

# Bioavailability of Elements

## Part I Earth 281

Main reference: Chapter 15 from Selinus O., Alloway B., Centeno J.A., Finkelman R.B, Fuge R., Lindh U., and Smedley P., 2013. *Essentials Of Medical Geology: Impacts Of The Natural Environment On Public Health* revised edition. p.805. Academic Press.

# Bioavailability of Elements in Soil

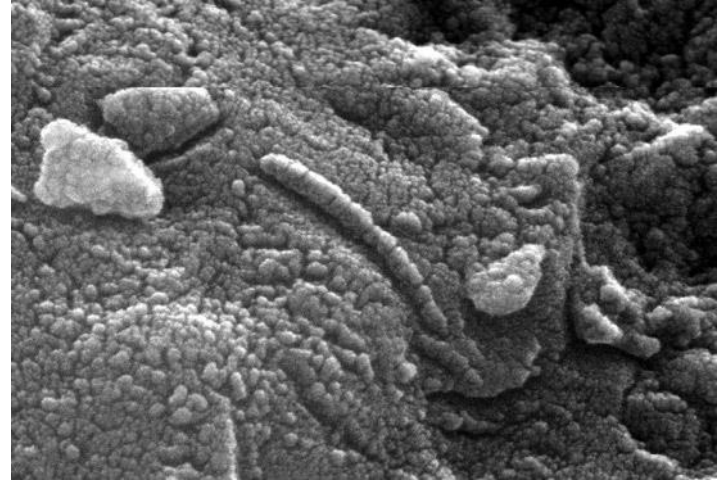
- In the study of medical geology, the rock-soil-plant/animal-human pathway is of major importance.
- The uptake of trace elements will depend mainly on plants physiology as well as soil geochemical properties.

# Soil formation

- Soil formation is closely linked to mechanical and chemical weathering of rock-forming minerals but can also includes biological/biochemical processes associated with plants, microorganisms and soil fauna eg. Worms or burrowing animals.

# Soil Formation

<http://www.delivery.superstock.com/>



<http://www.dvice.com/>



[www.goodwp.com](http://www.goodwp.com)

[worms4africa.co.za](http://worms4africa.co.za)

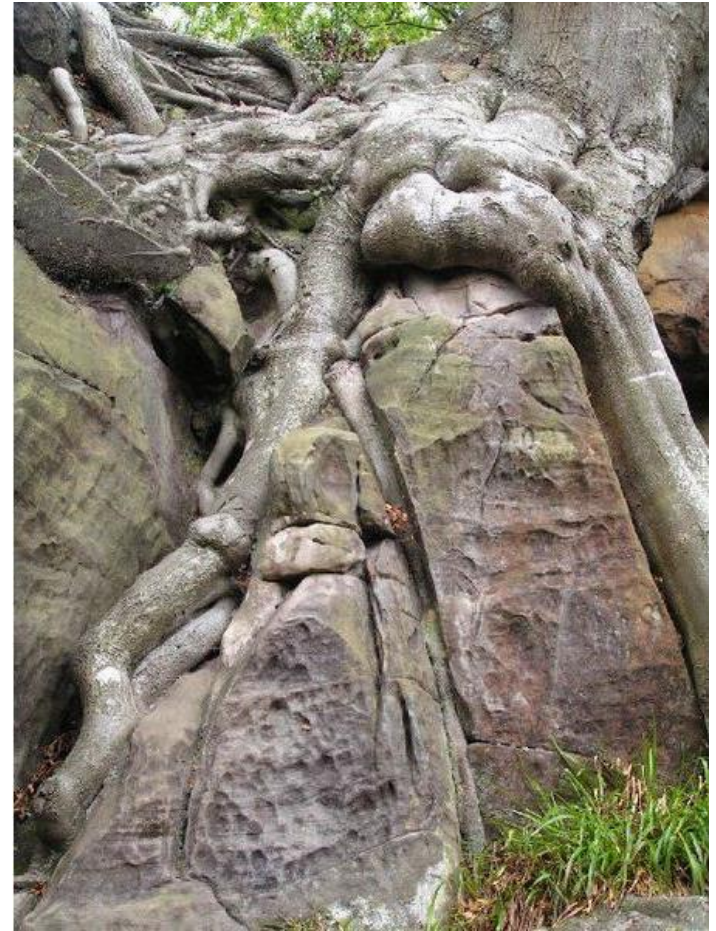


# Weathering

## Physical weathering

- splitting of rock material by frost, roots

### Gneiss Boulder Fractured by Frost Action



<http://img.bhs4.com/>

# Weathering

## Physical weathering

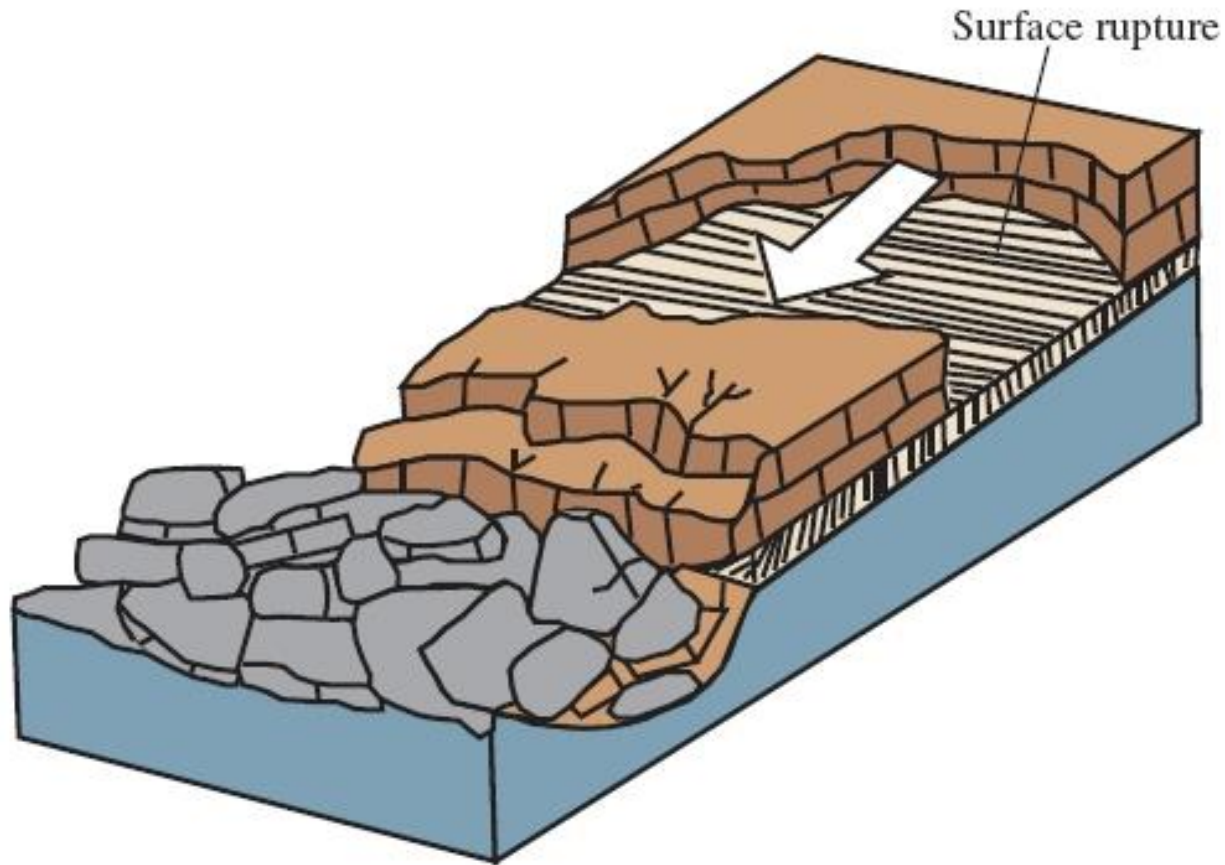
- comminution of and abrasion of rocks and mineral fragments during transport. Wave rock Australia



[facstaff.gpc.edu](http://facstaff.gpc.edu)



