

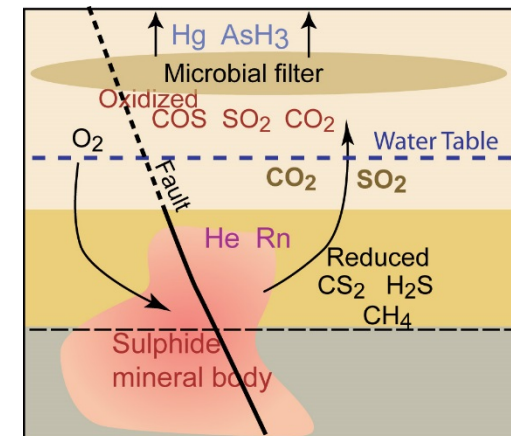
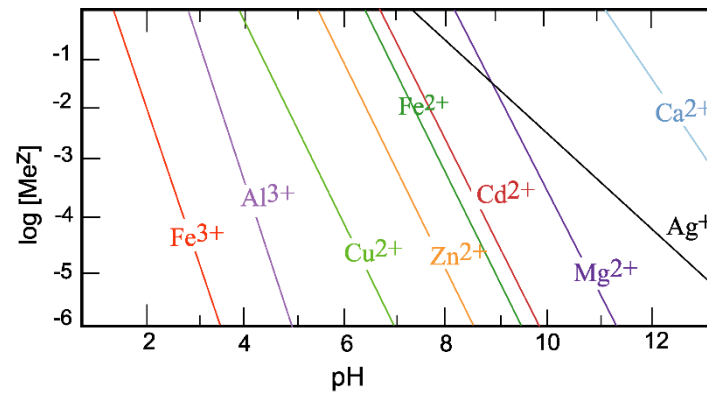
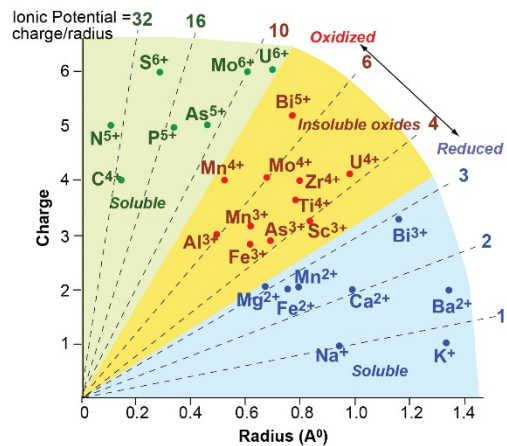
Workshop for Northern Star Resources

REGOLITH GEOCHEMISTRY DISPERSION MECHANISMS, METAL MOBILITY, AND GOLD!

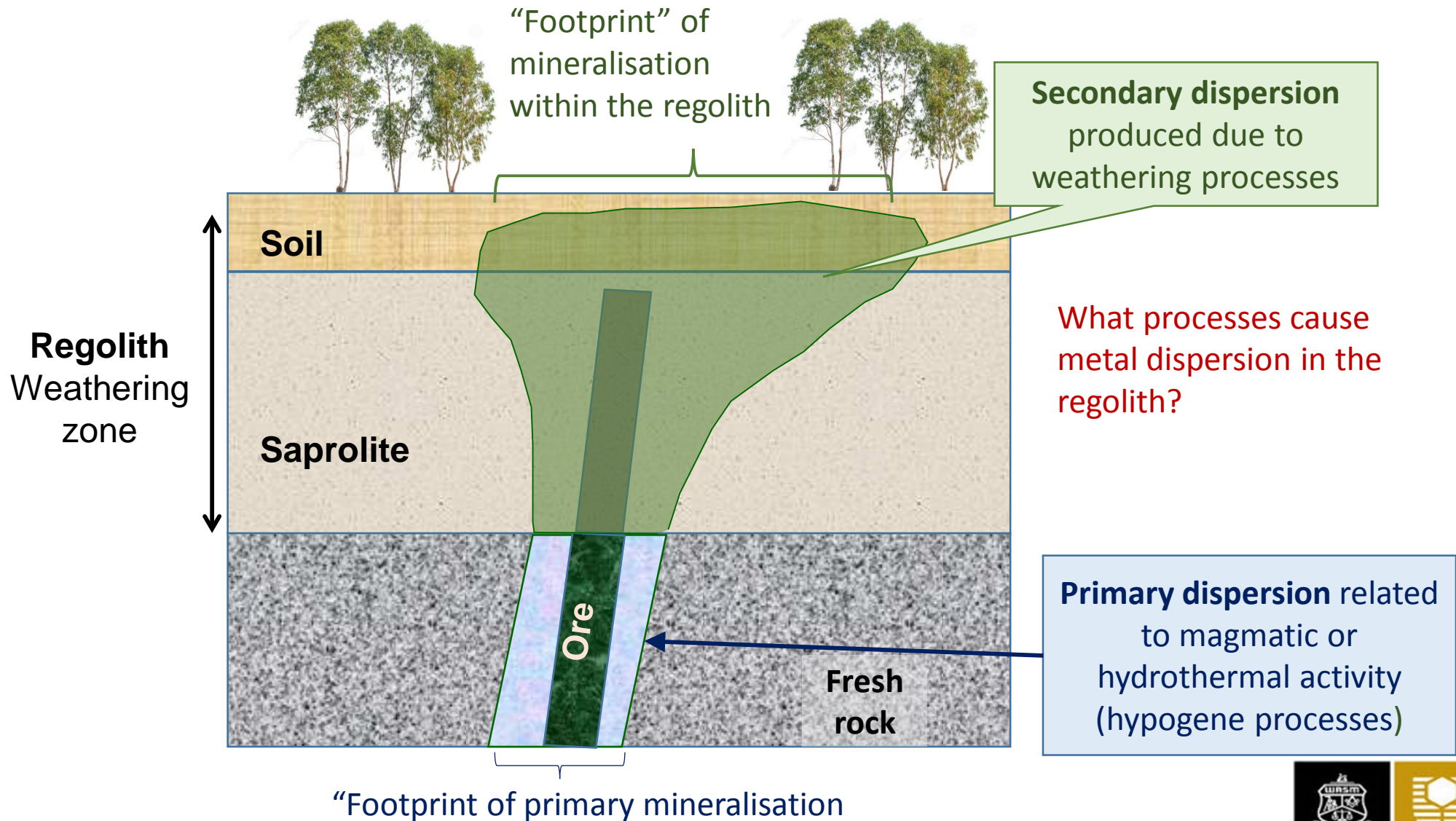
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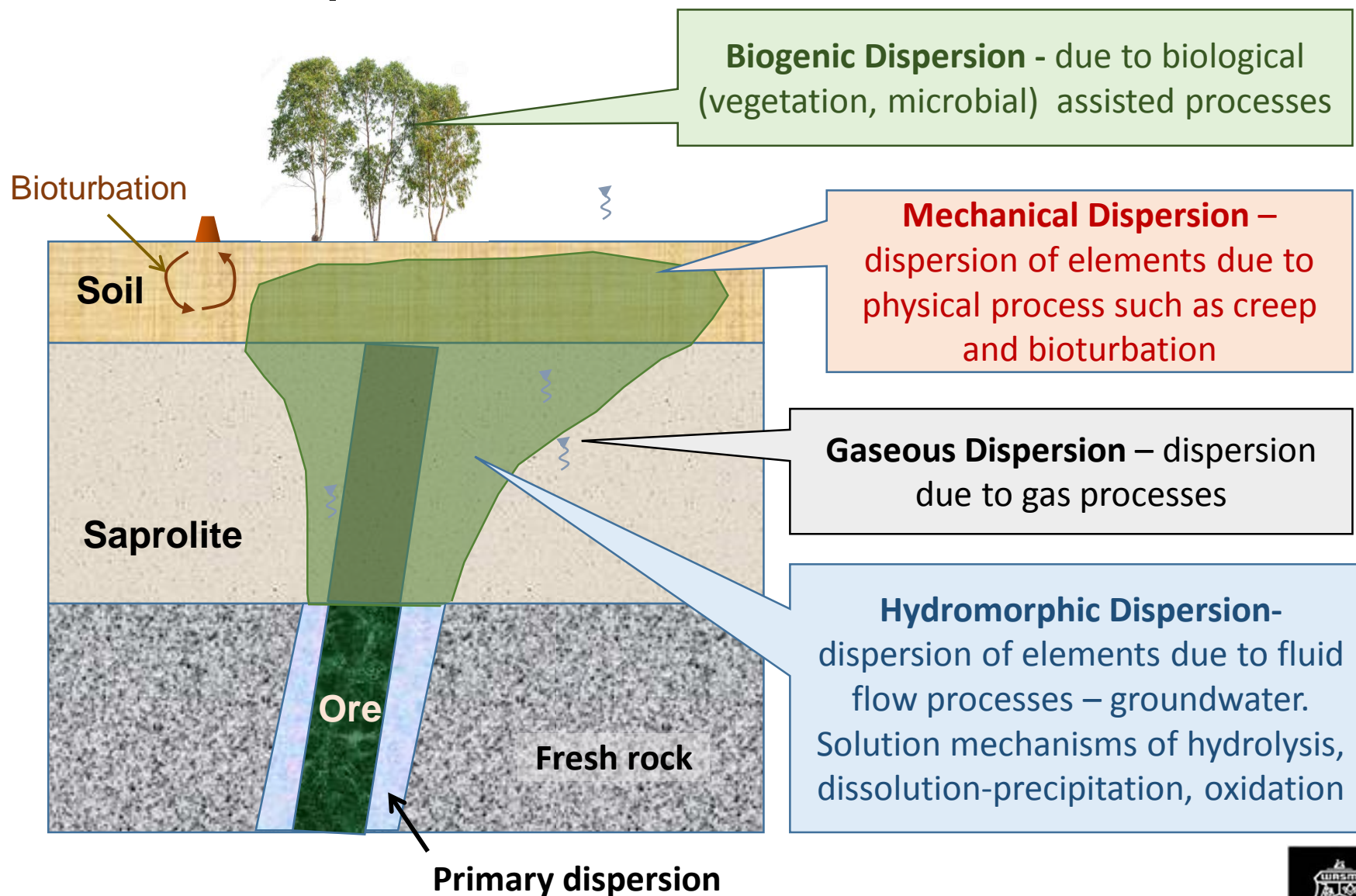
Western Australian School of Mines



