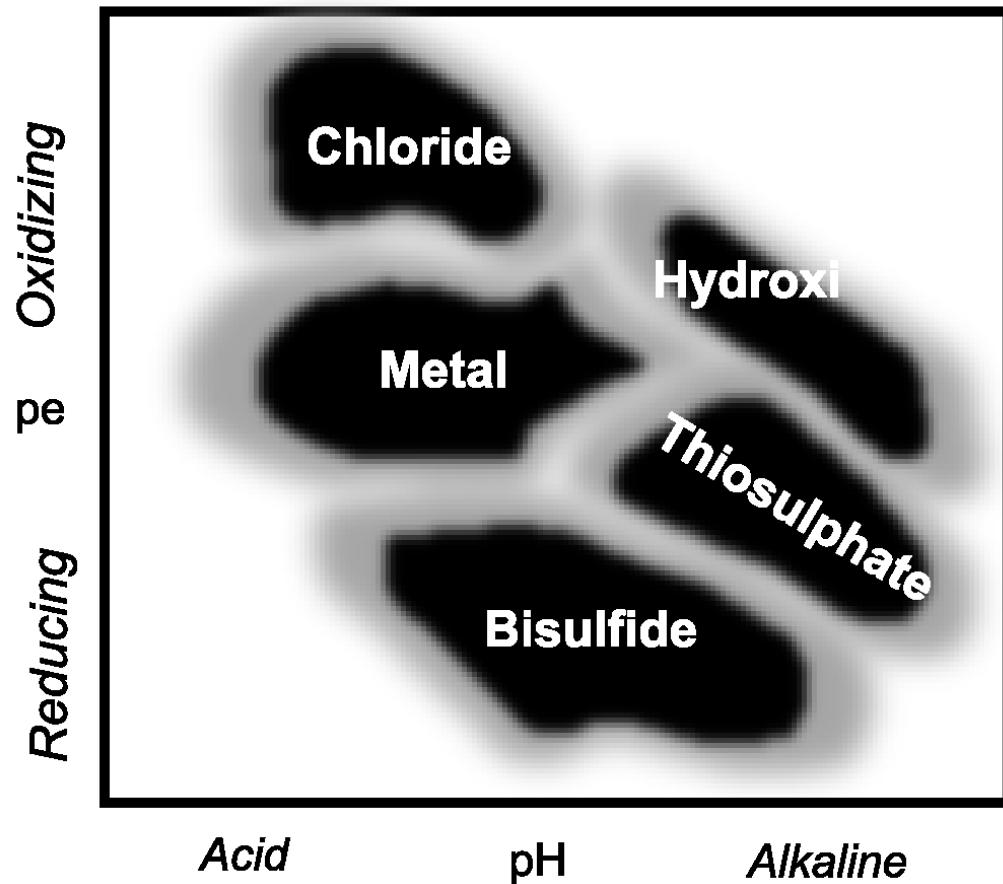


# Redox and complex stability of Au

Gold becomes soluble by forming complexes with different species –  $\text{AuCl}_2^-$ ,  $\text{Au}(\text{S}_2\text{O}_3)^{2-}$

Each Au complex has a redox-pH stability range

Complex can form at favourable redox conditions & destabilize at specific redox conditions e.g. drop or rise in pH or Eh



From Taylor & Eggleton (2001)



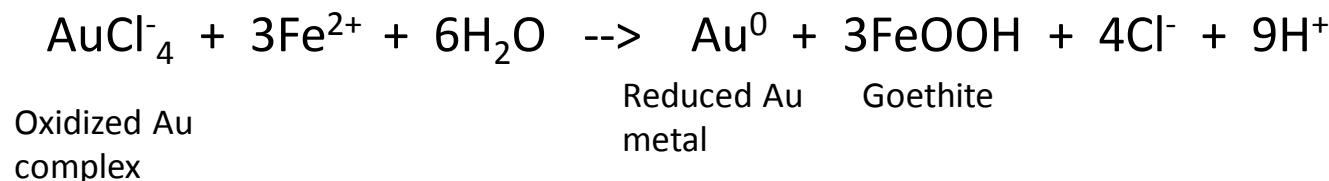
# Redox and Au mobility

Au has three redox states: Au(0) metallic, Au(I) and Au(III)

