Regolith Geochemistry & Mineralogy

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Regolith Geochemistry

- What factors control metal mobility?
- Why do river and groundwaters have higher concentrations of Ca, Na, Mg & K?
- Why is the near surface Australian regolith so rich in Al, Si & Fe minerals?
- Why do specific trace metals correlate strongly with Fe/Mn oxides & hydroxide rich materials?
- Can you predict how metals will behave in the regolith under specific conditions?

Regolith (Ρεγόλιθος)

- This entire mantle of unconsolidated material, whatever its nature or origin, it is proposed to call the regolith.
- Επιφανειακό κάλυμμα – υλικά ποικίλης προέλευσης (in situ – ex situ)

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Fundamentals of Geochemistry

The Periodic Table

- Alkali & alkaline earths: K, Rb, Sr, Cs, Ba, Li
- Transition metals: Sc, Ti, V, Cr Co, Ni, Cu, Zn, Pb, Sn, Bi
    - Different valence (oxidation) states; high electronegtivity
- Rare earth elements (lanthanides)
    - High charge, large radii
- High Field Strength Elements: Zr, Hf, Ta, Nb
    - High ionic charge +4 - +5; smaller radii
- Noble metals: Pt, Au, Pd, Rh, Os
    - Rare & unreactive
- Gases/Volatiles: He, Ne, Ar, Kr, Xe, C, S, Cl

Major & Trace Elements

- **Major Elements**
  - make up the majority of silicates (crust and mantle)
  - Si, O, Al, Fe, Mg, Na, K, Ca, (Mn), (Ti), (S), (P)
  - Reported as Wt % oxide or mg/Kg
- **Trace Elements**
  - the remaining elements, but vary depending on the geochemical system under study. For example, trace elements in igneous rocks not same as oceanic ones
  - Generally reported as ppm or mg/Kg

Elements in Exploration Geochemistry

- **Target or Ore elements**

  "Commodity" sought

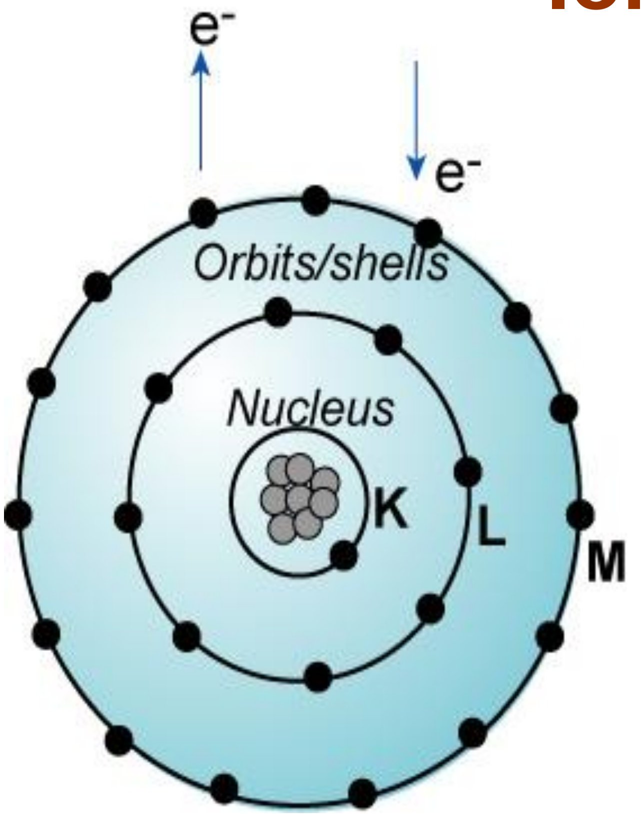
  e.g. Au, Cu, Ni, Pt, U, Zn etc

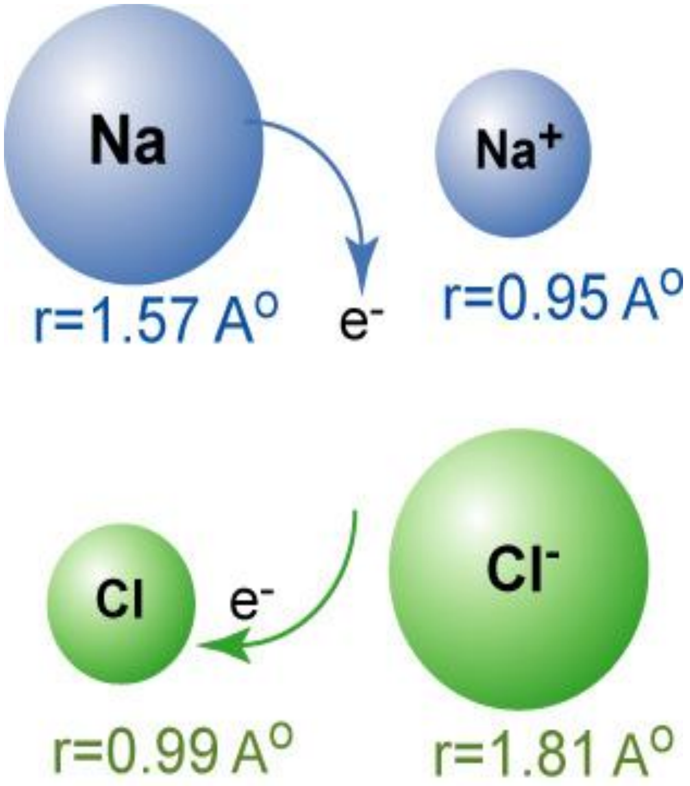
- **Pathfinder elements**

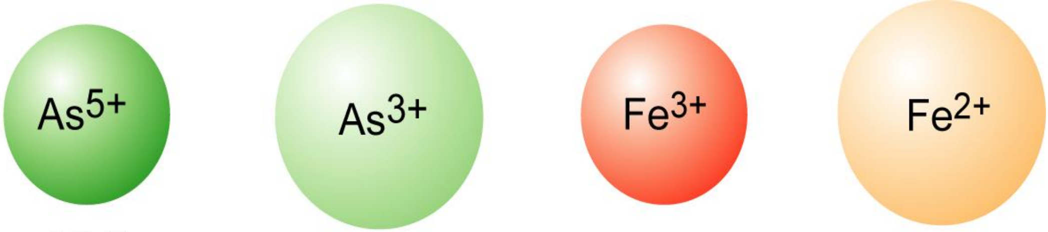
  Elements commonly associated in high or anomalous concentrations with target elements

  E.g. As, Mo, Bi, Sb, Sn, W, Cu

Ionic charge







	As^{5+}	As^{3+}	Fe^{3+}	Fe^{2+}
z/r	10.6	4.3	4.68	2.63

Element properties critical to low temperature geochemistry

- Electrons removed or added to outer orbitals of atoms > charged particles > **ions**
- **Cations (+ve)** but smaller radii**, and anions (-ve)**
  - **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: Cl^-, Br^-, O^{2-}, F^-, I^-, S^{2-}**
- **Charge on the ion – Na^+, Ca^{2+}, Al^{3+}, Zr^{4+}, P^5 - z**
- **Ionic radius – size of the ions - *r***
- **Ionic Potential: ratio of ionic charge to ionic radius *z/r***
- **Different charges or redox states for individual elements**

Factors affecting element mobility in the regolith

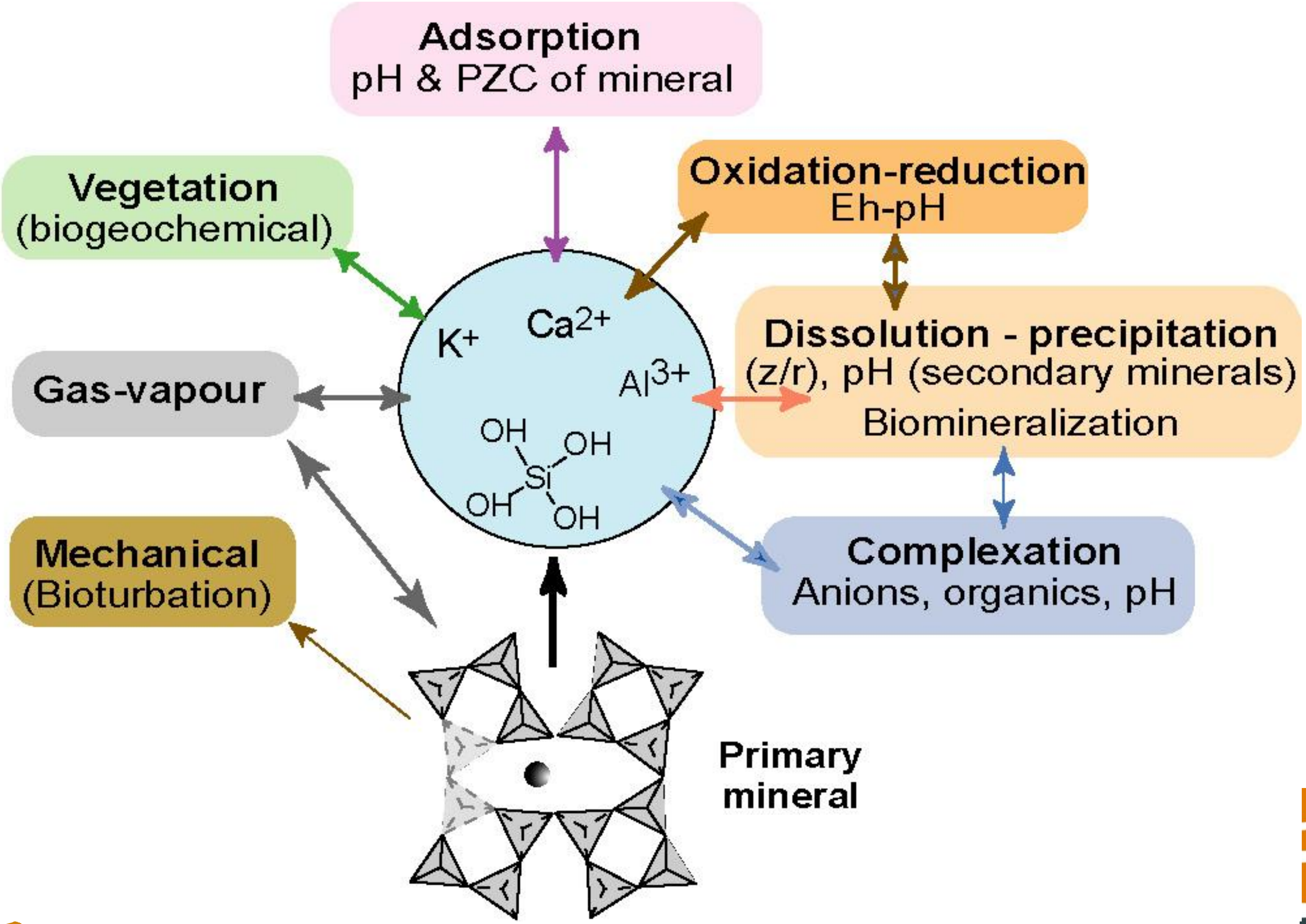
Distribution of elements in the regolith, especially weathering profile, are dependant on

- Weathering & stability of primary & secondary minerals
- Solution processes (solubility of elements)
  - **pH**
  - **Dissolution- precipitation**
  - **Oxidation-reduction**
  - **Solution-Gas**
  - **Complexation**
  - **Sorption**
- Gas-vapour
- Biological activity
- Mechanical activity

First the element has to come out of primary minerals..