# Different types of physical weathering



Slide-block

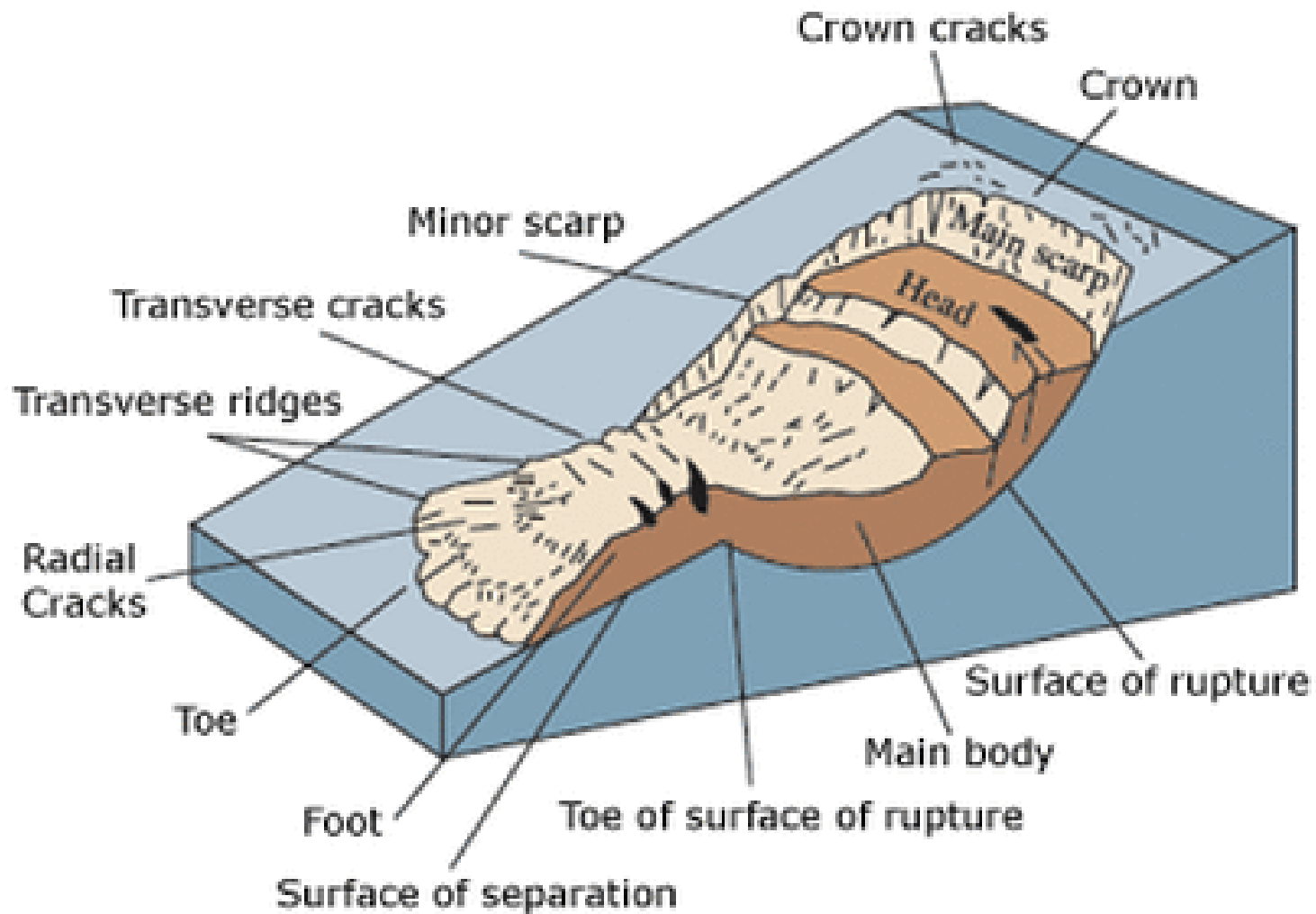


<https://www.bgs.ac.uk/landslides/burtonBradstock.html>

# Rock Fall

## Burton Bradstock in Dorset, UK





## Slump



<http://oaklandgeology.files.wordpress.com/2008/11/treecreep.jpg>







<http://stewart.sswiki.com/Chapter+12>

# Chemical Weathering Process



Rust\_from\_bathtub\_in\_Kyiv.jpg (1024×768)

1. Oxidation
2. Reduction
3. Hydration



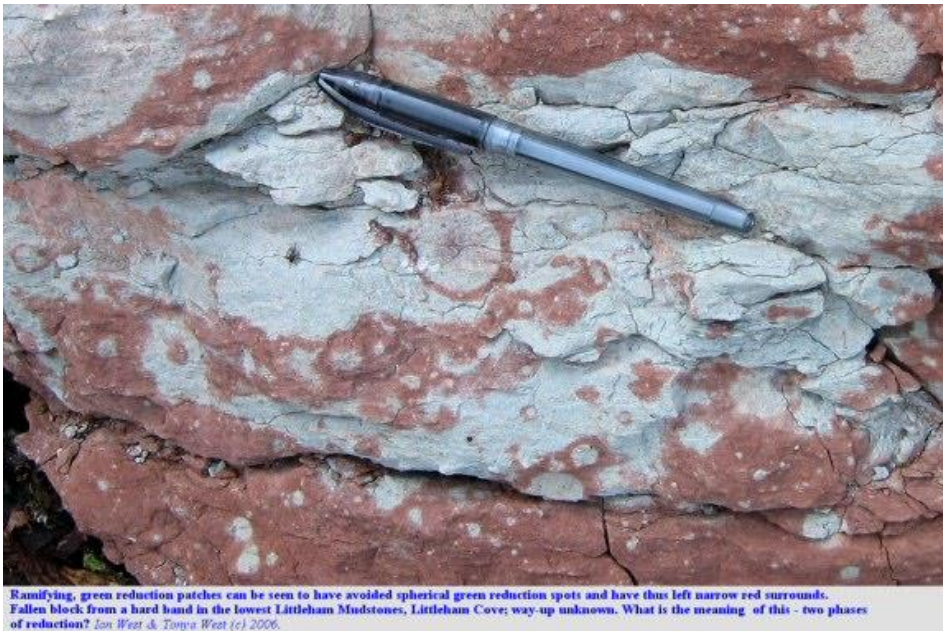
# Oxidation



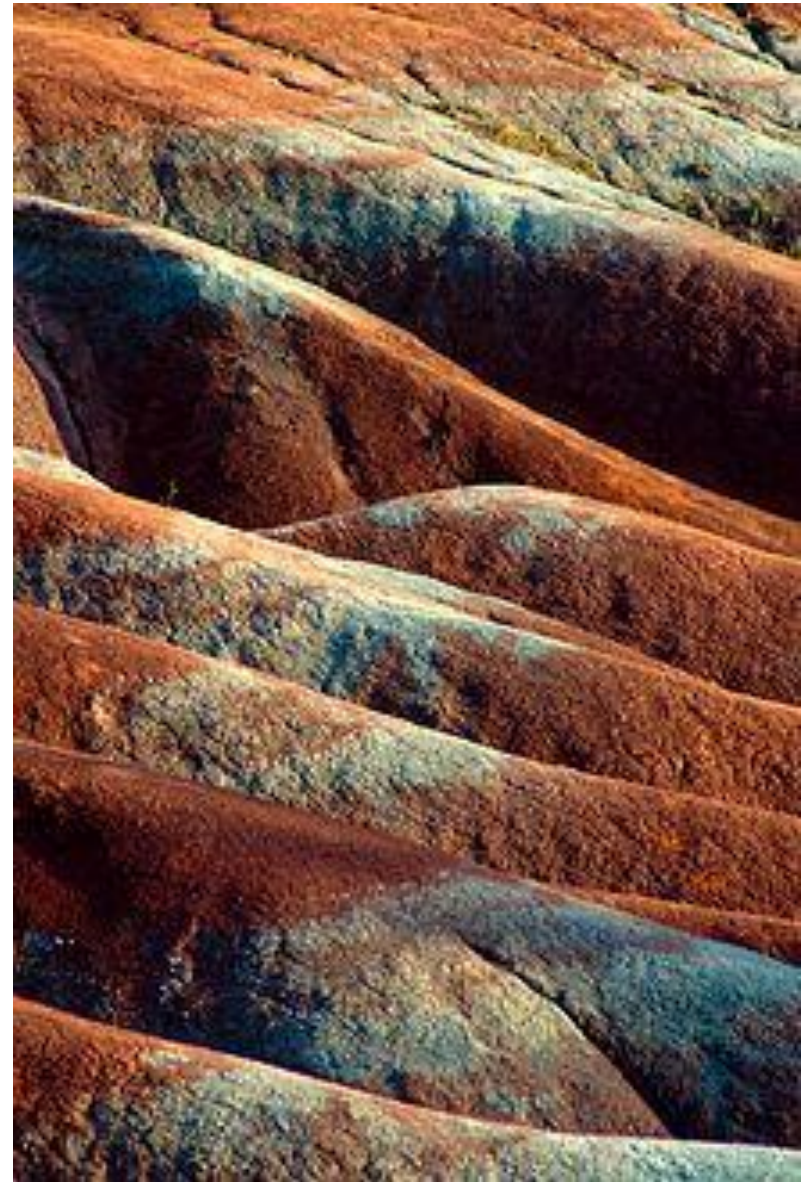
**Weathering rind in granite produced primarily by oxidation.**



# Reduction



<http://www.southampton.ac.uk/~imw/Budleigh-Salterton.htm>



Cheltenham\_Badlands\_closeup.jpg

Cheltenham Badlands, Ontario

Typical outcrop of the formation is exposed at Bronte Creek just south of the Queen Elizabeth Way

# Hydration

- Hydration refers to the absorption of water. The  $H^+$  and  $OH^-$  ions of water incorporate themselves into the atomic structure of a mineral to form a new version of it called a hydrate. If the original mineral had a chemical formula of  $X$ , the new suite of minerals will have chemical formulas of  $X \cdot nH_2O$ .
- For example, anhydrite ( $CaSO_4$ ) exposed to water hydrates into gypsum ( $CaSO_4 \cdot 2H_2O$ ).