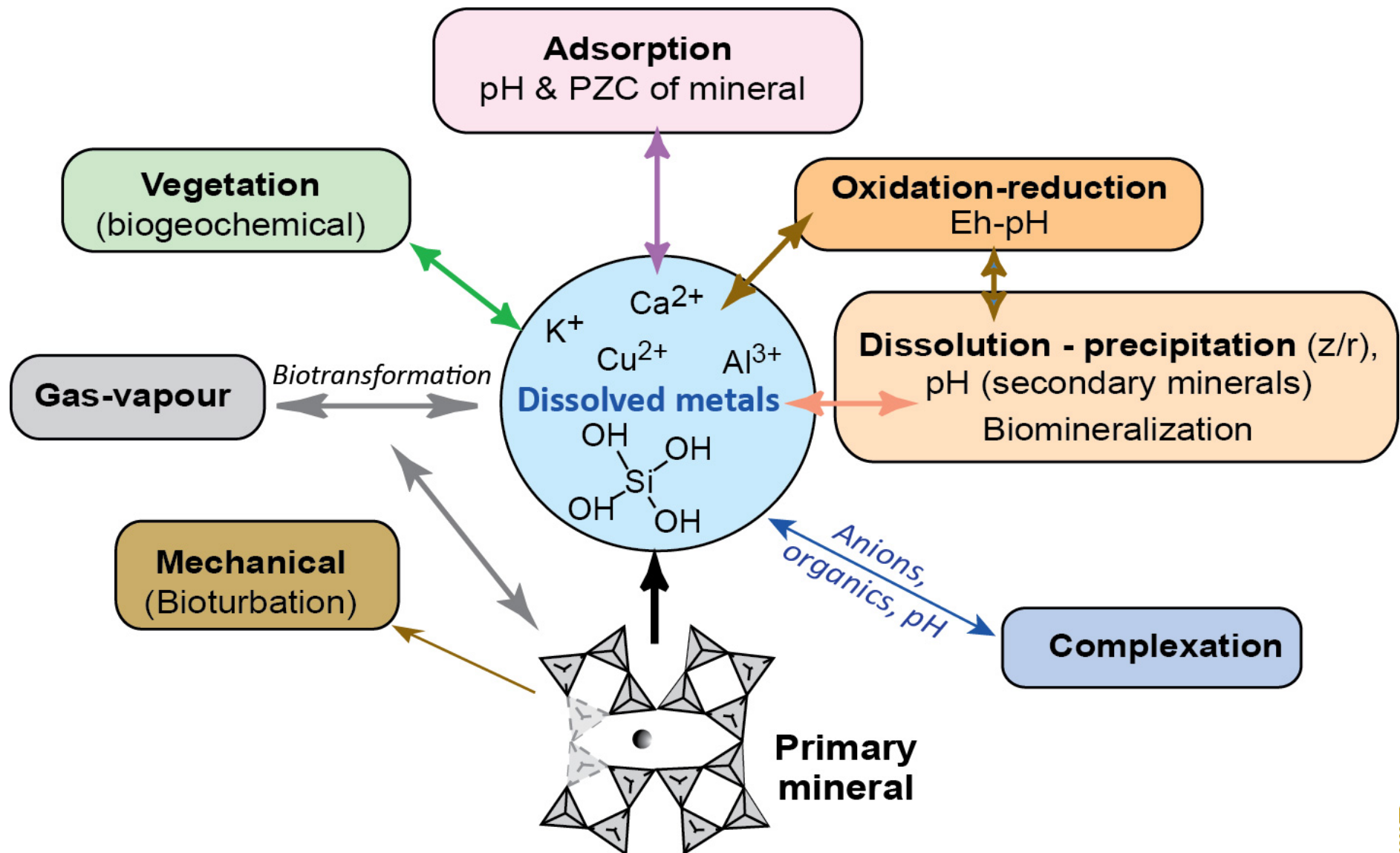
Types of Dispersion



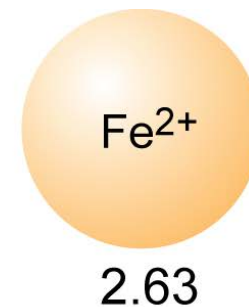
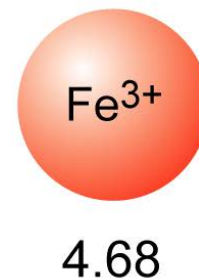
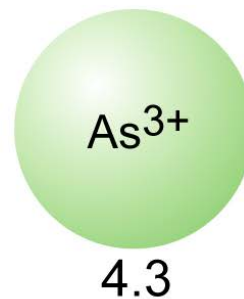
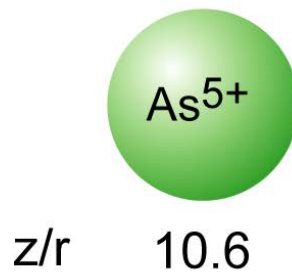
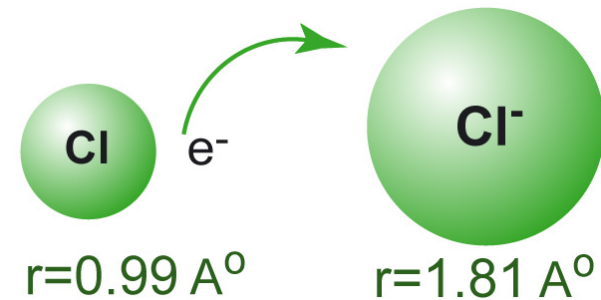
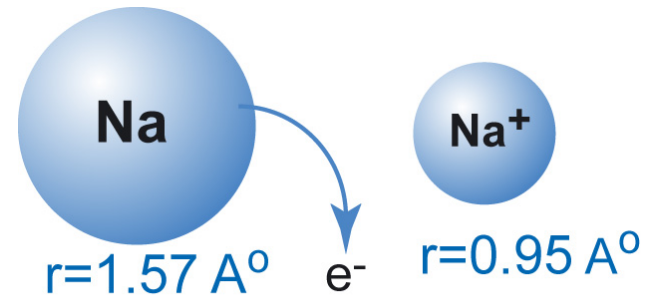
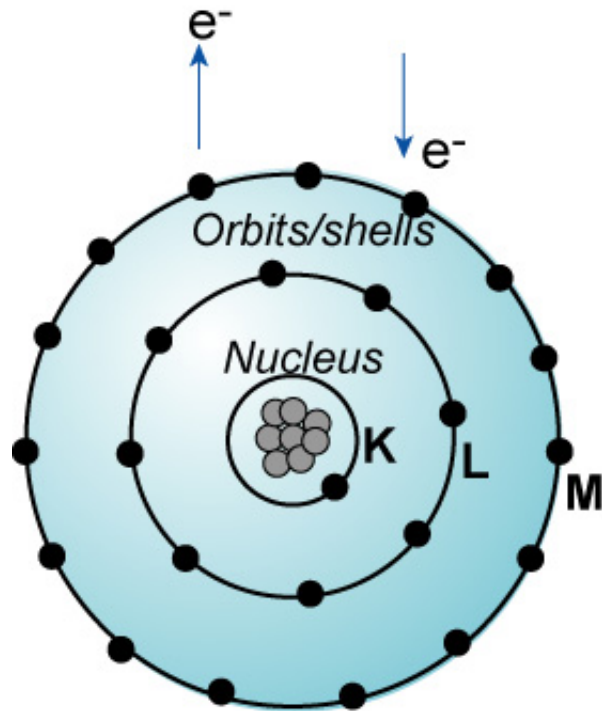
Surficial Dispersion Processes



Factors affecting ionic mobility once ion is free from primary mineral



Ionic principles – charge and radius