- **Rate of release** of elements – depends on stability of primary minerals
- Zr^{4+} release from zircon very slow (Zr-O bond strong)
- Ti^{4+} from pyroxene faster than Ti^{4+} from rutile or illmenite
- Release from within **secondary** minerals (kaolinite, goethite) is also dependant on stability of that mineral
- Solution process effects are minimal if element or ion is not “free” from the primary or secondary mineral
- Only mechanical effects are relevant to move elements as coarse mineral grains

Factors affecting metal mobility



Adsorption
pH & PZC of mineral

Vegetation
(biogeochemical)

Oxidation-reduction
Eh-pH

Gas-vapour

Dissolution - precipitation
(z/r), pH (secondary minerals)
Biomineralization

Mechanical
(Bioturbation)

Complexation
Anions, organics, pH

Primary mineral

Then reactions between solution and secondary minerals operate –

Divalent metal hydrolysis

- Hydroxides, oxides, sulphates & carbonates are the least soluble of metal salts, so solubility of metal hydroxide controls the solubility/mobility of metals in solution or solid (regolith) > precipitation of metal bearing secondary minerals (stable solids establish equilibrium with lowest metal concentration in water)
- Metal oxides & hydroxides hydrolyze in water yielding a variety of hydrolysis products – $M(OH)^+$, $M(OH)_2$, $M(OH)_3^-$…
- For most divalent metals (M^{2+} - Mg, Ca, Zn, Cu, Pb) dominant species at pH < 9 is M^{2+}
- The reaction $M(OH)_2 \leftrightarrow M^{2+} + 2(OH)^-$

  involves hydroxyls, and is therefore pH dependant, the concentration of M^{2+} decreasing with increasing pH
- Total amount of metal in solution is sum of all its hydrolysis products (species)
- $[Al]_T = [Al^{3+}] + [Al(OH)^{2+}] + [Al(OH)^+{}_2] + \ldots.$

Dissolution – precipitation > Solubility Products

$CaCO_3 <> Ca^{2+} + CO^{3-}$

Solution

Precipitation of a metal
- Salt
- Carbonate
- Oxide/Hydroxide
- Silicate

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Solubility Product (SP)

- The hydroxide is the **least soluble** salt of the metal
- Example: $Ca(OH)_2 \leftrightarrow Ca^{2+} + 2(OH)^-$ ($Ca(OH)_2 + 2H^+ = Ca^{2+} + 2H_2O$)
- Reported as Solubility Product (SP) – K_{sp}

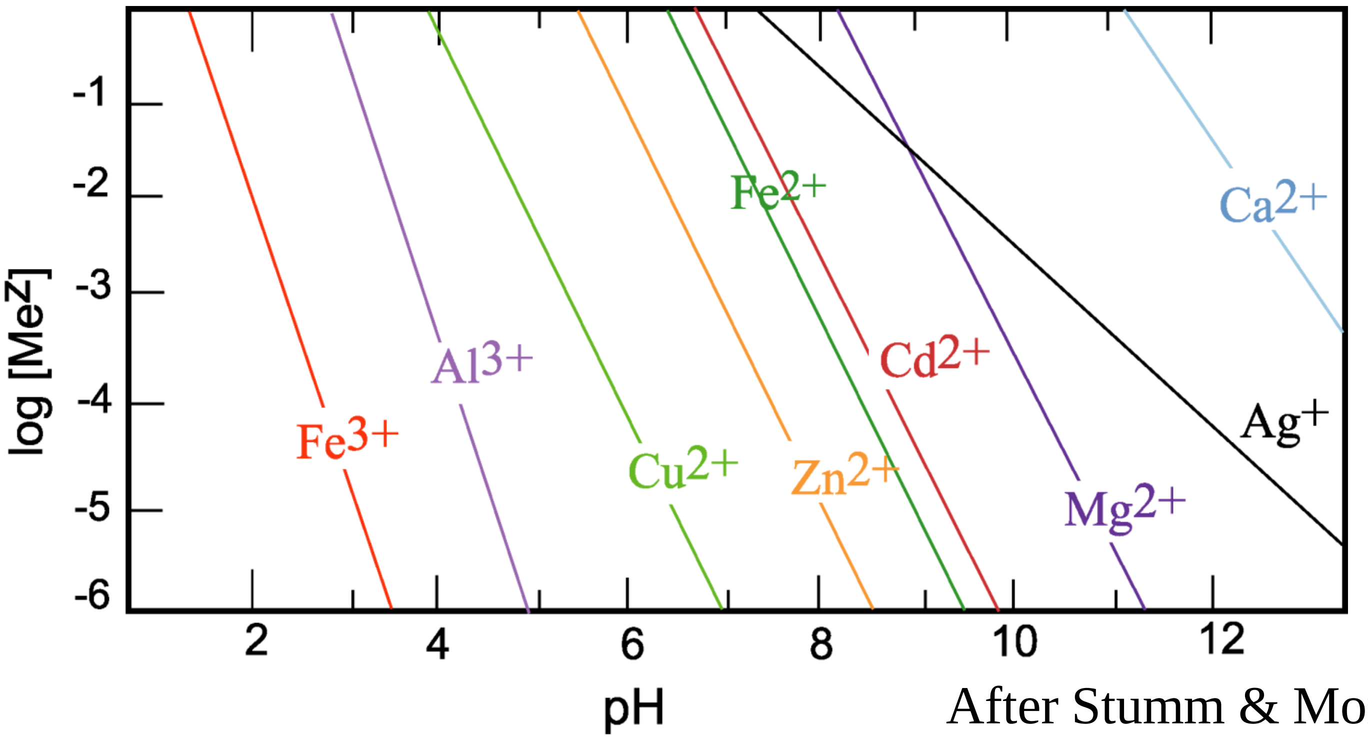
  $K_{sp} = [M^{2+}][OH^-]^2$ (moles/l)^3 or $K_{sp} = [Ca^{2+}][OH^-]^2$
- From experimentally determined K_{sp} of a reaction – concentration of metal in solution to **maintain equilibrium** with solid hydroxide can be calculated
- For simple reactions (i.e. nothing else is dissolved in water – highly unlikely!) equilibrium between concentration of M^{2+} in solution with solid hydroxide – corresponding equilibrium pH is known as pH of hydrolysis

Divalent metal hydrolysis

(oxides, hydroxides, sulphates)

- Divalent metals (M^{2+} - Mg, Ca, Zn, Cu) hydrolyze with dominant species < 9 pH being M^{2+}
- $M(OH)_2 = M^{2+} + (OH)^-$ reported as Solubility Product (SP) – **$K_{sp} = [M^{2+}][OH^-]^2$ (moles/l)^3**
- From experimentally determined K_{sp} of a reaction – concentration of metal in solution to maintain equilibrium with solid hydroxide (oxide & hydroxide least soluble, but also carbonates, phosphate, silicates etc) can be calculated

Metal Hydrolysis

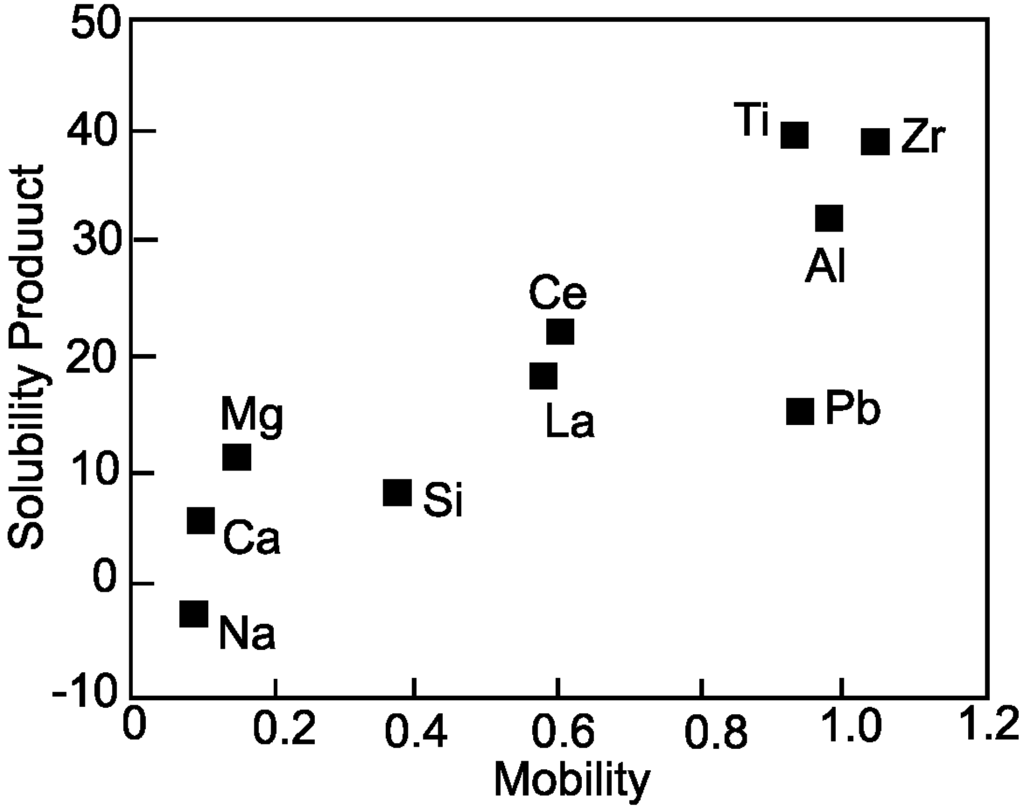


After Stumm & Morgan (1981)

- Concentration of M^{2+} in solution is dependant on pH of solution (groundwater) $M(OH)_2 + 2H^+ = Me^{2+} + 2H_2O$
- Slope of solubility curve depends on valence of metal
- For many cations, concentration decrease with increasing pH

Solubility Product – one estimate of mobility during weathering!