Gypsum crystals in the Giant Crystal Cave near Naica, Mexico

# Soil Weathering Ingredients

- First you need some Rock-Till-Soil
- Add Moisture
  - a.  $O_2 \rightarrow$  oxides Al O or Fe O
  - b.  $CO_2$  from atmosphere  $\rightarrow H_2CO_3$  (carbonic acid)  
or  $HCO_3^-$
  - c. Organic acids/compounds
  - d. Root respiration  $\rightarrow CO_2 \rightarrow H_2CO_3$



# Description of Soil Types

Soils can contain Horizons e.g. O, A, E, B, C and R

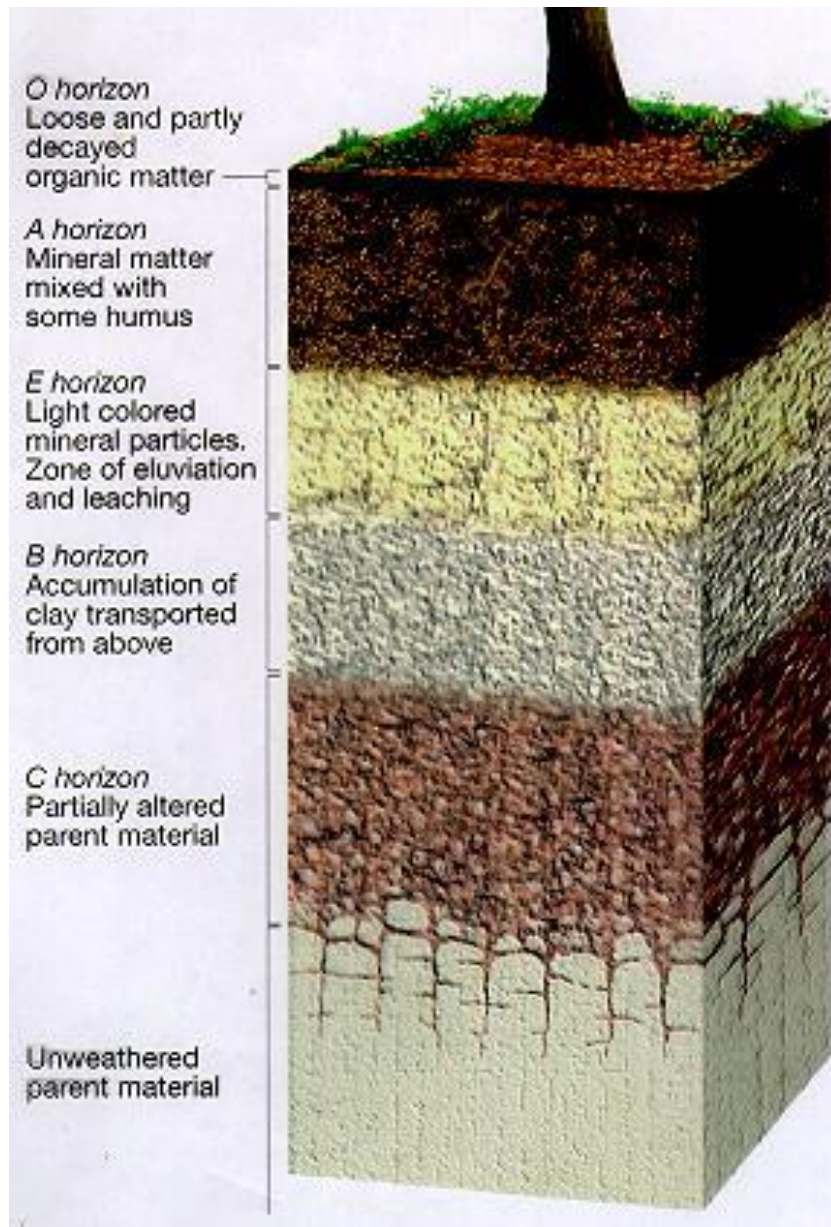
- Horizon O: mainly organic matter from decomposing plant/animal matter (dark C-N-P-S rich)

Humus – organic compounds; major reservoir of C, N, P, and S

- Horizon A: mixture of organic matter and mineral (dark – bioturbated and mixed by for eg. earthworms)

Rich in oxides Fe, Mn, and carbon

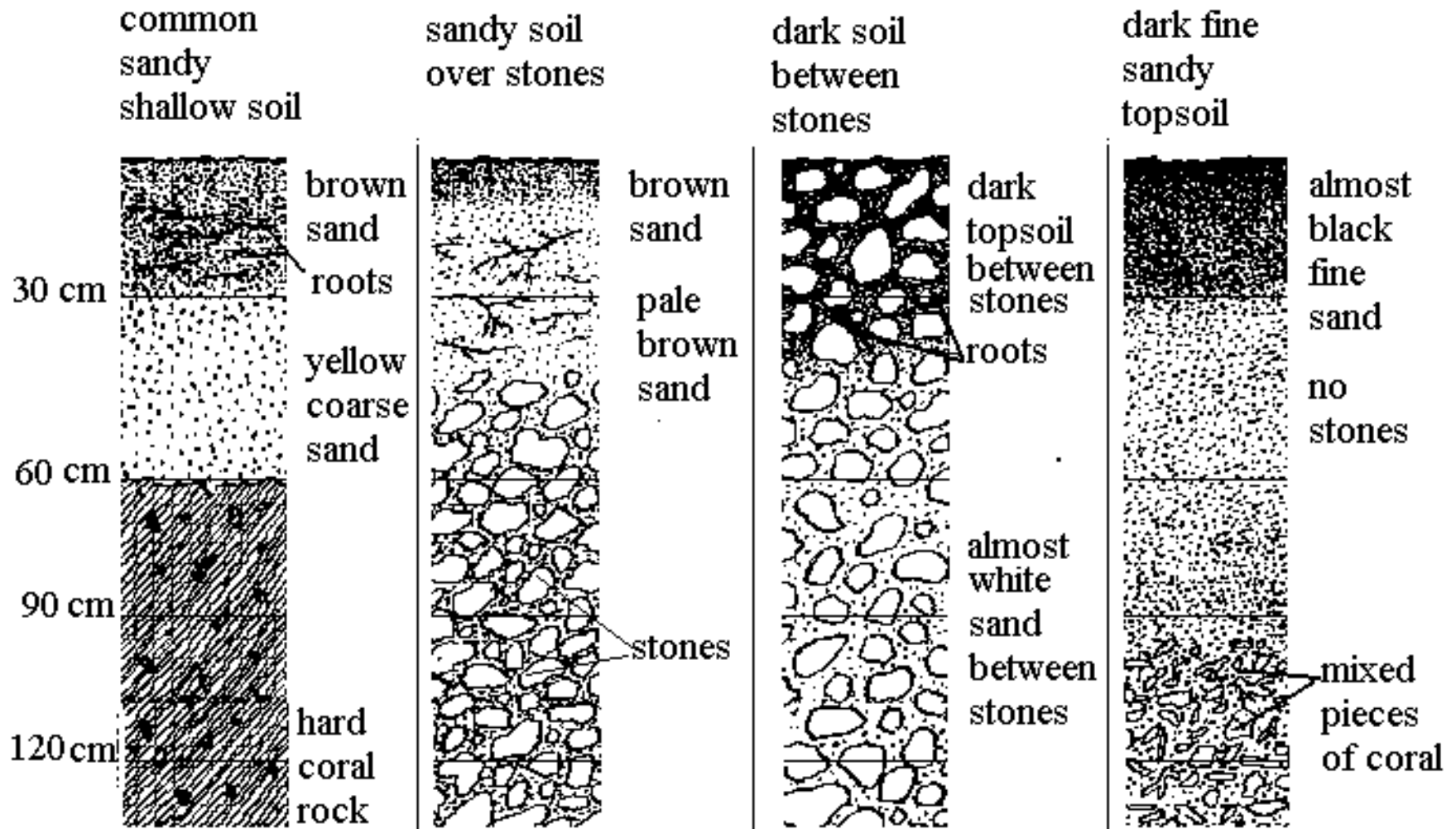
- Horizon E: Eluvial – lighter coloured and different textured soils
- Horizon C: Weathered rock
- Horizon R: Bedrock



A portrayal of the horizons within the profile of a typical forest soil (temperate Podsol)