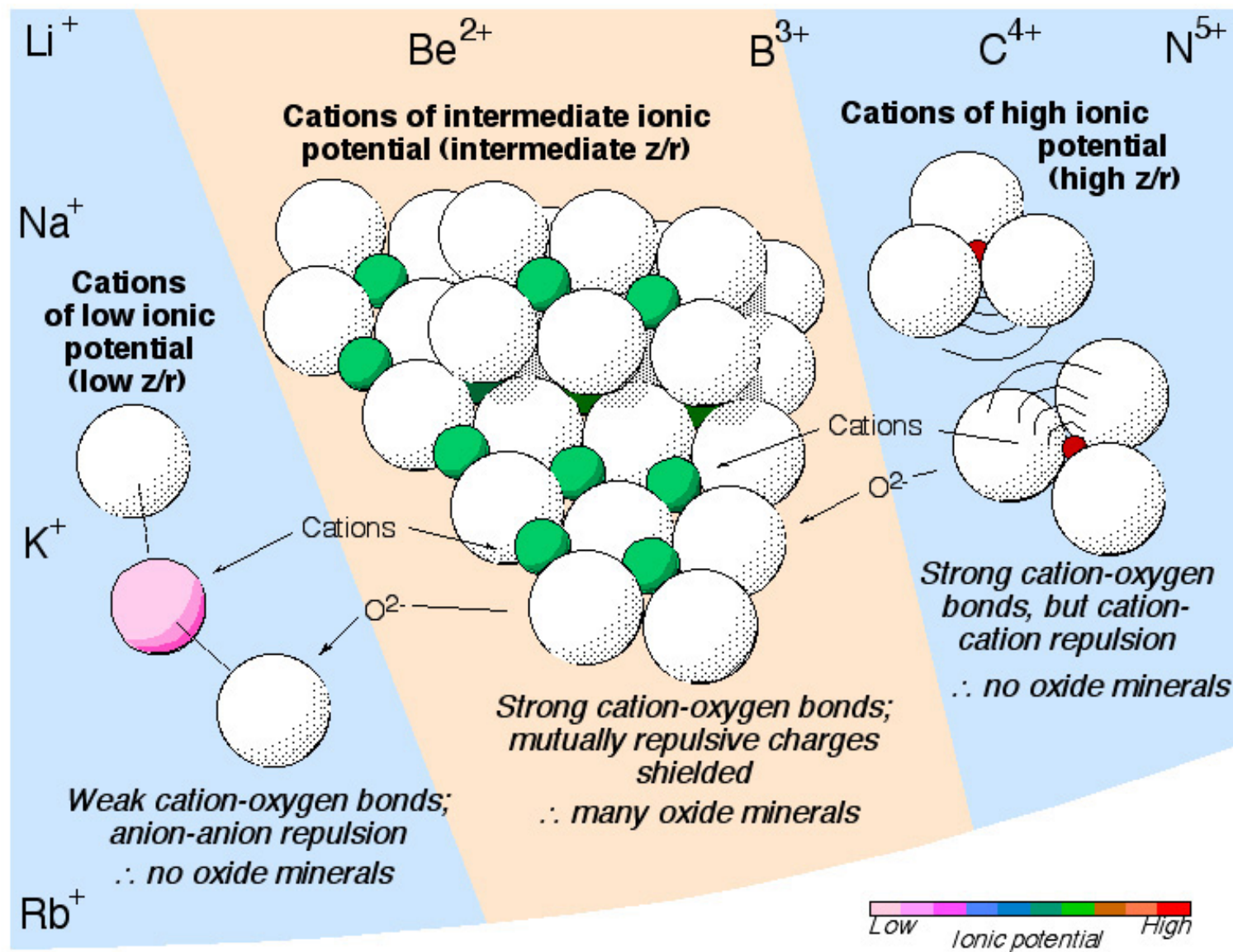


Element properties critical to low temperature geochemistry

- **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): Na^+ , K^+ , Mg^{2+} , Al^{3+} , Si^{4+} etc;
Soft cation (some electrons in outer shell): Cr^{3+} , Fe^{3+} , Ni^{2+} , Co^{3+} , V^{4+} etc;
- **Anions**: Simple: F^- , Cl^- , S^{2-} , Br^- , O^{2-} , I^-
- **Oxyanions**: metal ion that combines with oxygen to form anionic species: NO_3^- , SO_4^{2-} , PO_4^{3-} , MoO_4^{2-} , AsO_4^{3-} , SeO_4^{2-}