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



Mobility of selected elements from a bauxite profile (Data: R.A Eggleton)

Note that higher SP (less mobile) link with high z/r or Ionic potential

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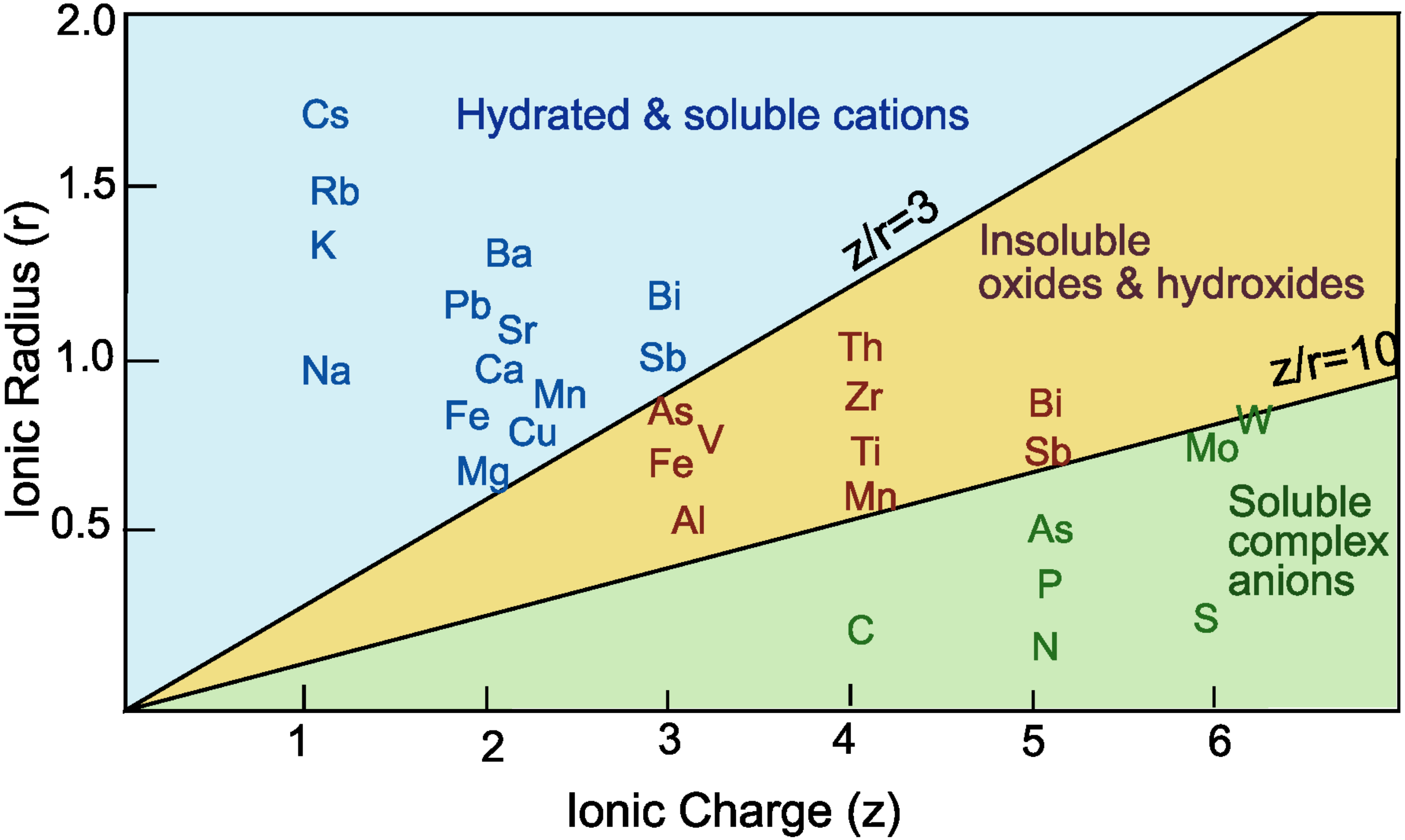
Ionic potential – prediction of solubility once element/ions in solution

- Low IP cations **(*z/r* < 4)** – Na^+, Ca^{2+} etc, bond weakly to O^{-2} because of weakly focussed charge; do not form stable oxides & prefer solution > soluble
- Intermediate IP cations **(*z/r* 3 -10)** – Al^{3+}, Fe^{3+}, Ti^{4+} etc, compact, moderate charge distributions form stable oxides > less soluble
- Large IP cations **(*z/r* >10)** – P^{5+}, N^{5+}, S^{6+} etc, bond tightly to O^{2-} > stable but soluble radicals like PO_4^{-3}, NO_3^- etc > high focused charge on cations repel each other in solids > not stable oxides > soluble

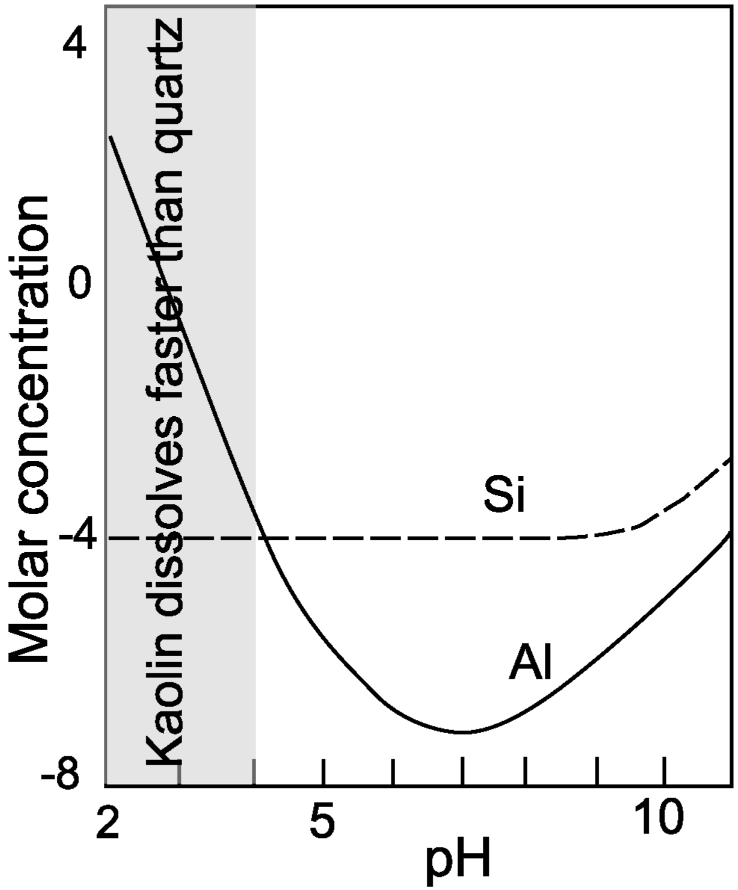
Another way to estimate mobility is via ionic potential (z/r) – relates to oxide/hydroxide stability



Modified after Plant (1992)

Major elements

Alumino- silicate solubility

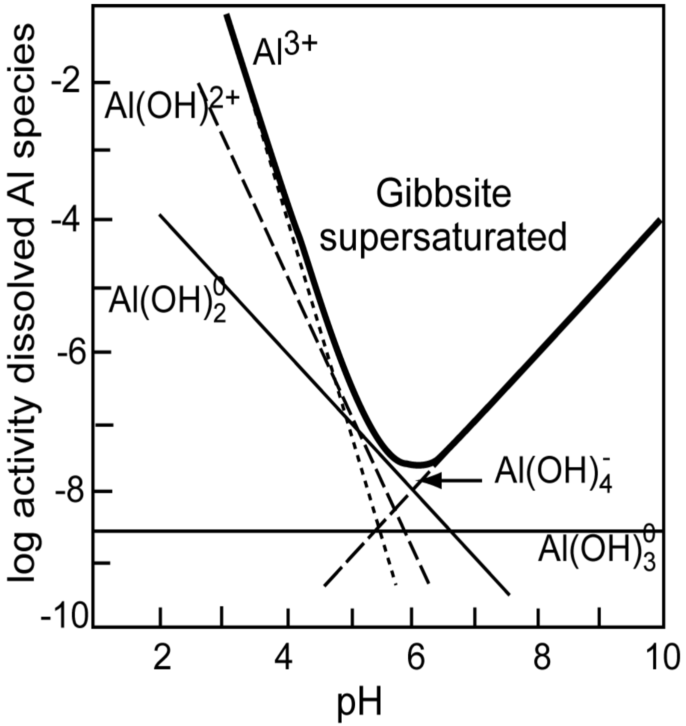


Al is mobile (soluble) < pH 4 or > pH 8 (based on alumino-silicate reaction).

Generally, natural waters are within this pH range and therefore Al and Si minerals dominate the regolith

In extreme acid conditions (pH< 4) Al goes into solution but Si may not (but it too does!)