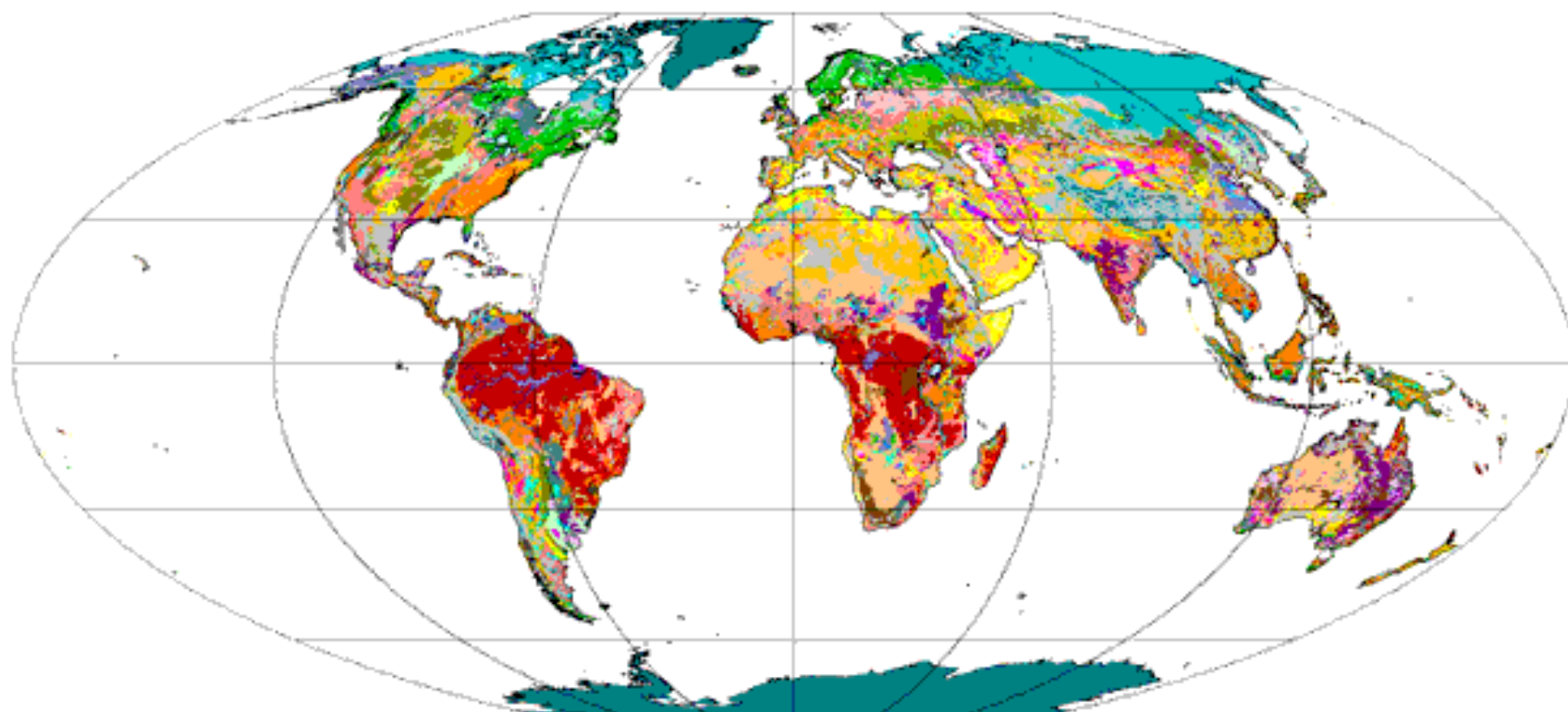
# Soil Horizons - typical profiles

## 6.26 Soil profiles





## DOMINANT SOILS OF THE WORLD

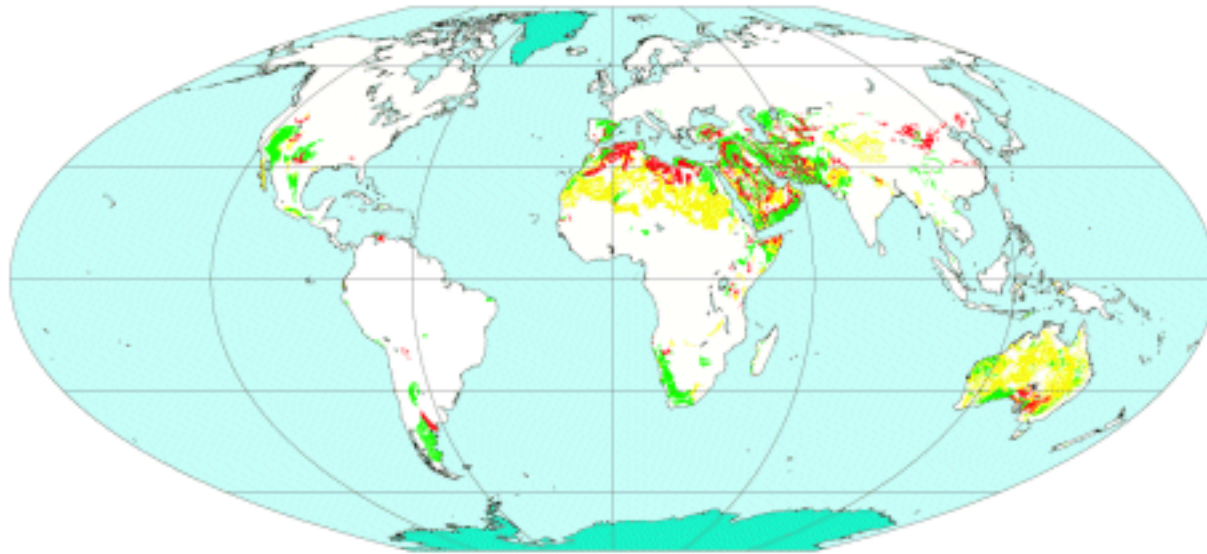


Flat Polar Quartic Projection

FAO-GIS, February 1998

# Two factors determining soil horizon appearance

- **Calcium carbonate** (calcimorphic soils):
  - Origin from weathered limestone (granite) or precipitation of calcite in pores of soil.
- **Waterlogging** (hydromorphic soils): creates anoxic condition, reduction of iron oxides the colour going from reddish colour to light brown, grayish and possibly bluish green
  - a) Grey, blue-green = reduction of iron oxides → Gley soil
  - b) Red, orange = oxidation → Podsol soil



**Dominant**

**Associated**

**Inclusions**

**Miscellaneous lands**  
(Inland waterbodies, Glaciers, No data)

Flat Polar Quartic Projection

FAO-GIS, February 1998

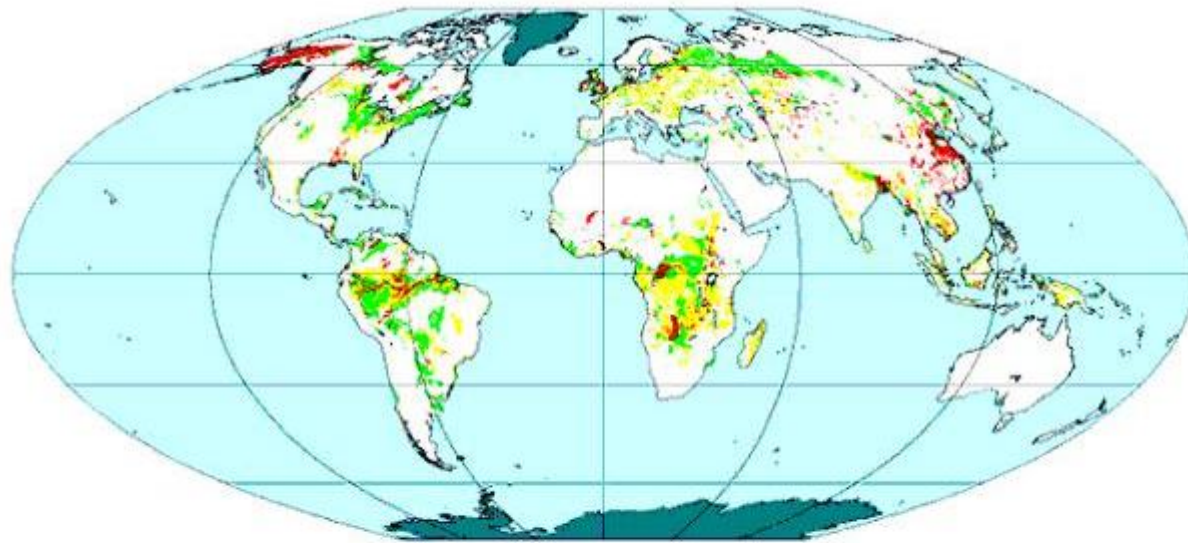
# Calcisols





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■ Dominant
 ■ Associated
 ■ Inclusions
 ■ Miscellaneous lands