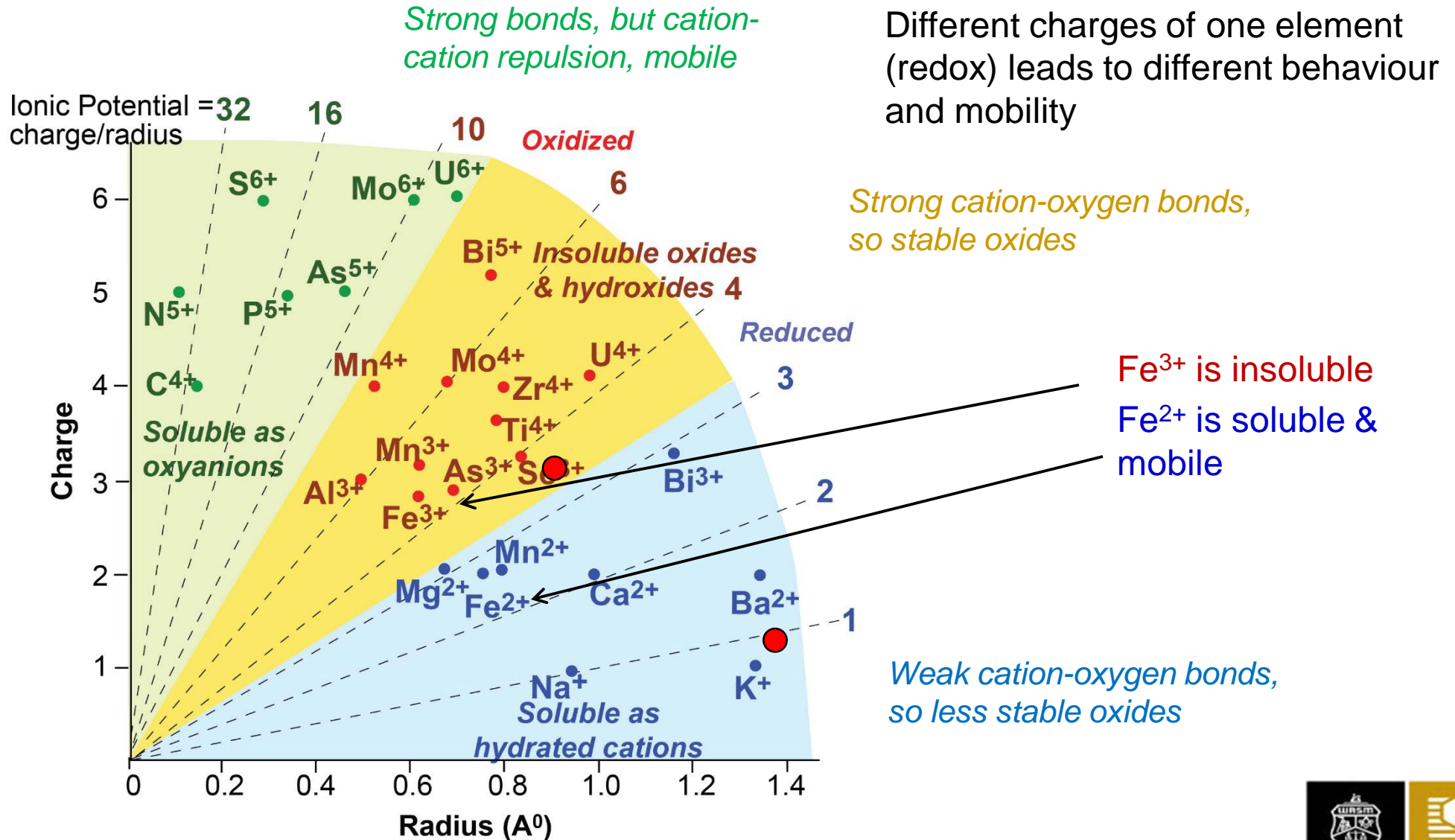
Ionic potential – prediction of solubility once element in solution



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: $\text{Ca(OH)}_2 \leftrightarrow \text{Ca}^{2+} + 2(\text{OH})^-$ ($\text{Ca(OH)}_2 + 2\text{H}^+ = \text{Ca}^{2+} + 2\text{H}_2\text{O}$)

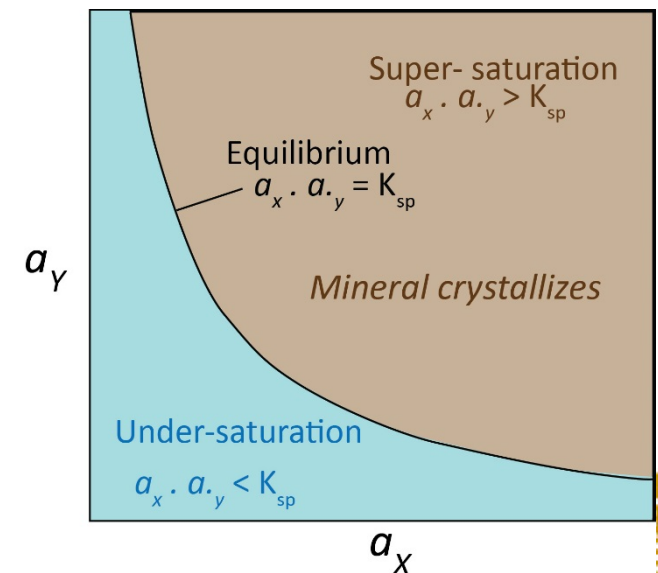
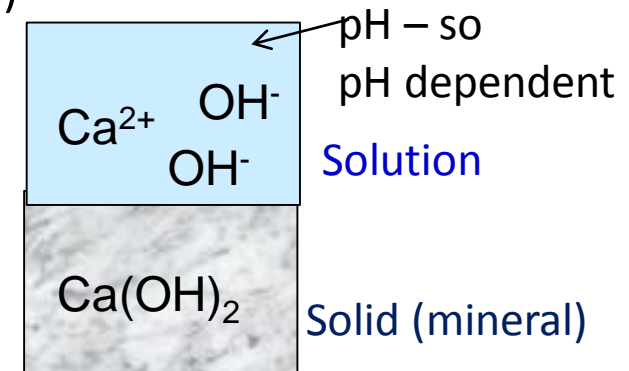
- Reported as **Solubility Product (SP) – K_{sp}**

$$K_{sp} = [\text{M}^{2+}][\text{OH}^-]^2 \text{ (moles/l)}^3 \text{ or } K_{sp} = [\text{Ca}^{2+}][\text{OH}^-]^2$$