Al solubility - Gibbsite



$$Al(OH)_3 <> Al^{3+} + 3OH^-$$

$$Al^{3+} + H_2O <> Al(OH)^{2+} + H^+$$

$$Al^{3+} + 2H_2O <> Al(OH)_2^+ + 2H^+$$

$$Al^{3+} + 4H_2O <> Al(OH)_4^- + 4H^+$$

- Concentration of dissolved Al species in equilibrium with gibbsite as a function of pH
- Hydrolysis products of each Al species plotted
- Al goes into solution at low pH and very high pH

Another way metal mobility is afffected is via Complexation

- Besides H_2O – other complexes exist in water
- **Central ion** (cation, Ca, Mg, Fe, Al, K) with **ligand** (anions, O, S, Cl, F, I, C)
  - OH complexes: $FeOH^+$, $Fe(OH)_2^+$
  - Halide complexes: $CuCl^-$, $PbCl_3^-$
  - Carbonates : $CaCO_3^0$, $MgCO_3^0$
  - Sulphate: $CaSO_4^-$
- Each metal complex has a stability constant – dependant on
  - pH &
  - concentration (activity) of metal & ligand

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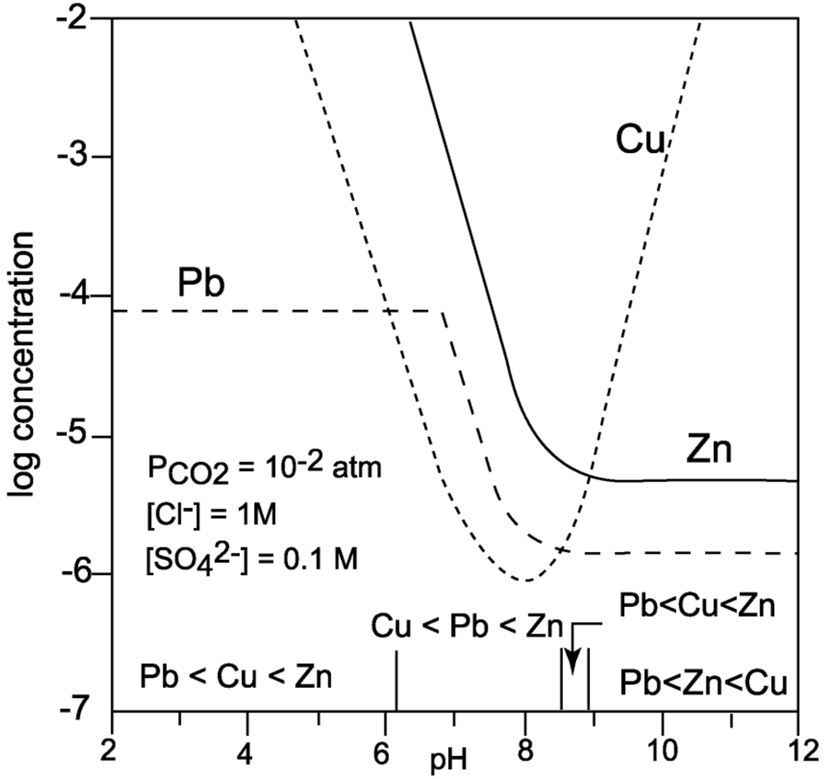
Complexes and metal mobility

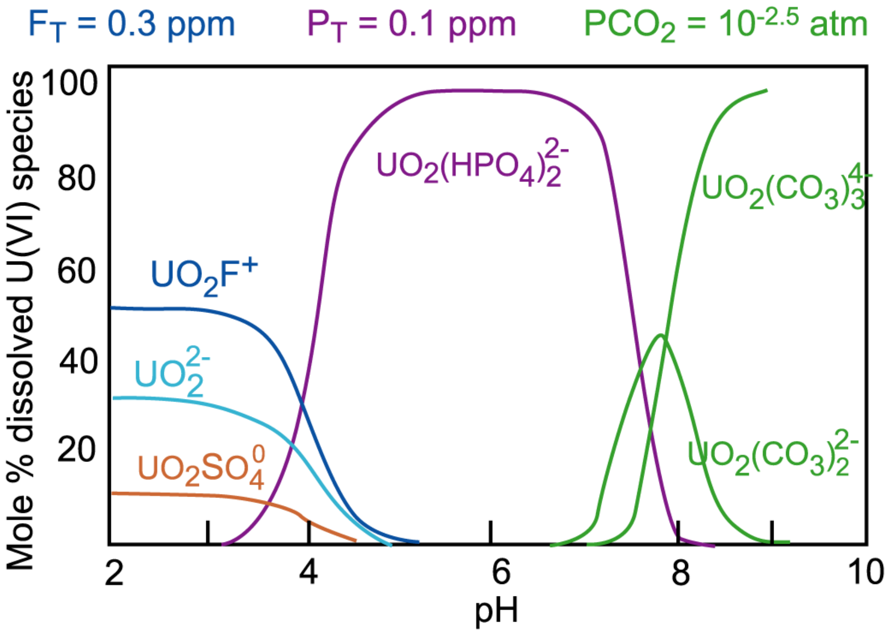
- Availability of complexes affect metal mobility > require specific concentration of anions & pH
- Metallic Au becomes mobile on complexation with
  - Halide (CN^-, Cl^-) in acid-oxidizing environments
  - Thiosulphate complexes ($S_2O_3^{2-}$) in alkaline conditions
  - Organics in organic rich environments
- U is mobile when complexing with CO_3^{-2} ($UO_2(CO_3)_2^{2-}$ and PO_4^{2-} ($UO_2(HPO_4)_2^{2-}$ in the pH 4-8
- Zn-Cu mobile with Cl^-
- Changes in pH can affect complex stability, metal mobility and precipitation of metal-complex minerals (e.g. precipitation of metal carbonates, metal sulphates)

Metal Mobility – pH and complexes



Theoretical calculations

Complex SO_4^{2-} Cl^-



After Langmuir (1979)

From Mann & Deutcher 1980

Organic Complexes

- Chelates – organic molecules capable of binding metals (multidentate ligands)
- Specific chelates bind metals e.g. Al, Fe and increase their mobility even in environments that they are predicted to be immobile purely on pH-Eh, SP
- Some chelates even extract metals from mineral structure
- e.g. Citric acid, fulvic and humic acids chelate ferric iron
- Relevant mechanism affecting metal mobility in upper parts of soils

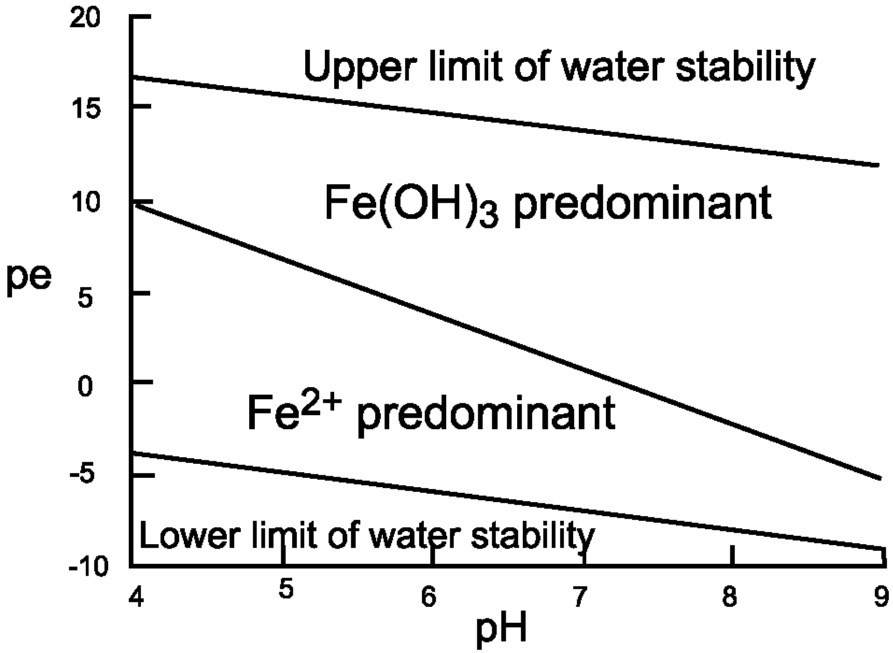
Oxidation – reduction (redox)

- Many elements in the regolith exist in two or more oxidation states
- 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
- **Electron transfer** process
  - Oxidation – loss of electrons from elements
  - Reduction – gain of electrons
- Catalyzed by microbial reactions

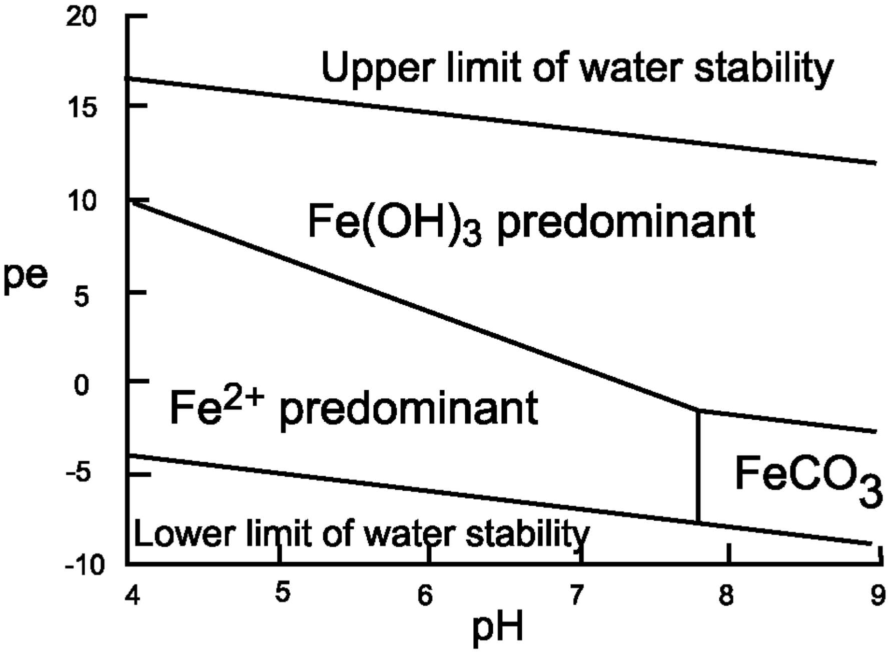
Redox potential & redox diagrams

- Tendency of an regolith environment to be oxidizing or reducing – measured in terms of **electron activity (pe)** or **electron potential (Eh)**
- Higher Eh , lower the electron activity
- Eh-pH or pe-pH diagrams provide a way of assessing the dominance and stability of different redox species in the environment
- Iron can be present in minerals or as a solute species depending on redox conditions

Iron redox diagram



Fe-O-H_2O system



Fe-O-H_2O-CO_2 system

Some redox elements in the regolith

- Iron: Fe^{2+} <> Fe^{3+} (FeOOH)
- Manganese: Mn^{2+} <> Mn^{3+}, Mn^{4+} (MnO_2)
- Carbon: C <> $(CO_3)^{2-}$ ($CaCO_3$), C^{+4}(CO_2)
- Sulfur: S^{2-} <> S^{6+} ($(SO_4)^{2-}$), S^0 (FeS_2)
- Arsenic: As^{3+} <> As^{5+} (AsO_4^{3-})
- Gold: Au^o <> Au^+, Au^{3+} ($AuCl_4^-$)
- Chrominum: Cr^{3+} <> Cr^{6+} (CrO_4^{2-})
- Uranium: U^{4+}(UO_2) <> U^{6+} (UO_2)