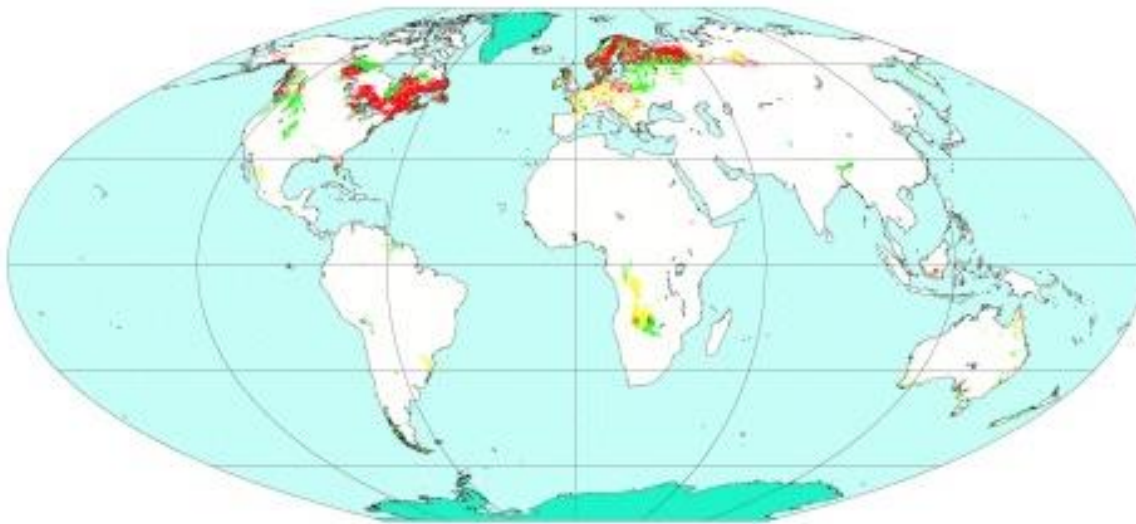
Flat Polar Quartic Projection

FAO-GIS, February 1998

# Gleysols



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



**Dominant**

**Associated**

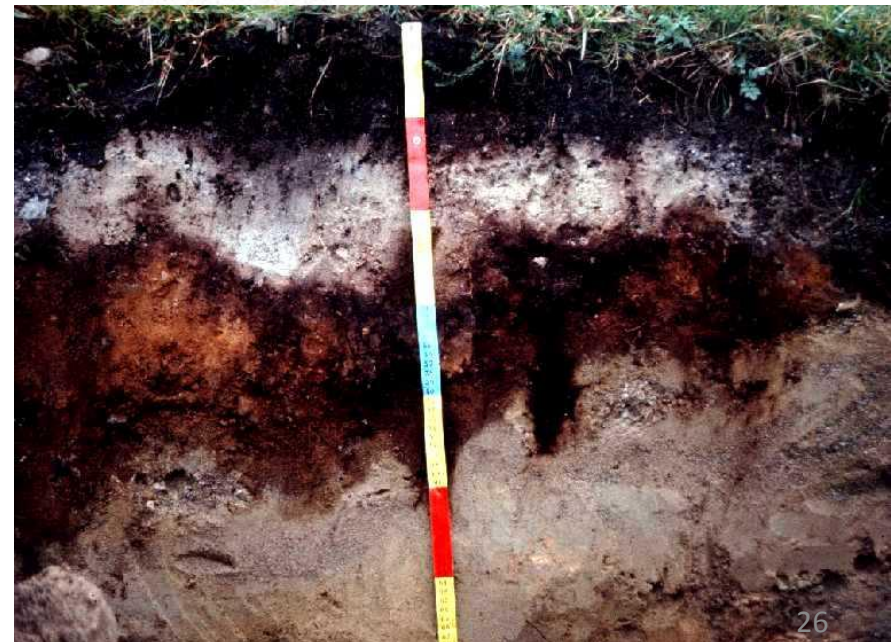
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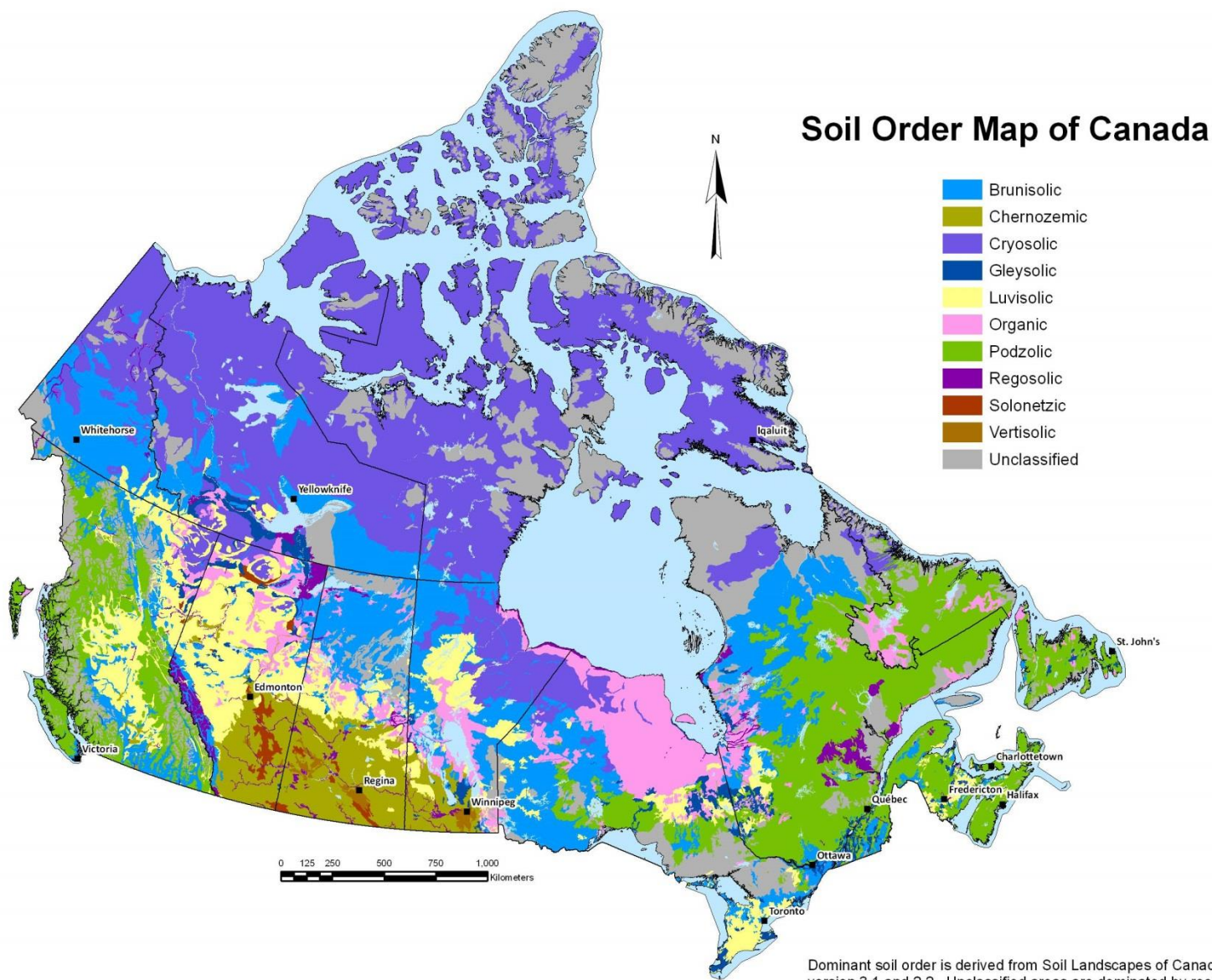
Flat Polar Quantic Projection

FAO-GIS, February 1996

# Podzols

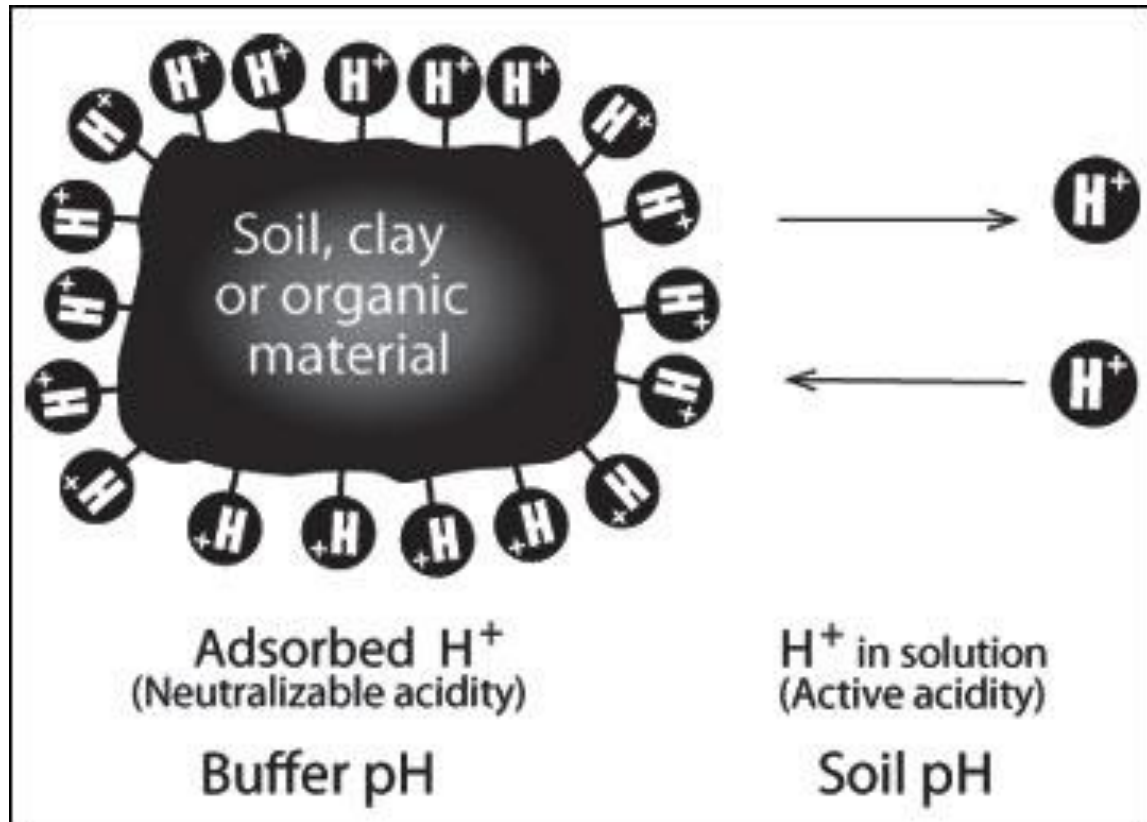






# Sorption

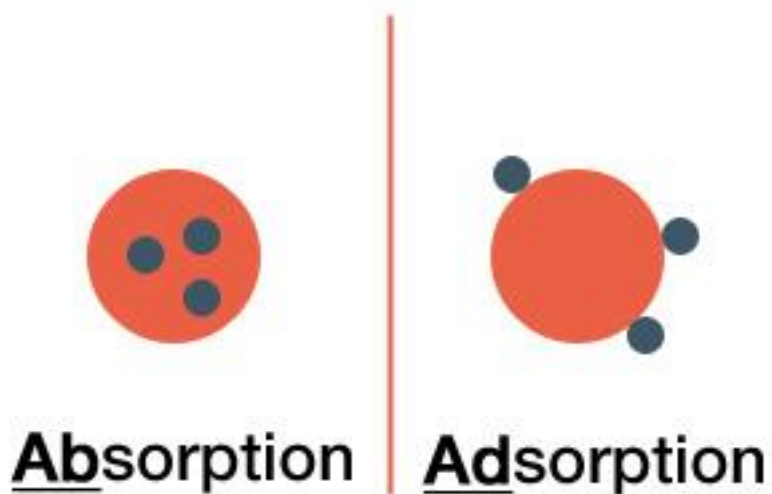
- The processes that determine the availability of elements, both naturally occurring and contamination.
- Processes that affect the 'sorption' of elements and their availability for plant uptake.