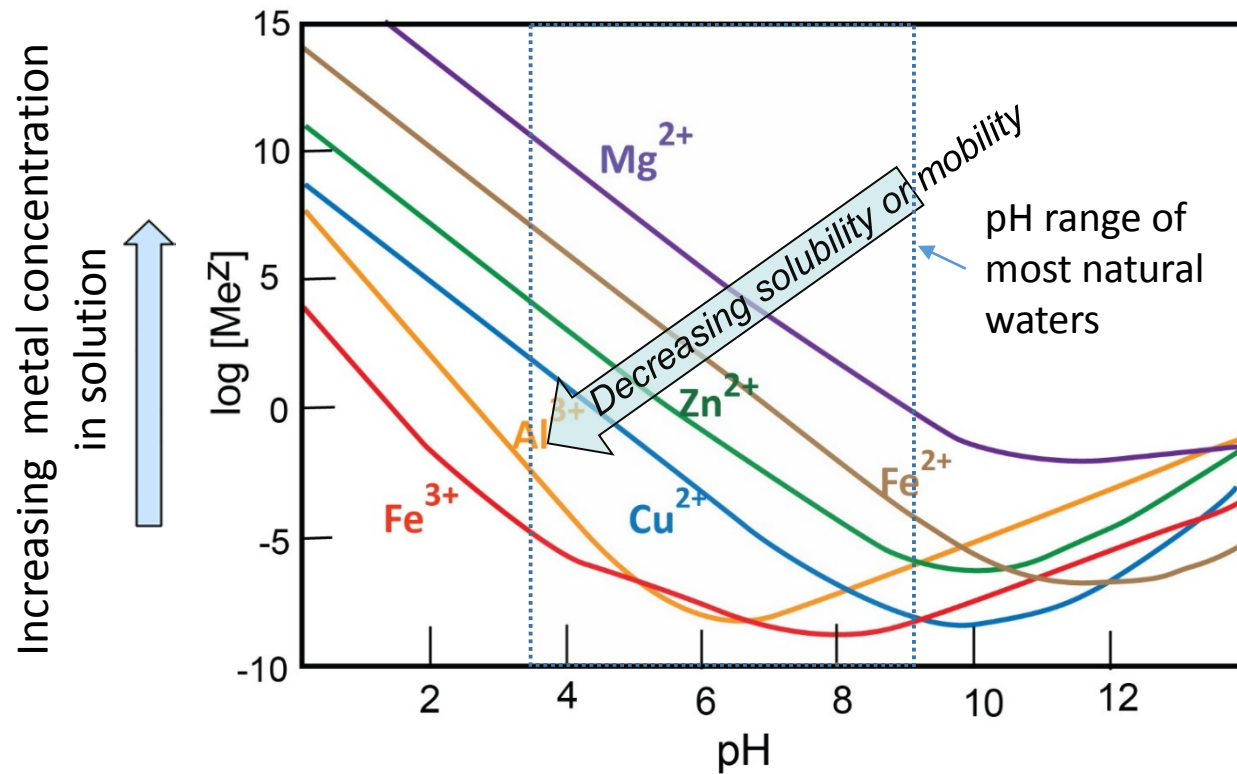
$$K_{sp} \text{ calcium hydroxide} = a_{\text{Ca}^{2+}} \cdot a_{\text{OH}^-}$$

K_{sp} = when Ca^{2+} concentration achieves *equilibrium* with Ca(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



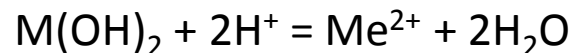
Metal Hydrolysis



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: Nordstorm & Alpers 1999)

Concentration of M²⁺ 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**

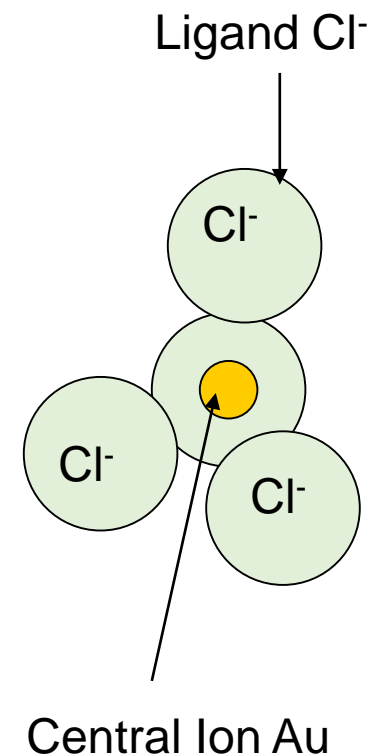
Besides H_2O – other complexes exist in water

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

- OH complexes: FeOH^+ , $\text{Fe}(\text{OH})_2^+$
- Halide (Cl^- , I^-): CuCl^- , PbCl_3^- , AuCl_4^-
- Carbonate (CO_3^{2-}): CaCO_3^0 , MgCO_3^0
- Sulphate (SO_4^{2-}): CaSO_4^{2-} ,
- Organic complexes: EDTA, oxalate

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

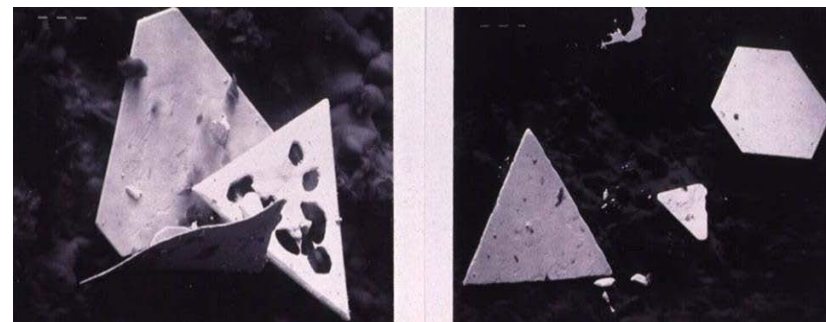
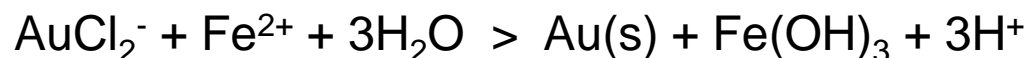
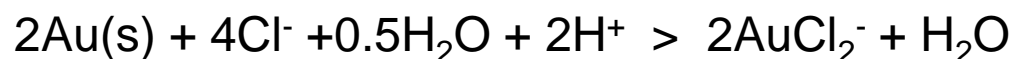
- pH
- concentration (activity) of metal & ligand





Aqueous Gold Species

Species	Solubility conditions	Product
AuCl^- , AuCl_4^-	Oxidized, saline, acid	High fineness Au
$\text{Au}(\text{CN})_2^-$	Presence of cyanide, oxidizing	Low fineness
$\text{Au}(\text{I}_2)^-$	Iodide from organics, oxidizing	High fineness
$\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$	Alkaline to weakly acid	Medium fineness
Au-organics	Organic environments, oxidizing	High fineness