Metallic Au goes into solution via complexing with Cl<sup>-</sup> or organics or thiosulfates, although the redox state changes to Au(III) or Au(I) e.g. gold in the Au-Cl<sub>4</sub><sup>-</sup> is Au(III), - it is oxidised

Au(III)-Cl complex is stable and mobile in oxidizing, acid conditions (see previous Eh-pH figure on stability of complexes)

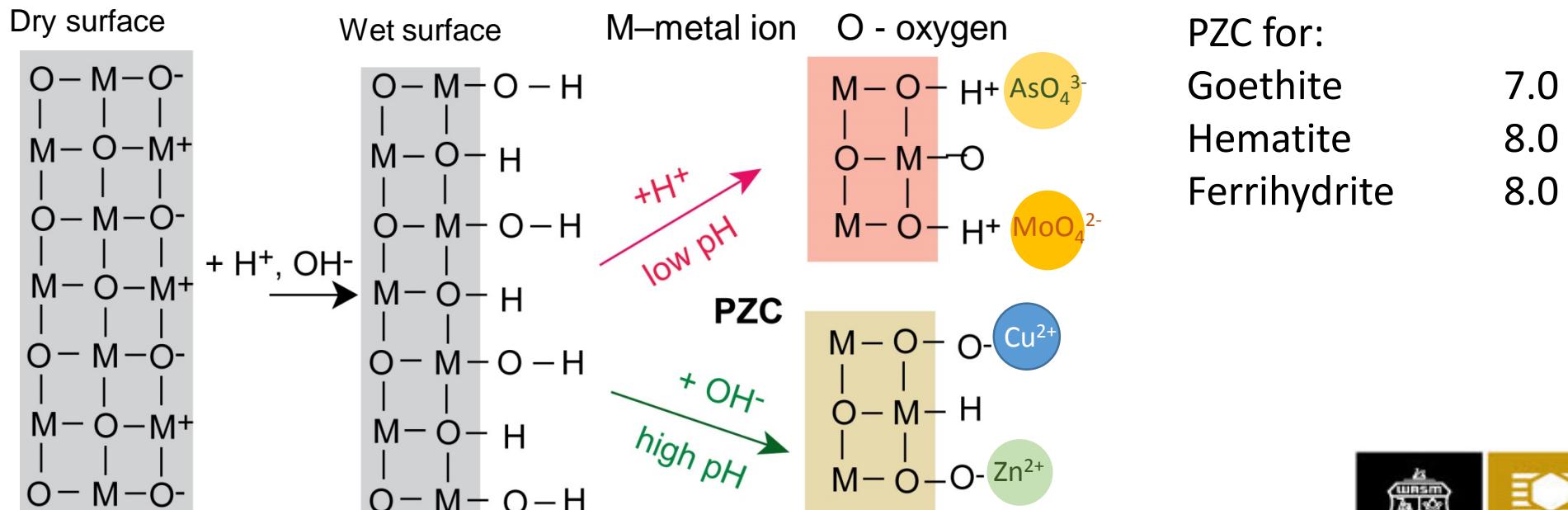
Au(III)-Cl complex can be *destabilised* if a reductant or reducing conditions are encountered, one being the reductants required during oxidation of Fe<sup>2+</sup> to Fe<sup>3+</sup> and hydrolysis to form iron oxides in lateritic profiles:



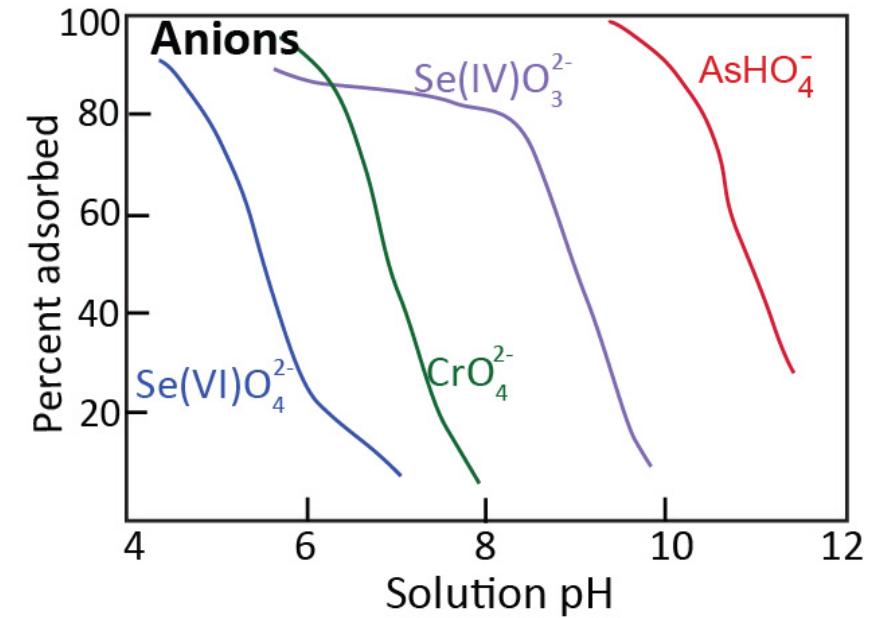
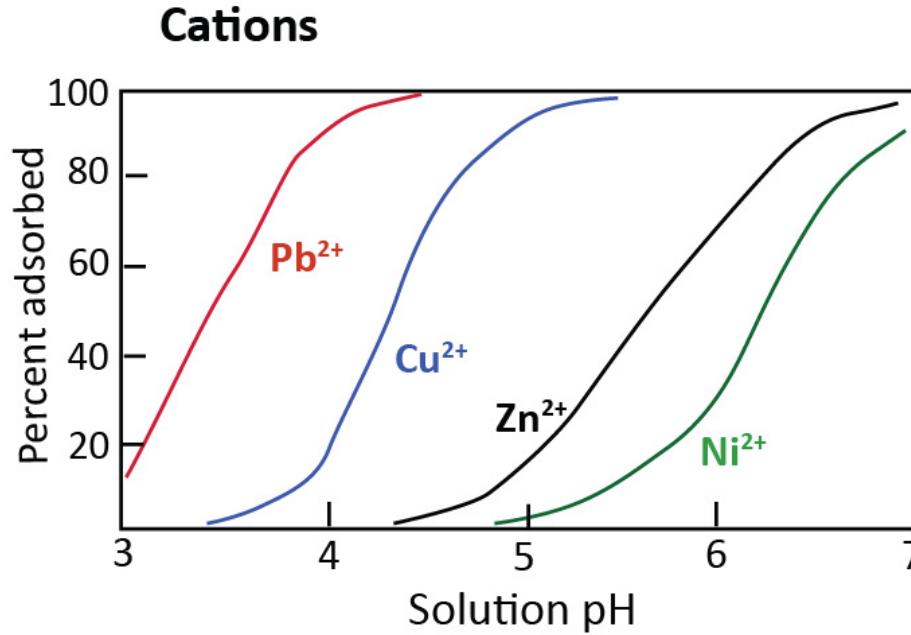
# Adsorption & Point of Zero Charge (PZC)

Adsorption is the binding of ions or molecules on the surface of a mineral

- Affects the mobility of metals & ions by making them immobile or mobile Outer surface of most regolith minerals are oxygens ( $O^{2-}$ ), therefore..
- In **acid** solutions, surface **+ve** charged In **alkaline** solutions, surface **-ve**
- The pH at which it occurs – zero charge on surface - point of zero charge (PZC) for the mineral