<http://extension.missouri.edu/p/MG4>

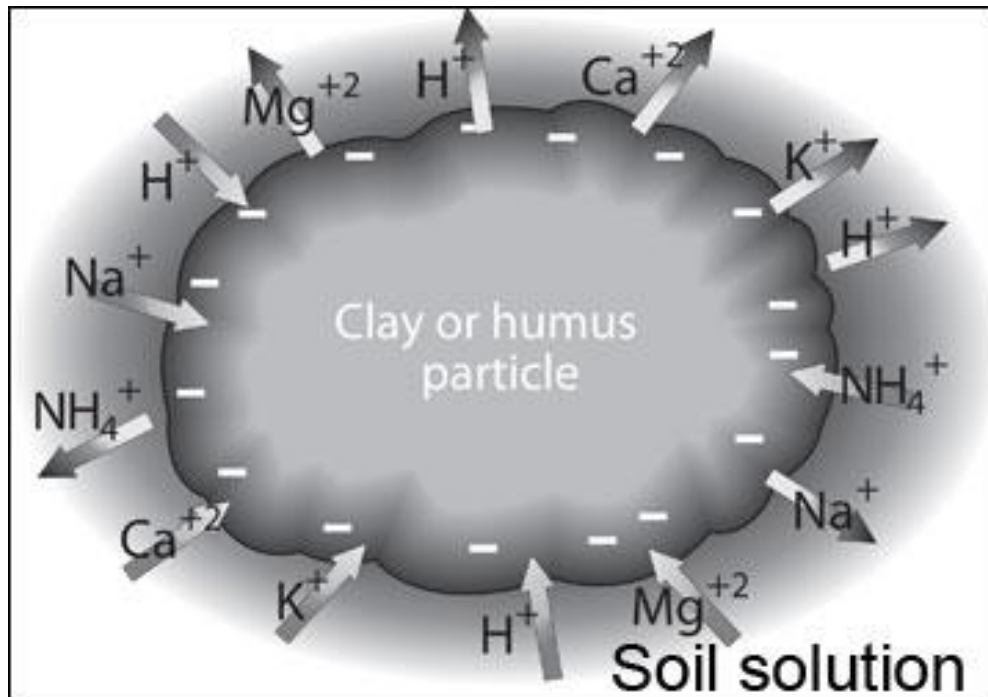
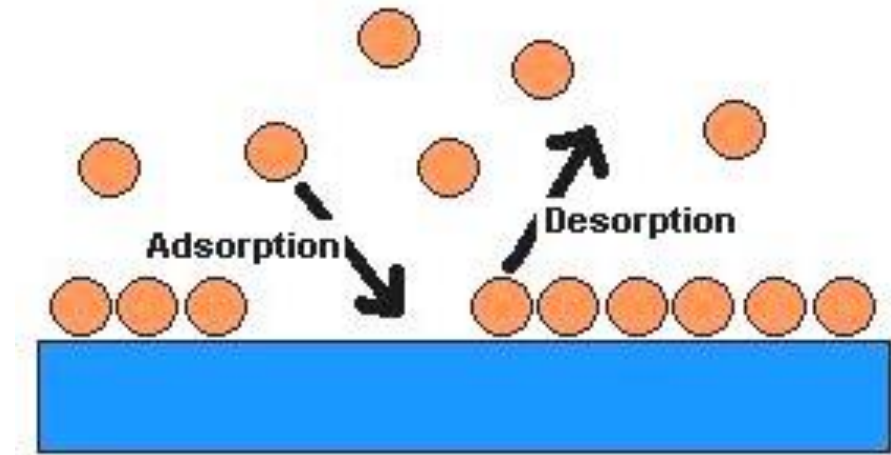
# Sorption Mechanisms

- Ionic exchange on mineral surface
- Co-precipitation
- Ligand exchange adsorption
- Insoluble precipitation
- Organic complexation





- Exchangeable nutrient cation adsorbed on the surface of soil particles and exists in equilibrium with cations in solution.



- Cations from soil particles replenish those taken up from the soil solution by plants creating a disequilibrium driven by a gradient.

# Factors affecting Desorption mechanisms of trace and major elements

- Speciation ( $\text{Fe}^{2+}$ ,  $\text{Fe}(\text{OH})_2^-$ ), and concentration of elements (gradients-chemical equilibrium)
- Composition of soil (clays, organic matter, iron, aluminum and manganese oxides)(CEC)
- Soil physical-chemical composition ( controls on pH, redox conditions, etc.)

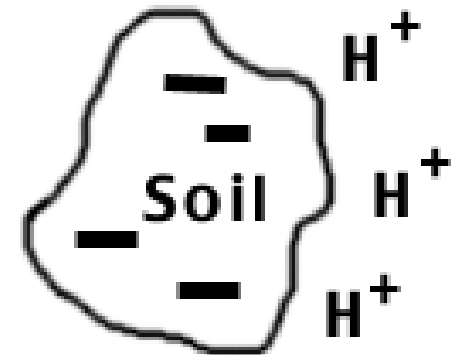
# Soil Chemical Properties

- pH
- Soil organic matter
- Chemically active mineral constituents
- Reducing/oxidizing (redox) conditions
- Adsorption and desorption of ions in soils



# pH

- Soil pH applies to the hydrogen ion ( $H^+$ ) concentration in the pore solutions.
- It is trying to maintain equilibrium with the dominantly negatively charged surfaces of particles.
- Soil pH in pore water range from 4 to 8; generally increases with depth
- $CO_2$  very important gas  
e.g. gain  $pCO_2$  low pH↓



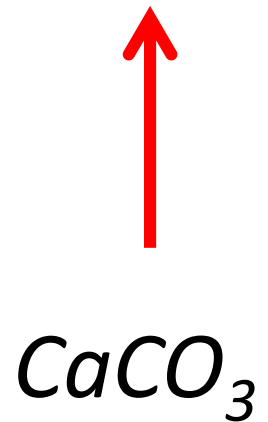
# pH

Soil pH controls behaviour of ions and many other processes in the soil

- Affected by reduction/oxidation (redox) conditions
  - e.g. Waterlogging which inhibits air penetration (CO<sub>2</sub>)
  - Reducing conditions (gleying) will increase pH
  - Oxidizing conditions will decrease pH
- Example: aerating your lawn will add atmospheric gases, lowering pH, which favours Metal (Me) mobility and availability to plant roots.
- Many plant foods pH↓ making Me's more available.

# Examples

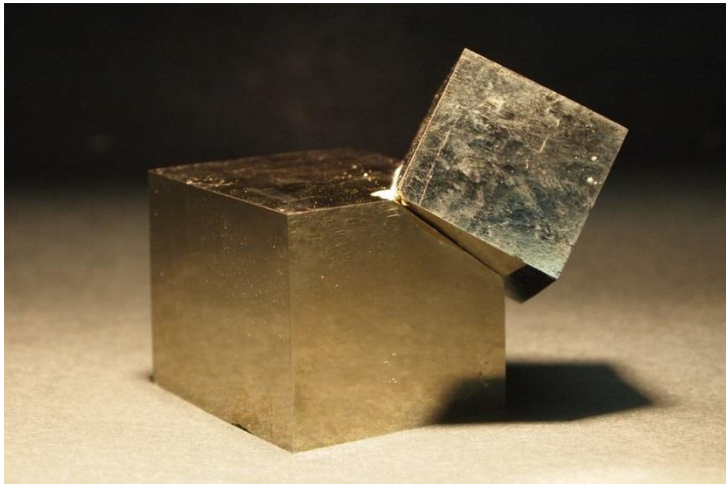
- Carbonates ( $\text{CaCO}_3$ ) can buffer pH change



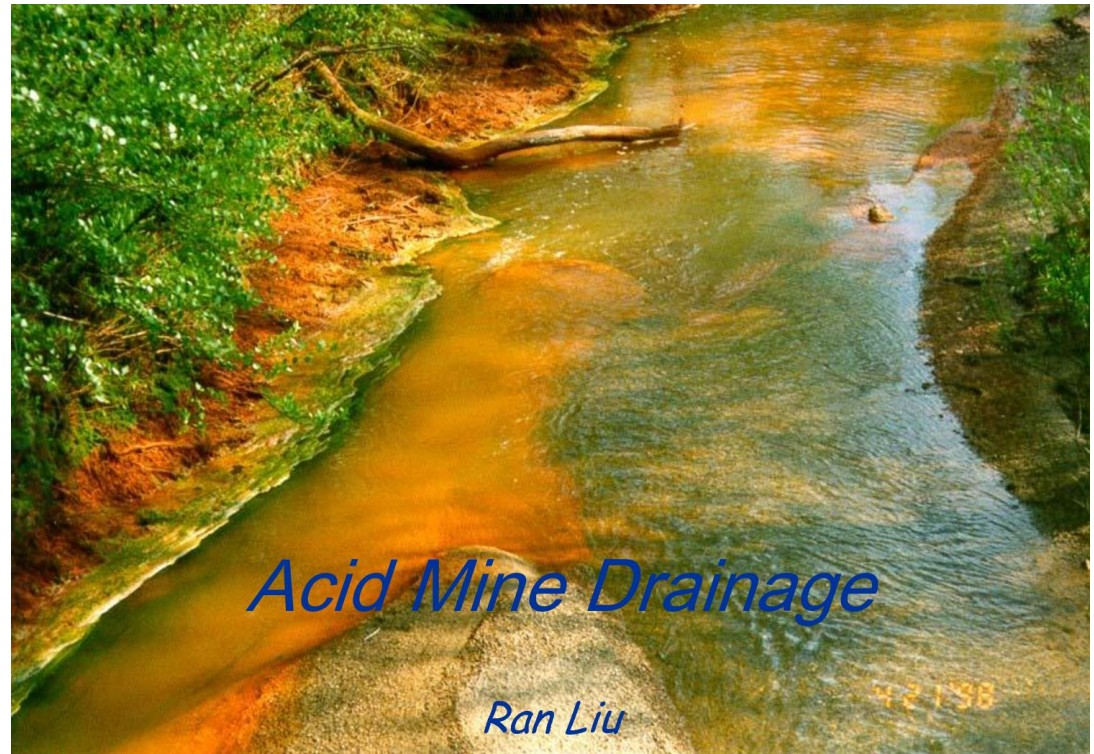


# Examples

- Pyrite ( $\text{FeS}_2$ ) oxidizes to  $\text{Fe}^{2+}$  and  $\text{SO}_4^{2-}$  to form sulphate ions and sulphuric acid causes a pH decrease.