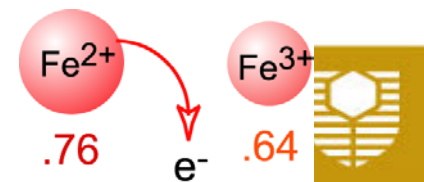




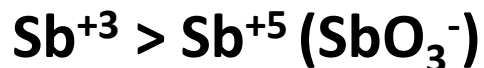
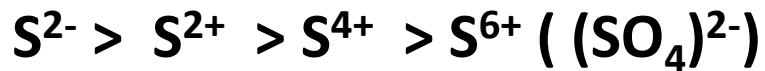
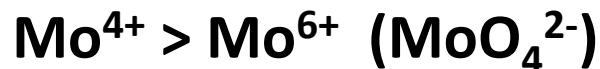
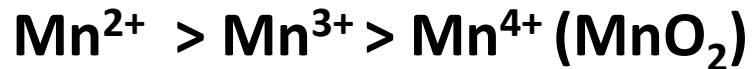
Another element property & surrounding conditions that affects its mobility is Oxidation – Reduction (redox)

- Many elements in the regolith exist in two or more oxidation states (e.g. Fe^{2+} and 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	Fe^{2+} to Fe^{3+} ; S^{2-} to S^0 to S^{4+} to S^{6+} ;	O_2 ;
Reduction	Gain of electrons	Fe^{3+} to Fe^{2+} ;	C in CH_2 ;



Some redox elements – pathfinders and target



Fe^{2+} more soluble than Fe^{3+}

As^{5+} more mobile (oxyanion) and toxic than As^{3+}

Sb^{5+} is more mobile (oxyanion) than Sb^{3+}

Se^{6+} more soluble but less toxic than Se^{4+}

Cr^{6+} more mobile and toxic than Cr^{3+}

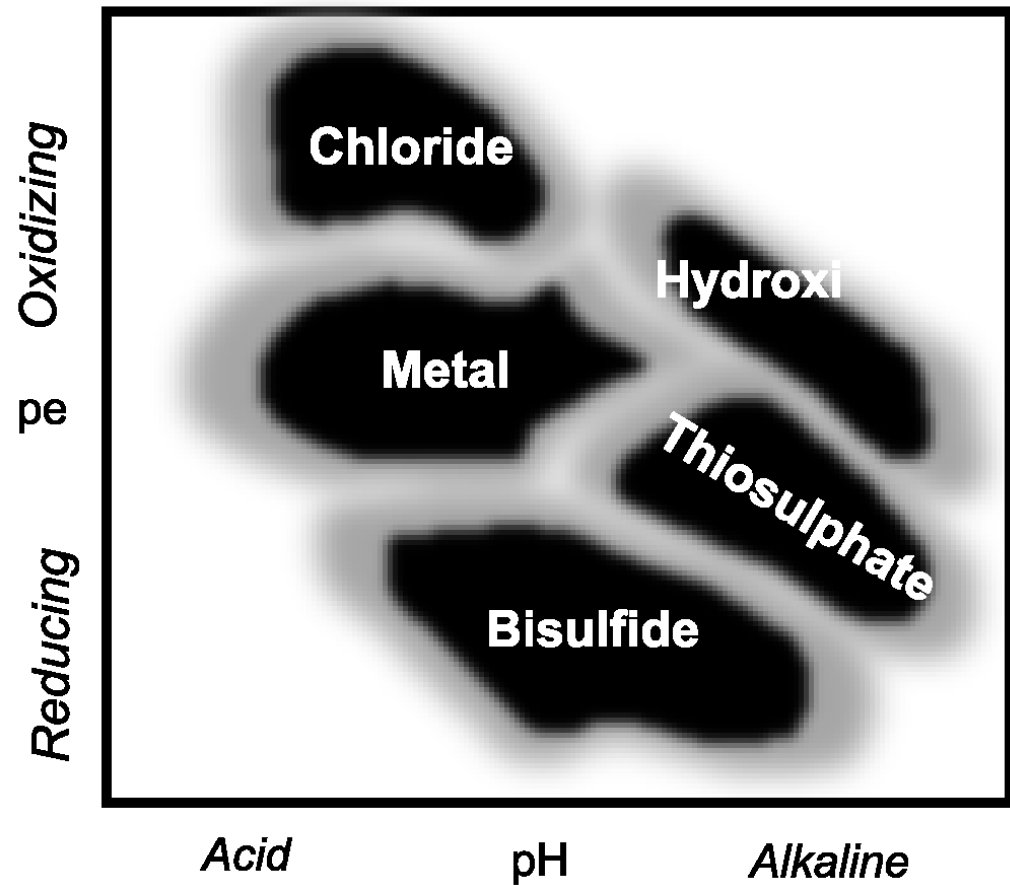


Redox and complex stability of Au

Gold becomes soluble by forming complexes with different species – AuCl_2^- , $\text{Au}(\text{S}_2\text{O}_3)_2^{2-}$

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)



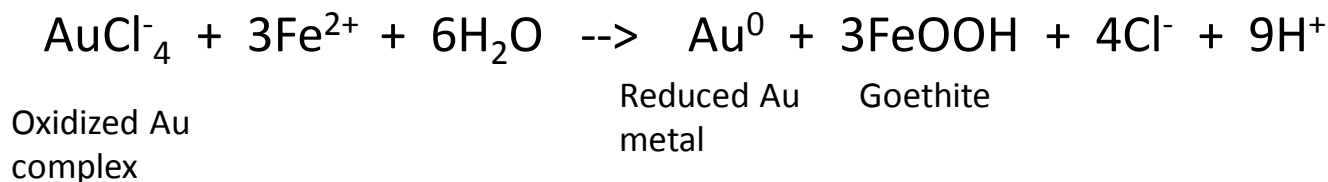
Redox and Au mobility

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

Metallic Au goes into solution via complexing with Cl^- or organics or thiosulfates, although the redox state changes to Au(III) or Au(I) e.g. gold in the Au-Cl_4^- 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^{2+} to Fe^{3+} and hydrolysis to form iron oxides in lateritic profiles:

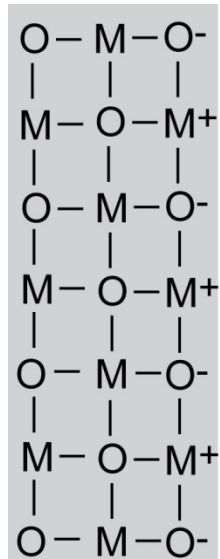


Adsorption & Point of Zero Charge (PZC)

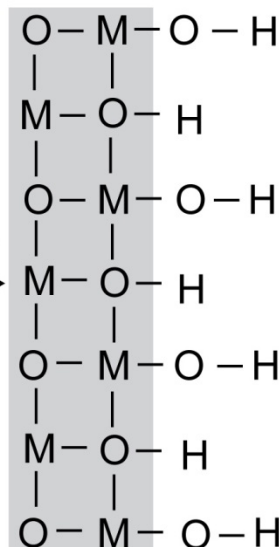
Adsorption is the binding of ions or molecules on the surface of a mineral