# Adsorption – pH vs cations and anions



Mineral surfaces, excess +ve at low pH, excess H<sup>+</sup> - attract anions (oxyanions)

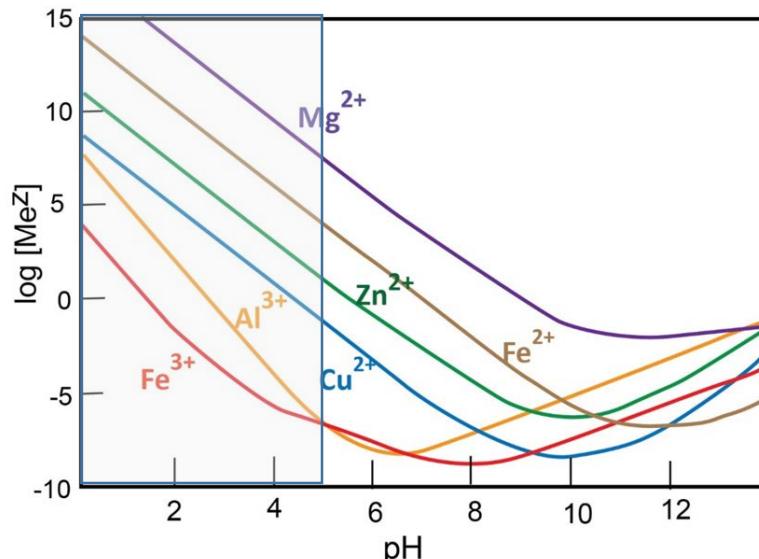
Mineral surfaces, excess -ve at high pH because excess OH<sup>-</sup> - attract cations

# Why are base metal cations (Cu, Zn, Pb) mobile around oxidizing sulfide deposits?

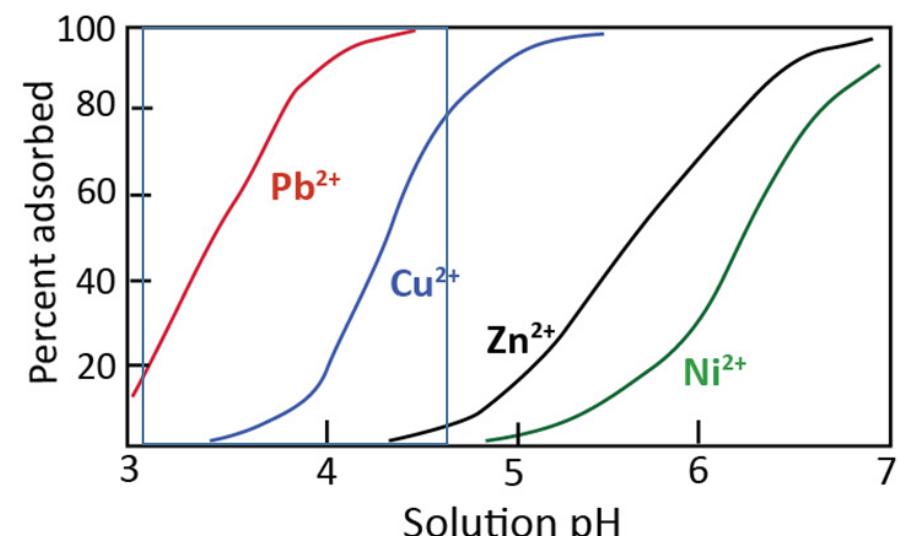
1. Oxidizing sulfides result in the production of acid conditions – release of H<sup>+</sup>



2. Generation of acidic environments around ore body results in greater mobility of Cu, Pb, Zn as per metal hydrolysis – note higher concentrations at lower pH.