More states exist for some elements but are relatively rare in the regolith environment. Each state can have several solute and solid species

Redox states and element mobility

Mobility and toxicity of redox elements varies depending on their redox state – redox potential of environment – *z/r* changes

- Fe^{2+} is more soluble than Fe^{3+} (z/r of $Fe^{2+} < 3$)
- Se^{6+} more soluble but less toxic than Se^{4+}
- As^{3+} is more mobile and toxic than As^{5+}
- Cr^{6+} is more mobile and toxic than Cr^{3+}

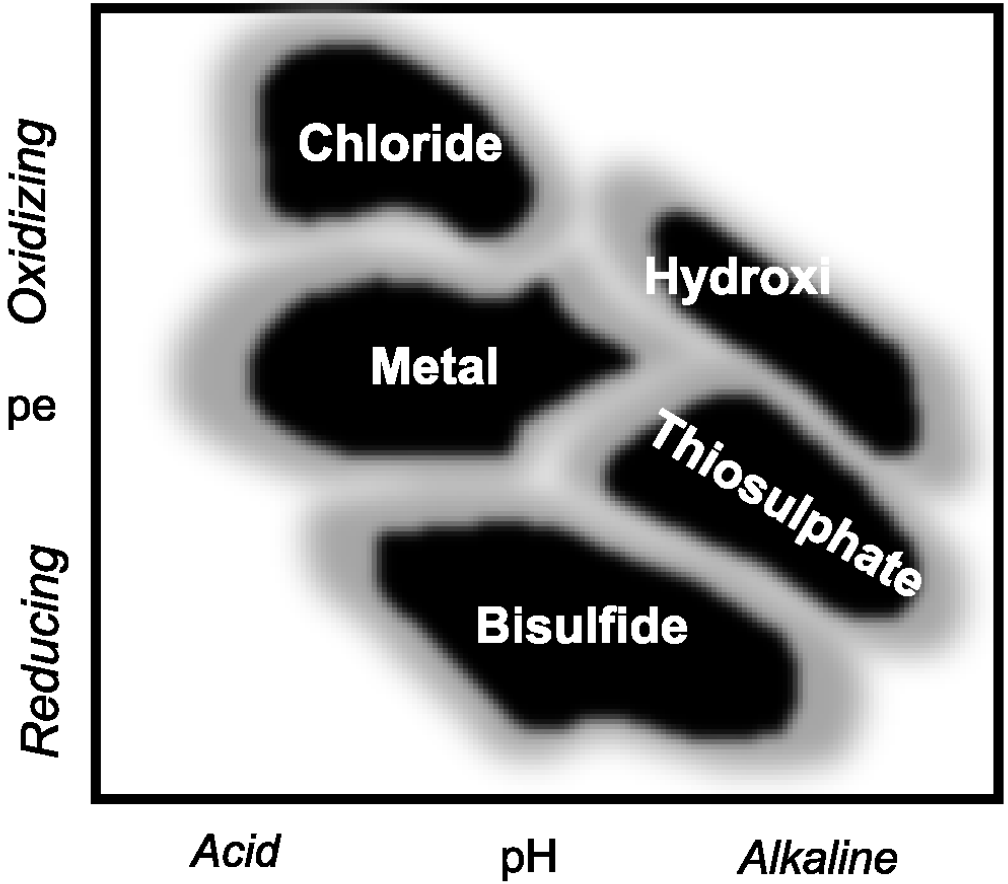
However, absorption can change the mobility of the elements irrespective of their oxidation state

Redox and complex stability

Gold becomes soluble by forming complexes with different species – $AuCl_2^-$, $Au(S_2O_3)^{2-}_2$

Each Au complex has a redox-pH stability range

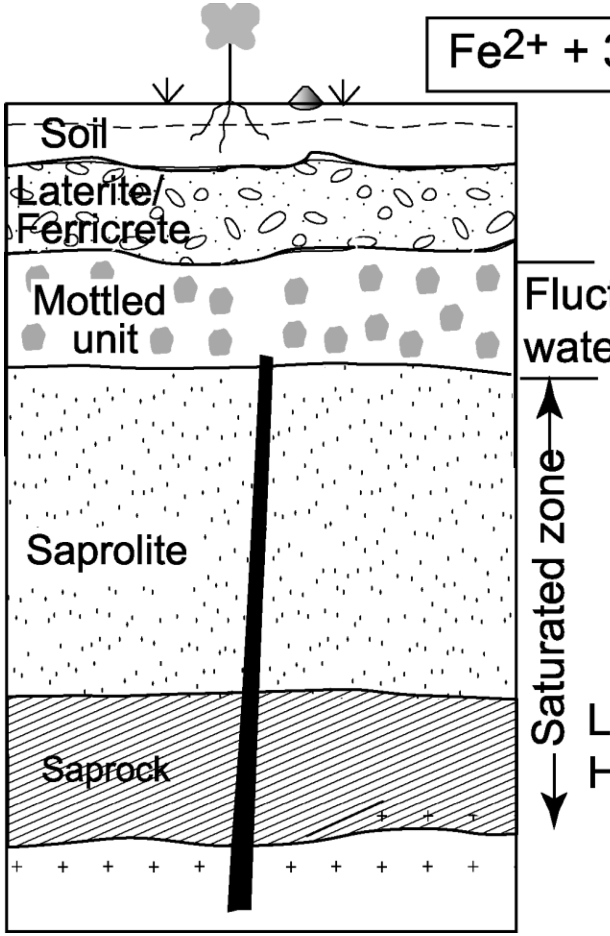
Complex can form at favourable redox conditions & destabilize at specific redoxs



From Taylor & Eggleton (2001)

A regolith profile example - ferrolysis

$Fe^{2+} + 3H_2O > Fe(OH)_3 + 3H^+ + e^-$



High Eh
Low pH

Formation of iron hydroxides lowers pH attacks kaolinite

Fe^{2+}
diffusing to
oxygenated water

Low Eh
High pH

Precipitation Fe oxides lower pH which affects metal mobility but also absorption of metals on Fe oxides

Sorption

Affects the mobility of metals and ions by making them immobile or mobile by bonding

- Adsorption: Species on the surface of mineral (layer silicates, oxides & hydroxides, organics)
- Absorption: species in the structure of mineral (diffusion?)
- Ion exchange: species A exchanges on or within structure of mineral with species B (charged bearing clay layer silicates – clay minerals, organics)

Mineral surface reactions

- Clay minerals, oxides, hydroxides, organics, carbonates in regolith have surface charge due to unsatisfied bonds at crystal surface and edges
- Some clay minerals also have permanent negative charges due to T and O substitutions
- These charges attract cations or anions that bond (adsorb or ion exchange) to the surface ions is specific ways – surface complexes

Point of Zero Charge (PZC)

- Outer surface of most regolith minerals are oxygens
- In **acid** solutions, surface **+ve** charged
- In **alkaline** solutions, surface **–ve**
- Change from –ve to +ve depends on mineral occurring at specific pH
- The pH at which it occurs – zero charge on surface - point of zero charge (PZC) for the mineral

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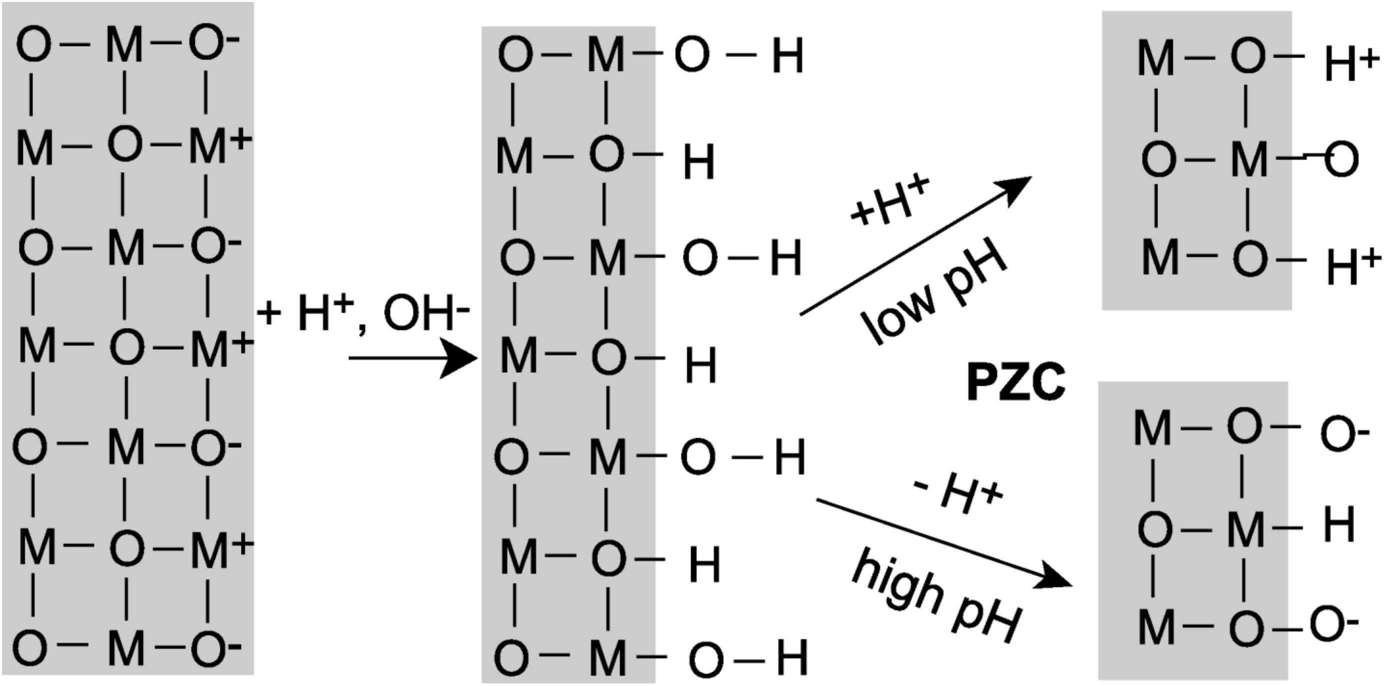
PZC and mineral surfaces