- 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

Dry surface



Wet surface



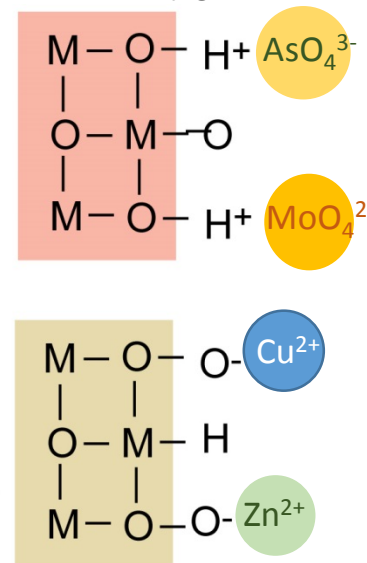
M-metal ion

O - oxygen

$+H^+$
low pH

PZC

$+OH^-$
high pH

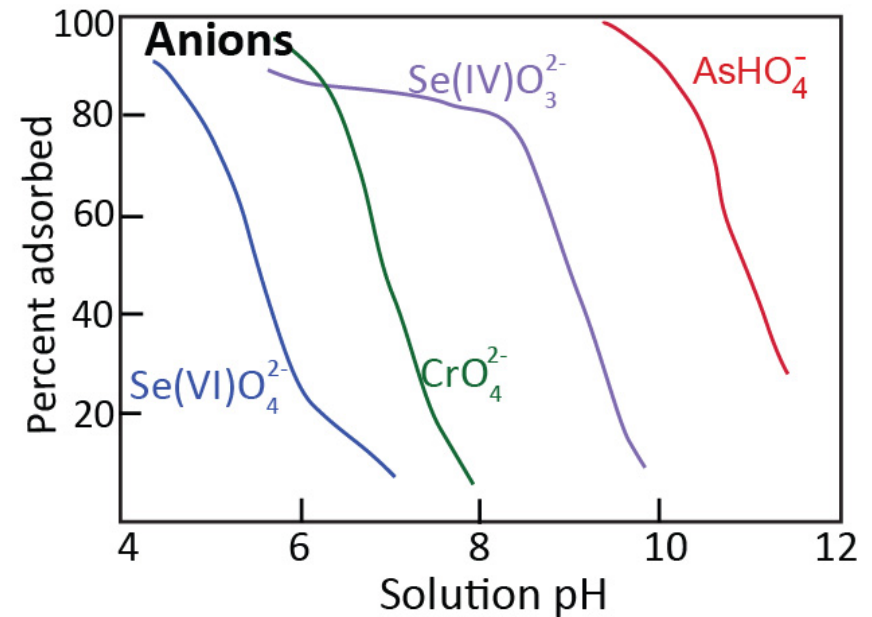
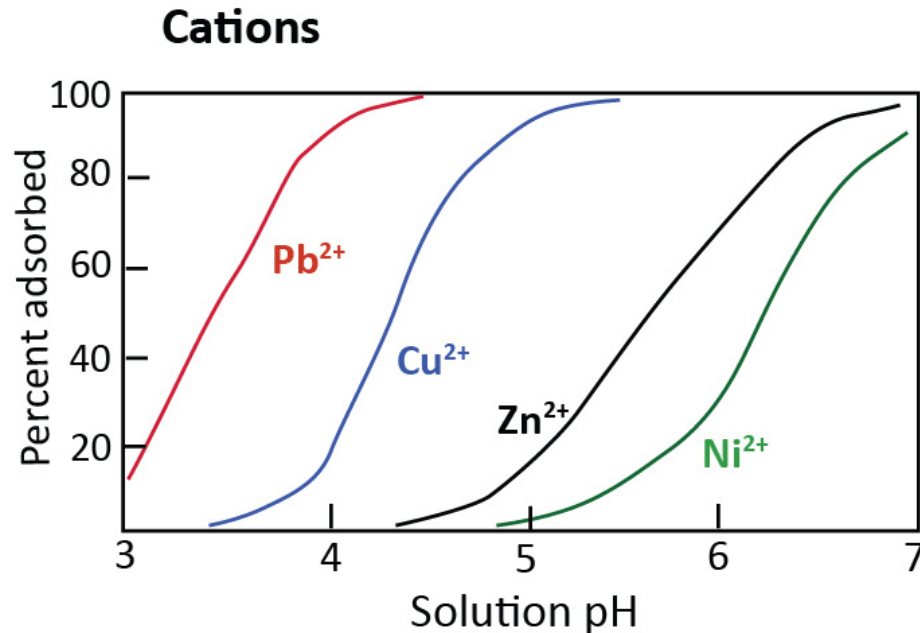


PZC for:

Goethite	7.0
Hematite	8.0
Ferrihydrite	8.0



Adsorption – pH vs cations and anions



Mineral surfaces, excess +ve at low pH, excess H^+ - attract anions (oxyanions)

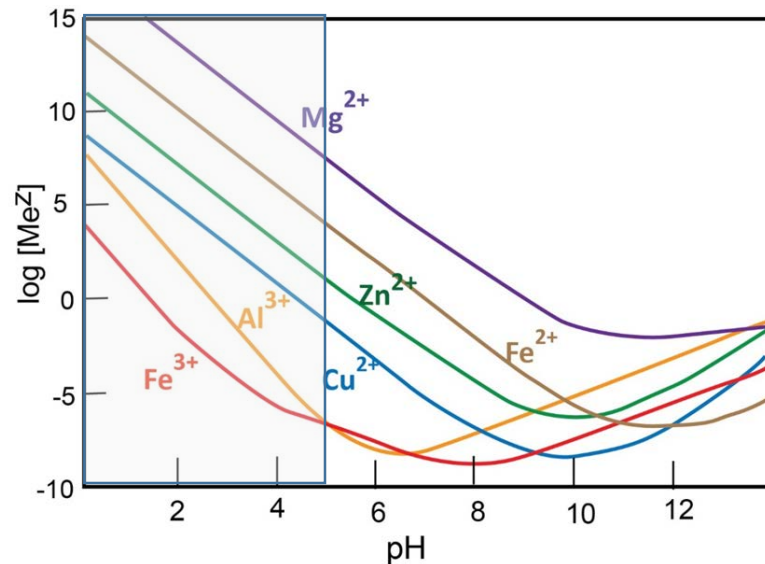
Mineral surfaces, excess -ve at high pH because excess OH^- - attract cations

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

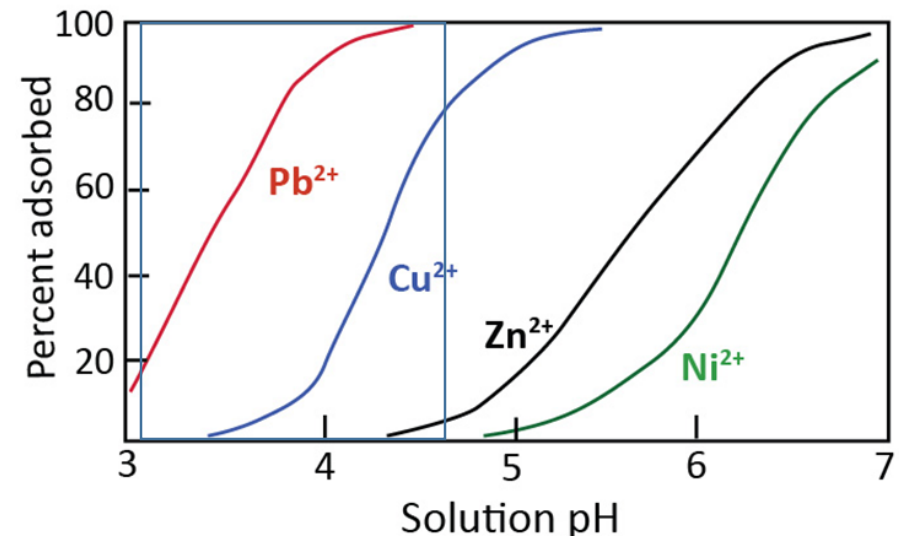
1. Oxidizing sulfides result in the production of acid conditions – release of H^+