3. Acidic pH, more H<sup>+</sup> on mineral surface sites, less attraction to bind positive cations such Cu<sup>2+</sup>, Zn<sup>2+</sup>, Pb<sup>2+</sup> so less absorption



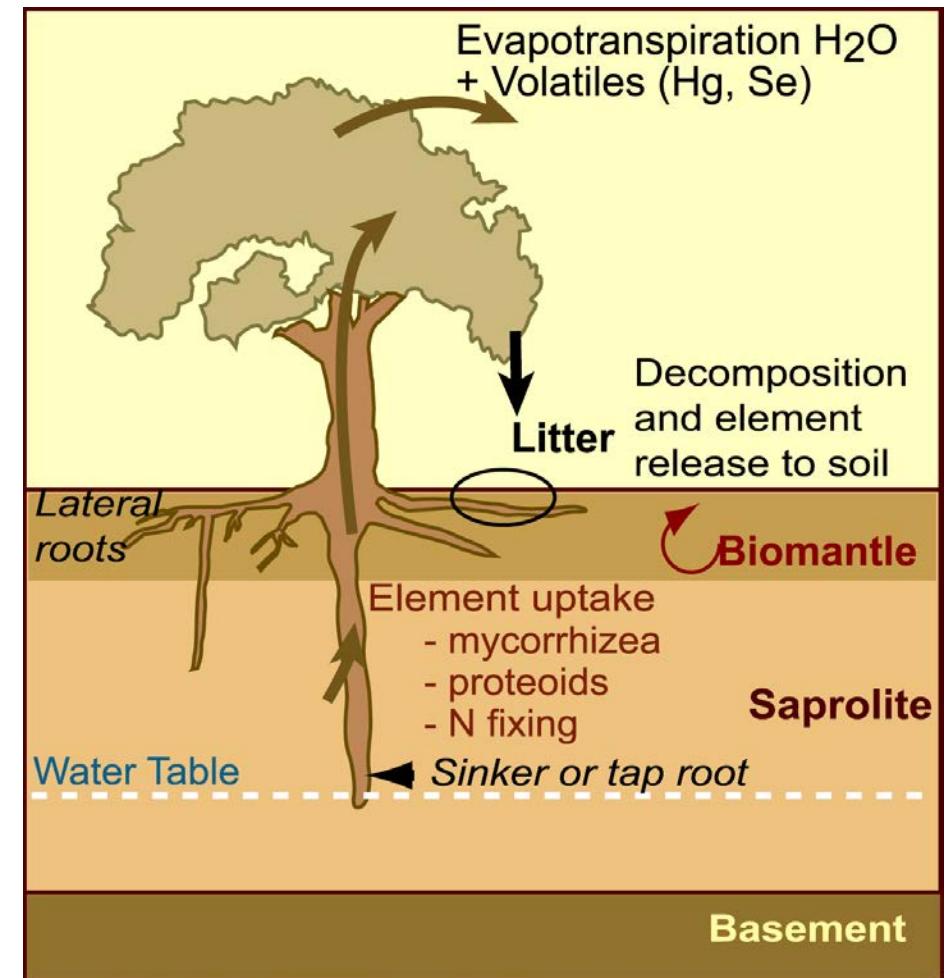
# Vegetation Transfer & Mobility

Transfer elements from subsurface via root systems, generally adapted to local nutrient status

Elements can be transferred to above ground and released on the surface after tree death & litter – continuing on geological time scales!