[www.earthsciences.hku.hk](http://www.earthsciences.hku.hk)

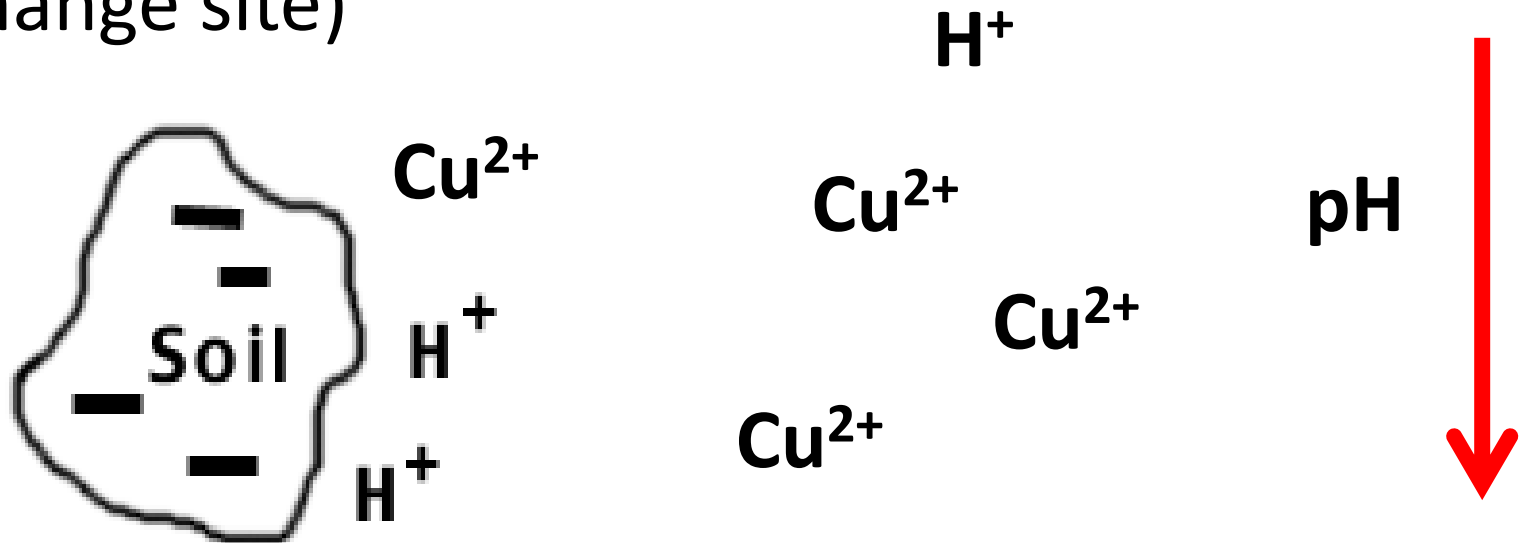


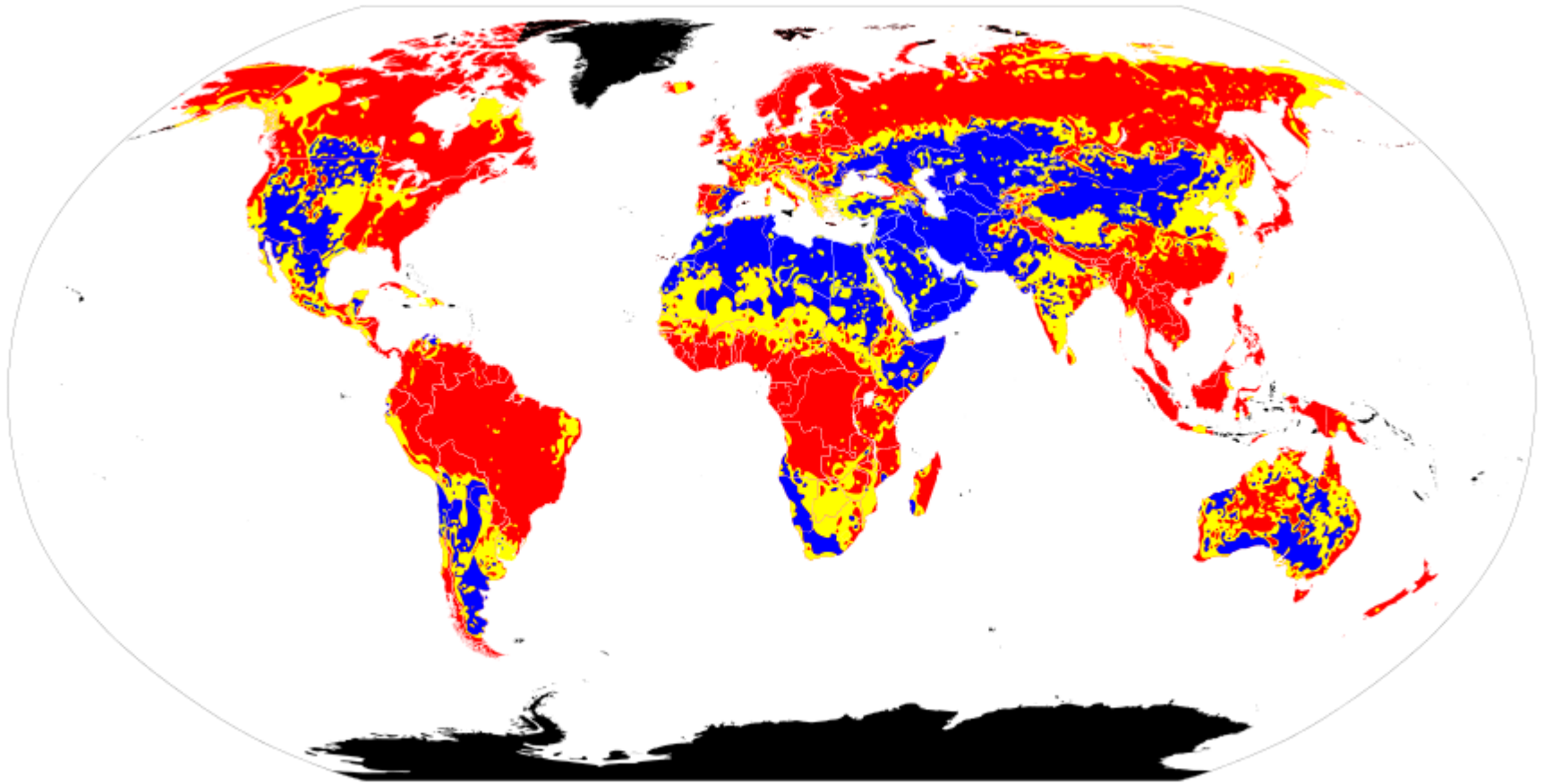
CarnegieMellon

ENGINEERING

# Examples

- Cationic divalent ( $\text{Cu}^{2+}$ ) elements are more mobile and more available in low pH because less strongly adsorbed on soil solids ( $\text{H}^+$  increases -- takes the place of cationic divalent elements on exchange site)





## **Global variation in soil pH.**

Red is acidic soil. Yellow is neutral soil.

Blue is alkaline soil. Black is no data.



# Soil Organic Matter

*Soil (living), Regolith (decomposed rock)*

- Soils contain living organisms, organic debris and humus.
- All soils contain organic carbon though the content varies widely.  
e.g.: Intensively cultivated soil <1%; grasslands 10%; poorly drained gleying sites 70%; Hot and dry environments (low).