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^+ on mineral surface sites, less attraction to bind positive cations such as Cu^{2+} , Zn^{2+} , Pb^{2+} so less absorption



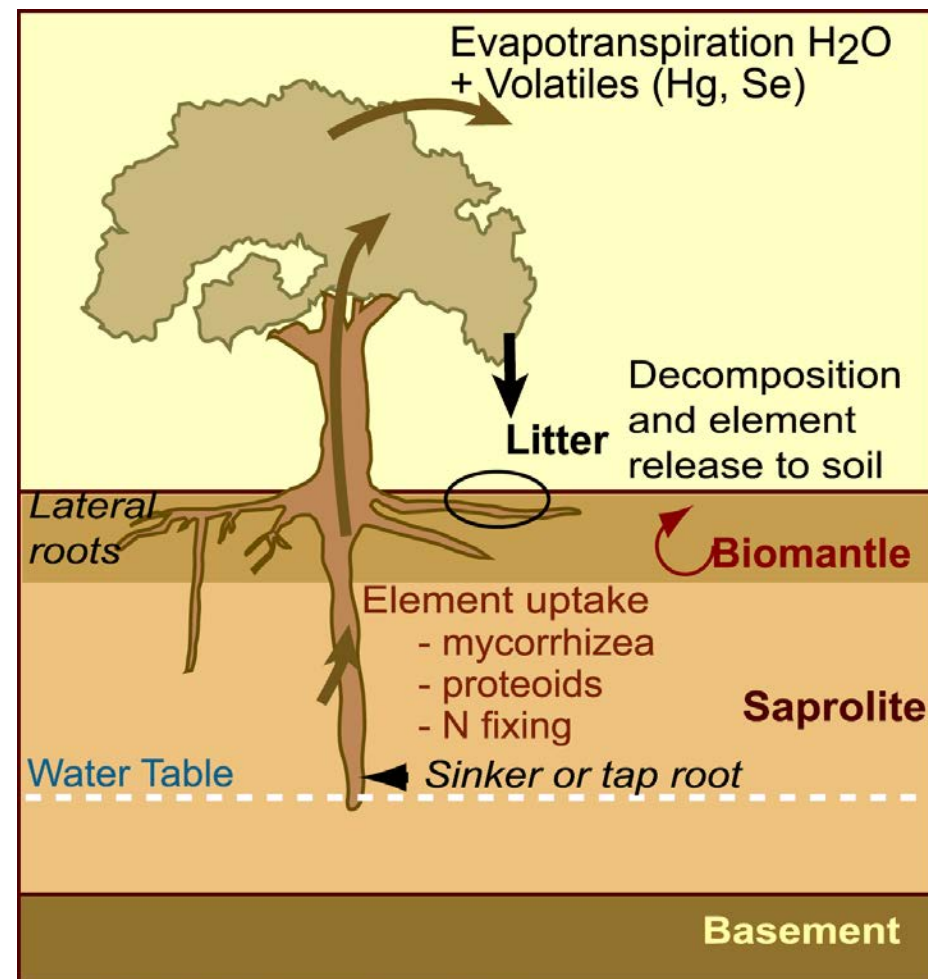
Vegetation Transfer & Mobility

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

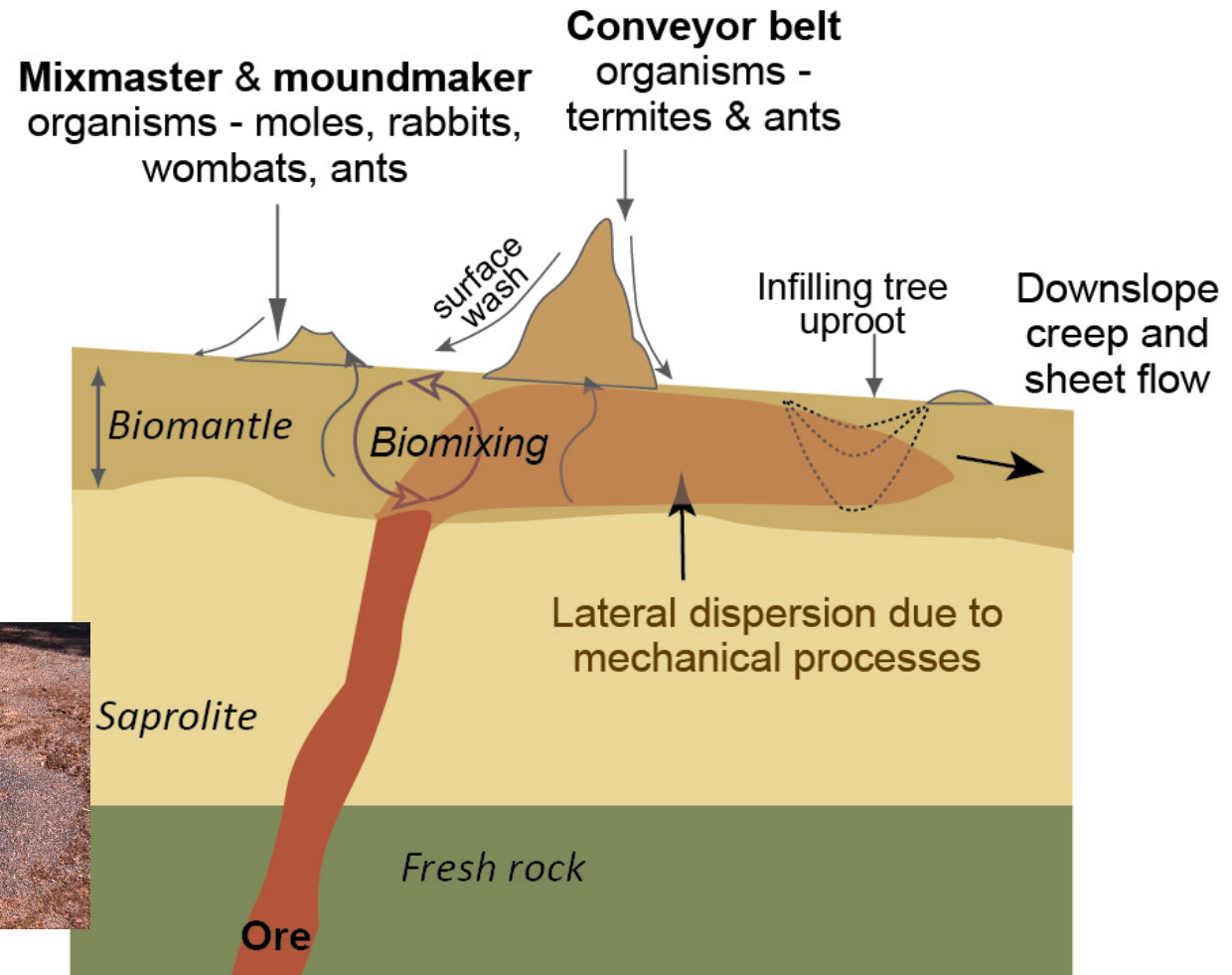
Sinkers tap deeper groundwater for nutrients in summer



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