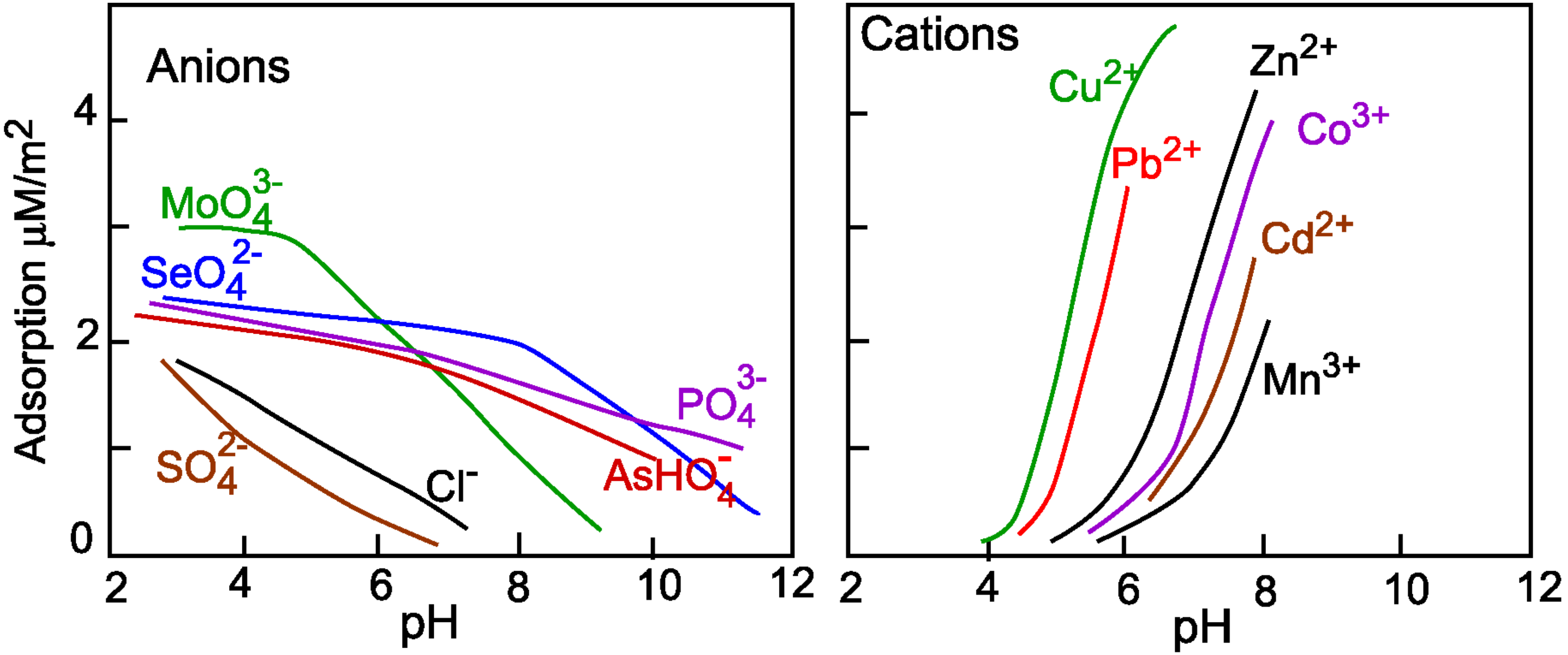


M – metal ion   O - Oxygen

Quartz	1.0
Birnessite	2.0
Smectite	2.0
Kaolinite	4.5

Goethite	7.0
Hematite	8.0
Ferrihydrite	8.0

Adsorption – pH vs cations & anions



Mineral surfaces – excess +ve at low pH = excess H$^+$ - attract anions

Mineral surfaces – excess –ve at high pH = excess OH$^-$ - attract cations

Also dependant on high concentration of other anions –Cl$^-$

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Modified from Thornber (1992)

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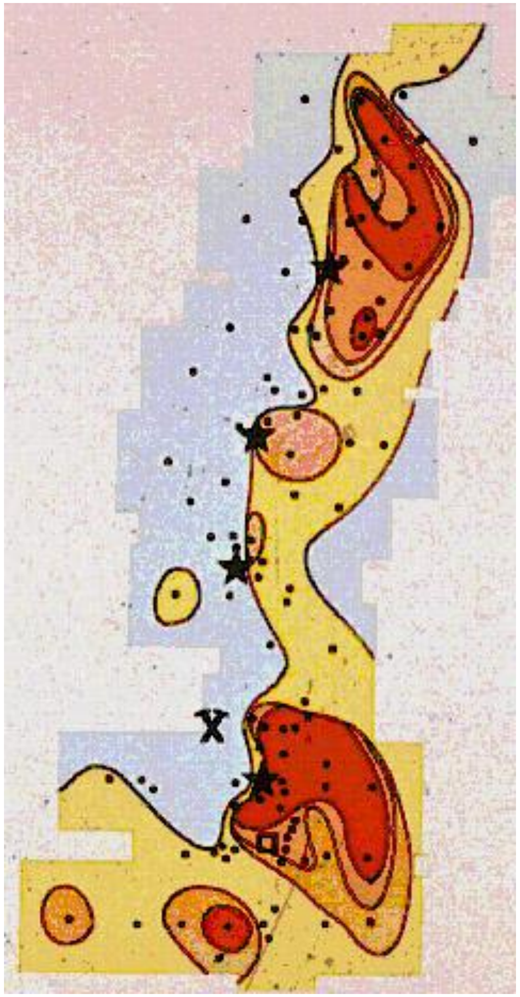
Sorption and element distribution

- Generally strong relationship between Fe-Mn concentrations (Fe-Mn oxides) and metals in upper parts of profile and ferruginous materials
- Fe-Mn oxides adsorb metals from solution (lag, ferricrete sampling)
- The mobility of trace metals is then controlled by solution pH and stability of host mineral

Arsenic distribution of laterite survey



Image/Data: Ray Smith

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Another way some elements can migrate
Gas or volatiles

- Gases –
  - Sulphide weathering: CO_2, COS, SO_2
  - Radioactive: ^{222}Rn & ^{4}He
  - Hydrocarbons: $CH_{4,}$ C_4-C_{10}
  - Noble gases (Ne, X, Kr)
- Volatile and metal hydride species – Hg, I, As, Sb
- Metal transfer – attached to gas bubbles moving through water column and unsaturated regolith – Cu, Co, Zn, Pb – not conclusive yet
- Higher transfer or mobility rates along conduits: Faults, fractures & shears > faster diffusion & advection
- Minor and selected element process

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Plants can transfer or increase mobility

- Vegetation requires essential and trace elements (micro-nutrients) for physiological processes
- Plants act as "biopumps" for specific metals – N, O, Ca, Cu, Zn, Mo, Ni, Au
- Hyperaccumulators take up more 100-1000μg/g
- Phytoremediation employs vegetation as uptake conduit

Macronutrients	Micronutrients	Other element absorbed
N, P, K, Ca, Mg, S	Fe, Mn, **Cu, Zn**, B, **Mo**, Cl, **Ni**, Si, **Se**	**Au, As**, Cr, **Pb**

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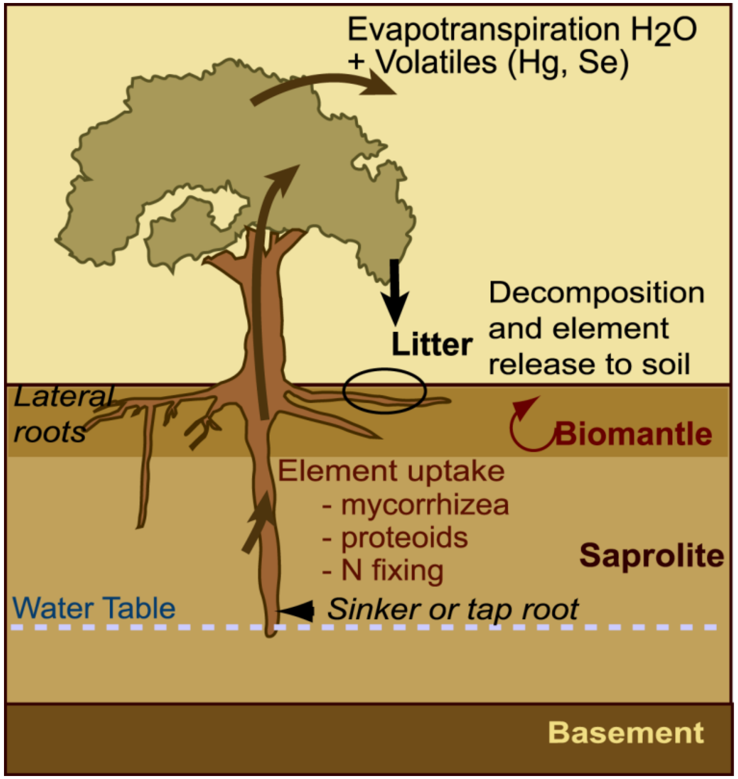
Vegetation Transfer & Mobility

- 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

Microbial Assisted Mobility
- Mineral Dissolution

- Sulphide oxidation (Fe^{2+} & S^o oxidation rate)
- Lichens-bacteria accelerate silicate weathering
- Phosphate minerals – P nutrient
- Organic contaminanted environments – increase mineral dissolution rate
- Complex metals – siderophores – increase metal mobility
- Aid reductive dissolution of insoluble oxides – release sorbed metals into solution
- Biotransformations – As, Sb, Hg, Se etc.