Dimorphic root systems – laterals and sinkers

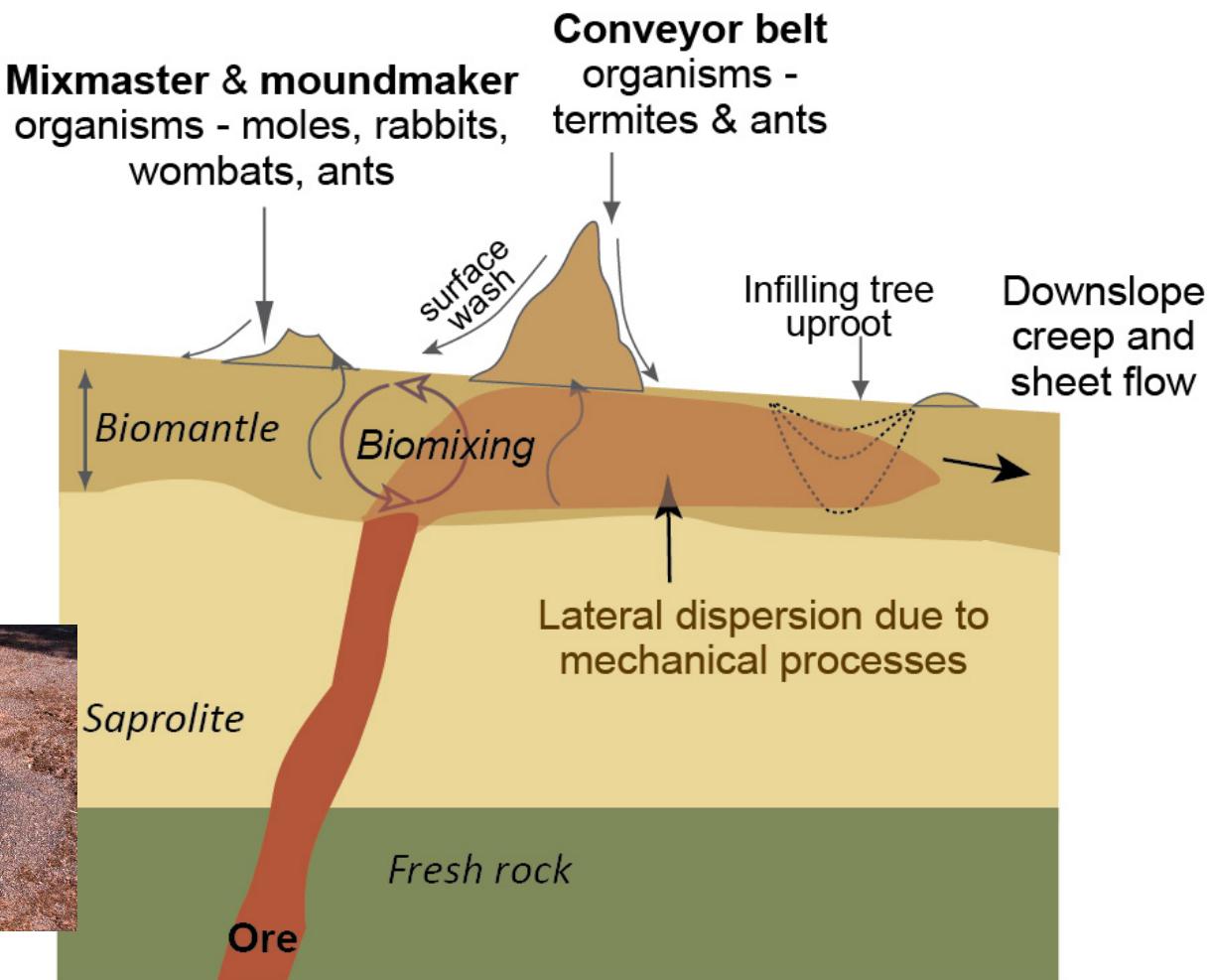
Sinkers tap deeper groundwater for nutrients in summer



# Mechanical Dispersion or Transfer

Biomantle – biomechanically active part of regolith

Biotransfer of subsurface material to surface (bioturbation) and then moved laterally downslope by gravity assisted mechanical processes – particles (lag)



# Landscape mobility

Mechanical: Zr (zircon), Ti (rutile), other heavies, Si (quartz, silcrete), Fe-Al-adsorbed trace metals (ferruginous particles)

Groundwater: Soluble cations & anions > complexed ~ redox

Valley cretes, acid sulfate soils, saline seeps