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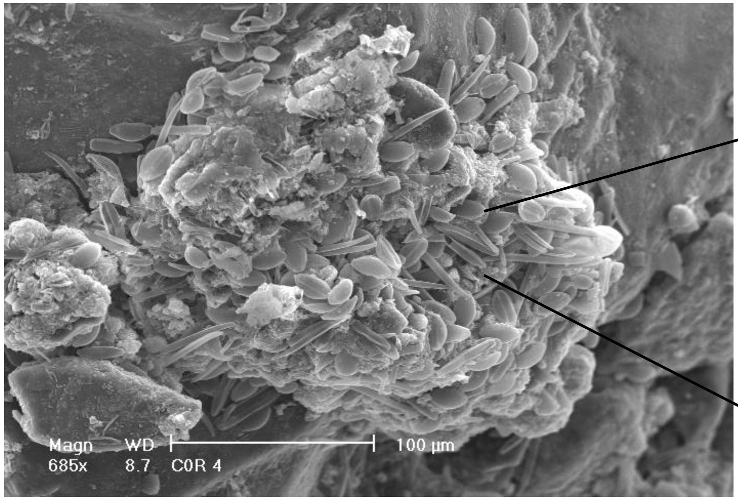
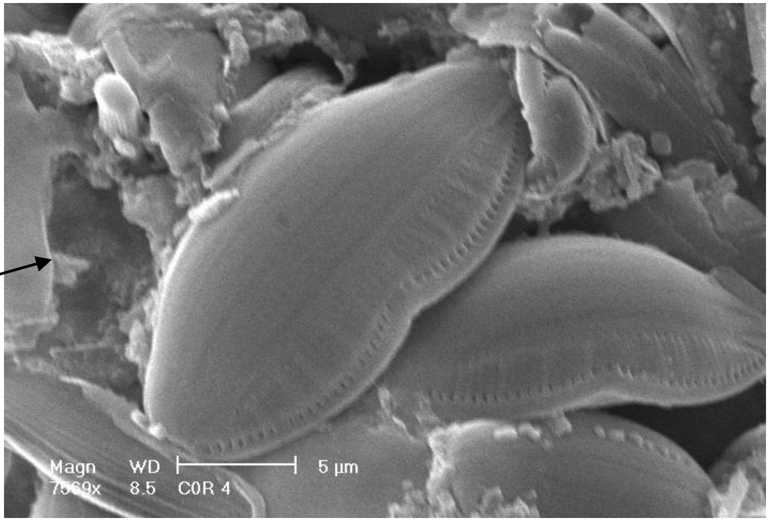
Microbial Assisted Immobility
Biomineralization

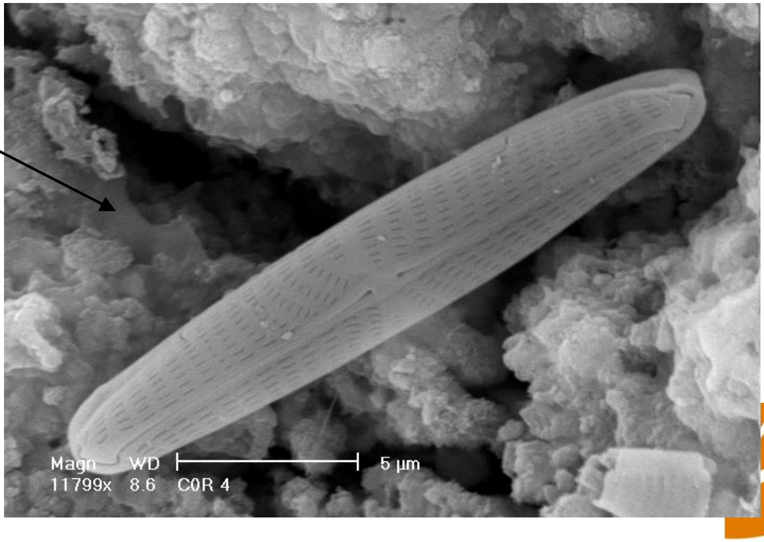
- Intracellular biomineralization
  - Fe: Bacterial magnetite
  - Zn, Fe & S: sulphides
  - Ca : carbonates
- Extracellular biomineralization
  - Fe & Mn: Fe oxides & hydroxides
  - Fe, Zn & S : Sulphates & sulphides
  - P & Fe: Phosphates
  - Gold!

Microbial Immobilization - Si

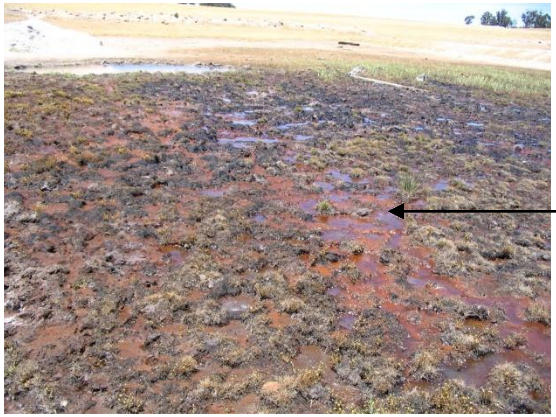


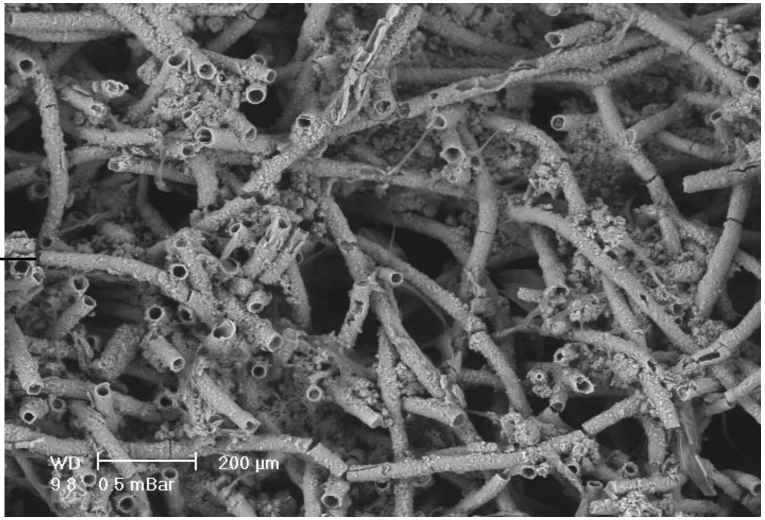
Siliceous diatom clusters from surface of acid sulfate soils





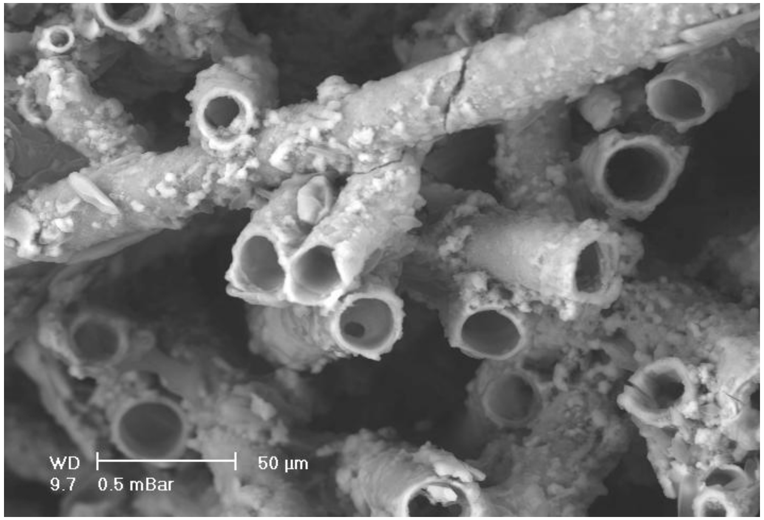
Microbial Immobilization of Fe





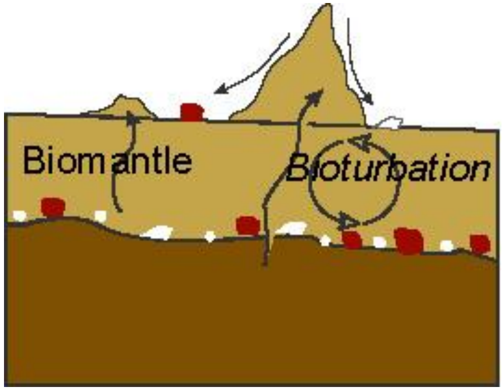
Surface reddish ppt - AAS

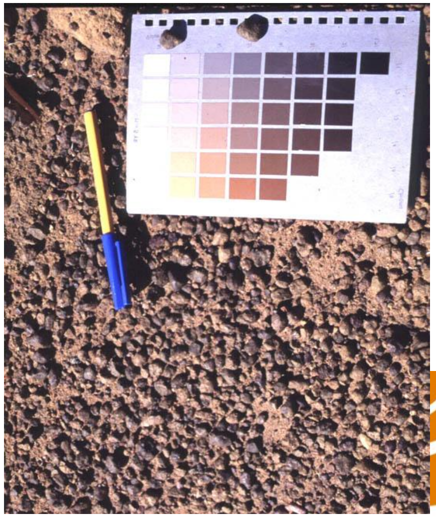
Iron oxidizing bacteria (*Leptothrix*) - tube like structures - encrustrations of Fe hydroxides



Mechanical Transfer

- Biomantle – biomechanically active part of regolith
- Biotransfer of subsurface material to surface (bioturbation, vegetation) and then moved laterally downslope by mechanical processes – particles (lag)
- “Immobile” elements are so made mobile because mechanical activity does not distinguish on SP, redox or adsorption





Major element mobility in profiles

Rock type	**Order of decreasing loss**
Till	**Na > Al > K > Si > Ca > Fe > Mg**
Basalt	**Ca > Mg > Na > K > Si > Al > Fe > Ti**
Granite	**Ca > Na > Mg > Fe > K > Si > Al > Ti**
Gabbro	**Ca > Mg > Fe > Si = Al = Na > Ti > K**
Based on SP	**Na > K > Ca > Mg > Si > Al > Fe > Ti**

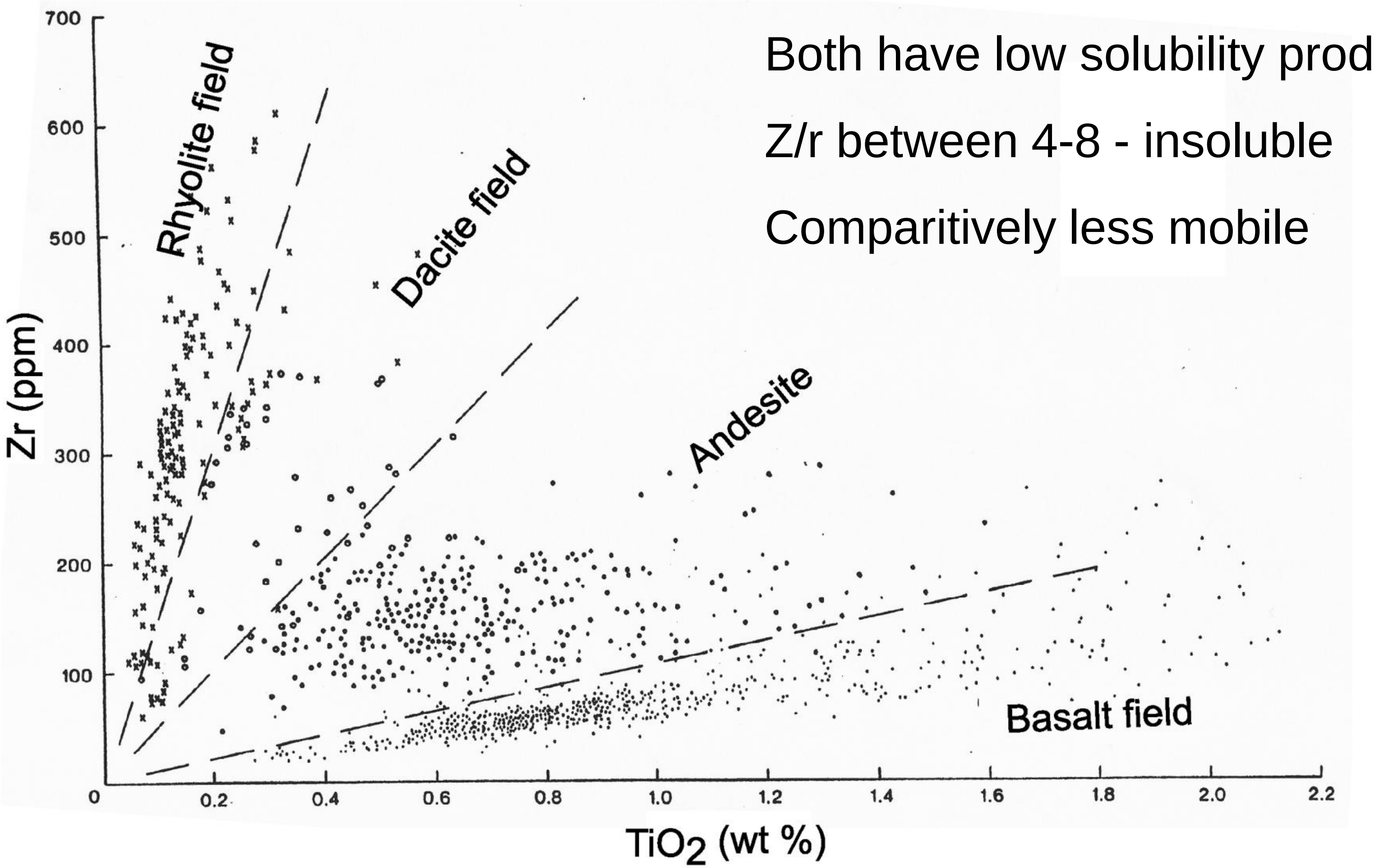
The rock discrimination plot (Hallberg plot)

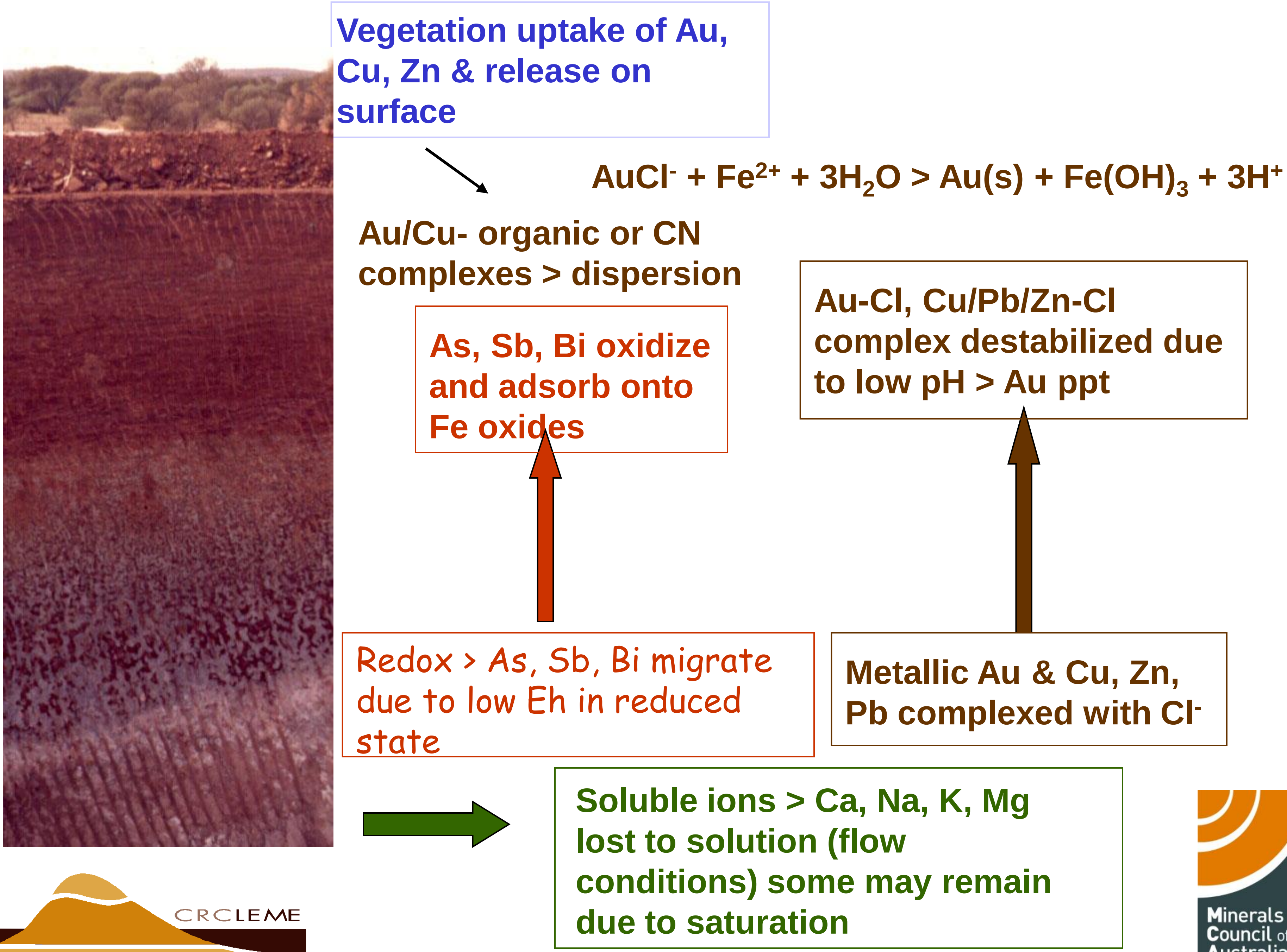
Zr and Ti in stable primary minerals

Both have low solubility products

Z/r between 4-8 - insoluble

Comparitively less mobile





Vegetation uptake of Au, Cu, Zn & release on surface

$AuCl^- + Fe^{2+} + 3H_2O > Au(s) + Fe(OH)_3 + 3H^+$

Au/Cu- organic or CN complexes > dispersion

As, Sb, Bi oxidize and adsorb onto Fe oxides

Au-Cl, Cu/Pb/Zn-Cl complex destabilized due to low pH > Au ppt

Redox > As, Sb, Bi migrate due to low Eh in reduced state

Metallic Au & Cu, Zn, Pb complexed with Cl^-

Soluble ions > Ca, Na, K, Mg lost to solution (flow conditions) some may remain due to saturation

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Landscape scale mobility (absolute accumulation)

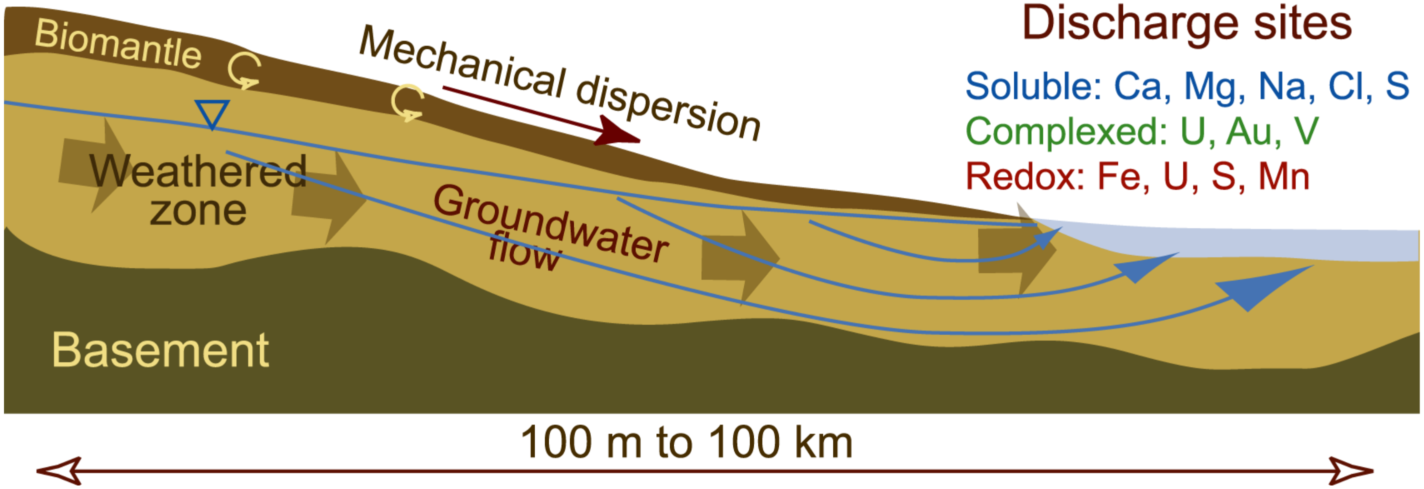
- Mechanical dispersion downslope – aggregate, biomantle & landform controlled
  - Quartz (Si), Ferruginous (Fe), aluminious (Al) and siliceous (Si) particles (lag) transport
  - Fe particle aggregates likely to transfer trace metals (adsorbed)
- Solute transport via groundwater to discharge sites – flow zones and climatic controls
  - Ca, Mg, Ba, S, Cl, Fe, Si, U, V dispersion to lower sites
  - Solutes either removed via rivers or accumulated as crusts or precipitates

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



Discharge sites

Soluble: Ca, Mg, Na, Cl, S

Complexed: U, Au, V

Redox: Fe, U, S, Mn

Valley Calcretes – U and V deposits

Ca, U, V influx via groundwater from large area into smaller area of paleo-valleys

Images: C Butt

Geochemical Analysis Techniques

- **XRF and INNA** – dry powder methods
- **Micro-XRF** – synchrotron based – great for quantitative micron sized chemical maps
- **AAS, ICP-MS, ICP-AES** – wet methods – need sample dissolution with reagents (generally acids)
- **Electron microprobe (EDXA)** – micron sized quantitative major element analysis
- **Laser ablation ICPMS** – micron sized quantitative trace metal analysis
- **SHRIMP** and **TIMS** – high resolution isotopic analysis

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