# Soil Organic Matter

*Soil (living), Regolith (decomposed rock)*

- Soil organic matter is the main reservoir for carbon, nitrogen, phosphorus, and sulphur in soils. (see Carbon, Nitrogen cycles, Bioavailability Lecture Part II)
- It can be divided into two component: humic and non-humic substances.
  - Non-humic – unaltered biochemicals: amino-acid, carbohydrates, organic acids, lignin, lipids, and waxes
  - Humic – formed in secondary synthesis reactions – acidic yellow/black, poly electrolytes of high molecular weight



<http://bit.ly/M1HUJuv>



**Table 15.1** Summarized values for pH and organic carbon in soils in England and Wales, Northern Europe (Baltic area), and the United States

Country	Number of samples	Minimum	Median	Maximum
England and Wales <sup>a</sup>				
pH (water)	5,679	3.1	6.0	9.2
Organic C (%)	5,666	0.1	3.6	65.9
Baltic area <sup>b</sup>				
pH (water)	774	3.7	6.1	8.7
Organic C (%)	774	1.8	7.1	97.2
United States <sup>c</sup>				
pH (water)	3,045	3.9	6.1	8.9
Organic C (%)	3,045	0.09	1.05	63.0

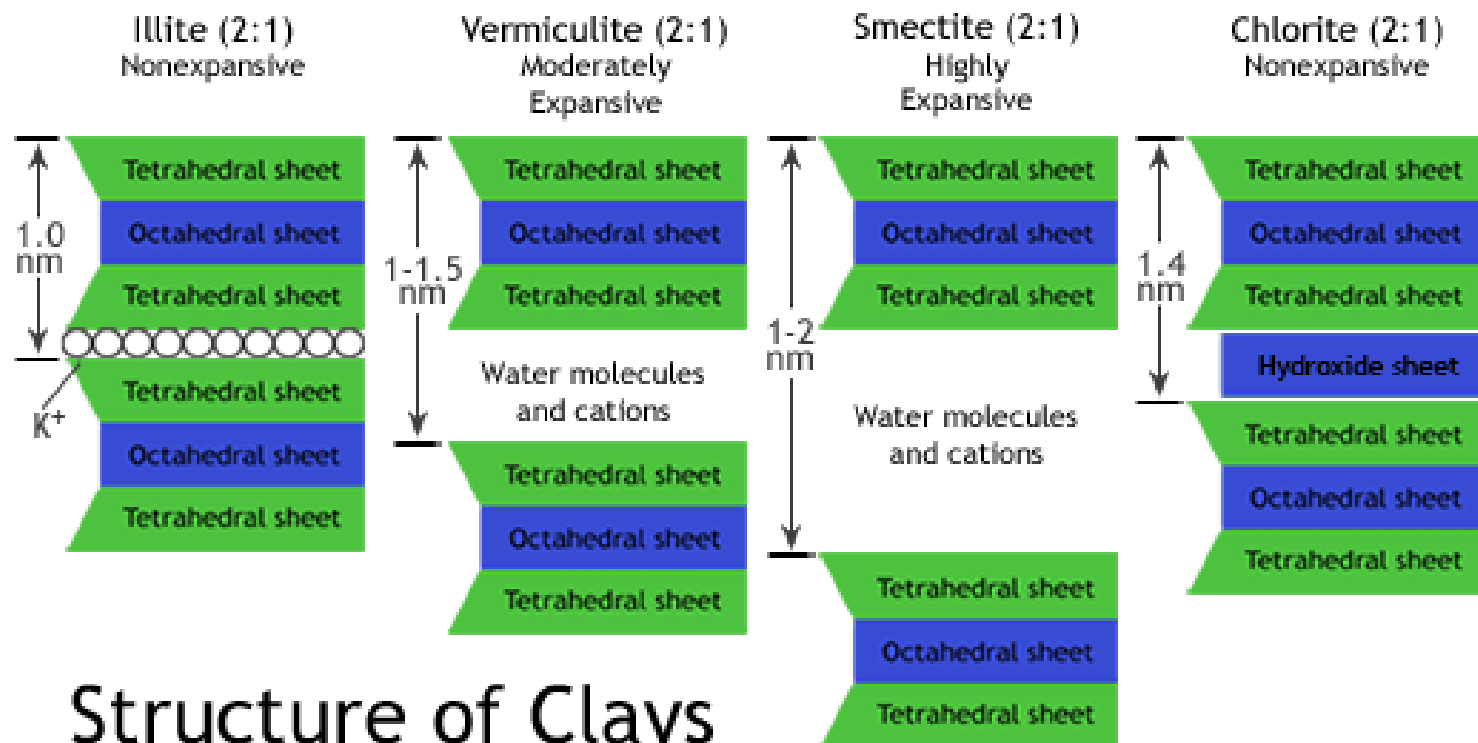
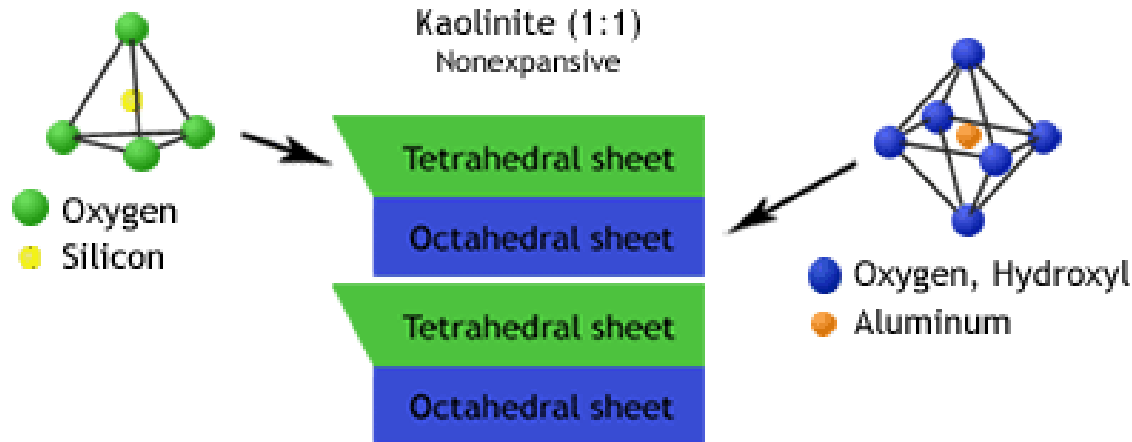
<sup>a</sup>Soils collected on 5 × 5 km grid (From McGrath and Loveland 1992)

<sup>b</sup>Soils collected on a 2,500-km grid over an area of 1,800,000 km<sup>2</sup> from 10 European countries surrounding the Baltic Sea (From Reimann et al. 2000)

<sup>c</sup>Soils from sites with healthy crops remote from obvious contamination (Holmgren et al. 1993)

# Chemically Active Mineral Constituents

- Clay mineral
  - Large surface area
  - Negatively charged on their surface (adsorption of cations)
- The structure creates a permanent charge imbalance – Net negative charge



# Structure of Clays

Created by Josh Lory for [www.soilsurvey.org](http://www.soilsurvey.org)

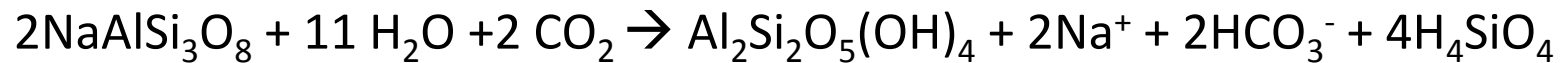
# Chemically Active Mineral Constituents

Clays form from weathering of “plutonic” –  
magmatic or crustal minerals

Feldspar (albite)

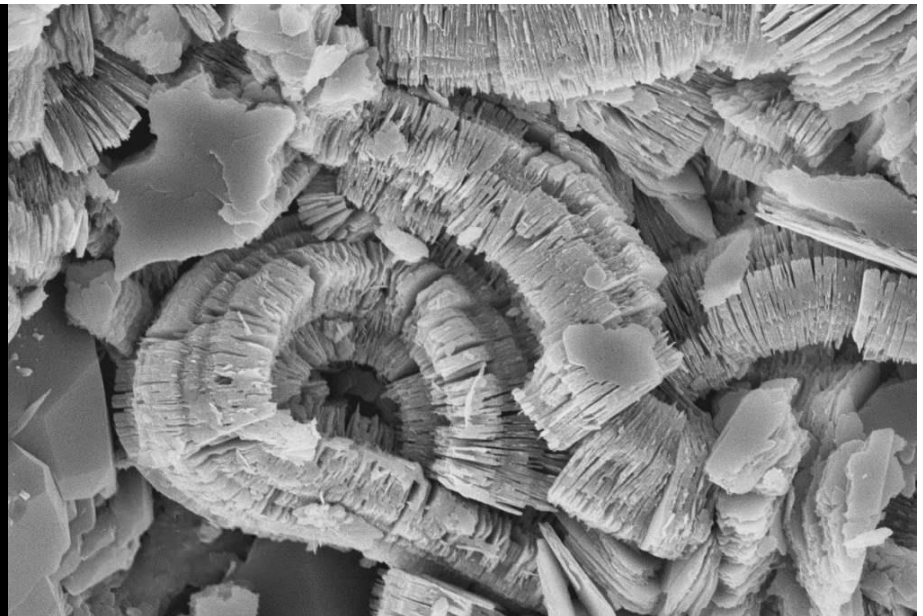
Kaolinite Silicic

Acid (weak acid)



<http://mindatnh.org/Kaolinite%20Gallery.html>

Kaolinite



<http://originoflife.net/micrographs/>

Kaolinite micrograph<sup>45</sup>



# Chemically Active Mineral Constituents

- Clays have other uses than in biochemical reactions. For example:
  - Pottery, fine china, ceramics of all kinds
  - Filters
- Oxides of iron, manganese, and aluminum
  - Colour of soils: brown (degree depends on iron content/dehydration)
  - Mobile depending on waterlogging conditions (redox conditions)

# Chemically Active Mineral Constituents

e.g.: Hydrated forms (water rich/wet season)



- Goethite (soil “rusty” iron) and Lepidocrocite (limonite → rust) are Polymorphs (same formula different crystal state)



- Dehydration leads to stability
- Old soils e.g.: tropical areas  
Old Fe oxides and Al dominate  
→ Bauxite deposits – iron regoliths
- Nutrients: young ferri soils scavenge other compounds e.g. like phosphate ( $\text{HPO}_4^{2-}$ ) and Arsenates ( $\text{AsO}_4^{3-}$ ) and releases them easily (good and bad from a health point of view –As lecture)

# Chemically Active Mineral Constituents

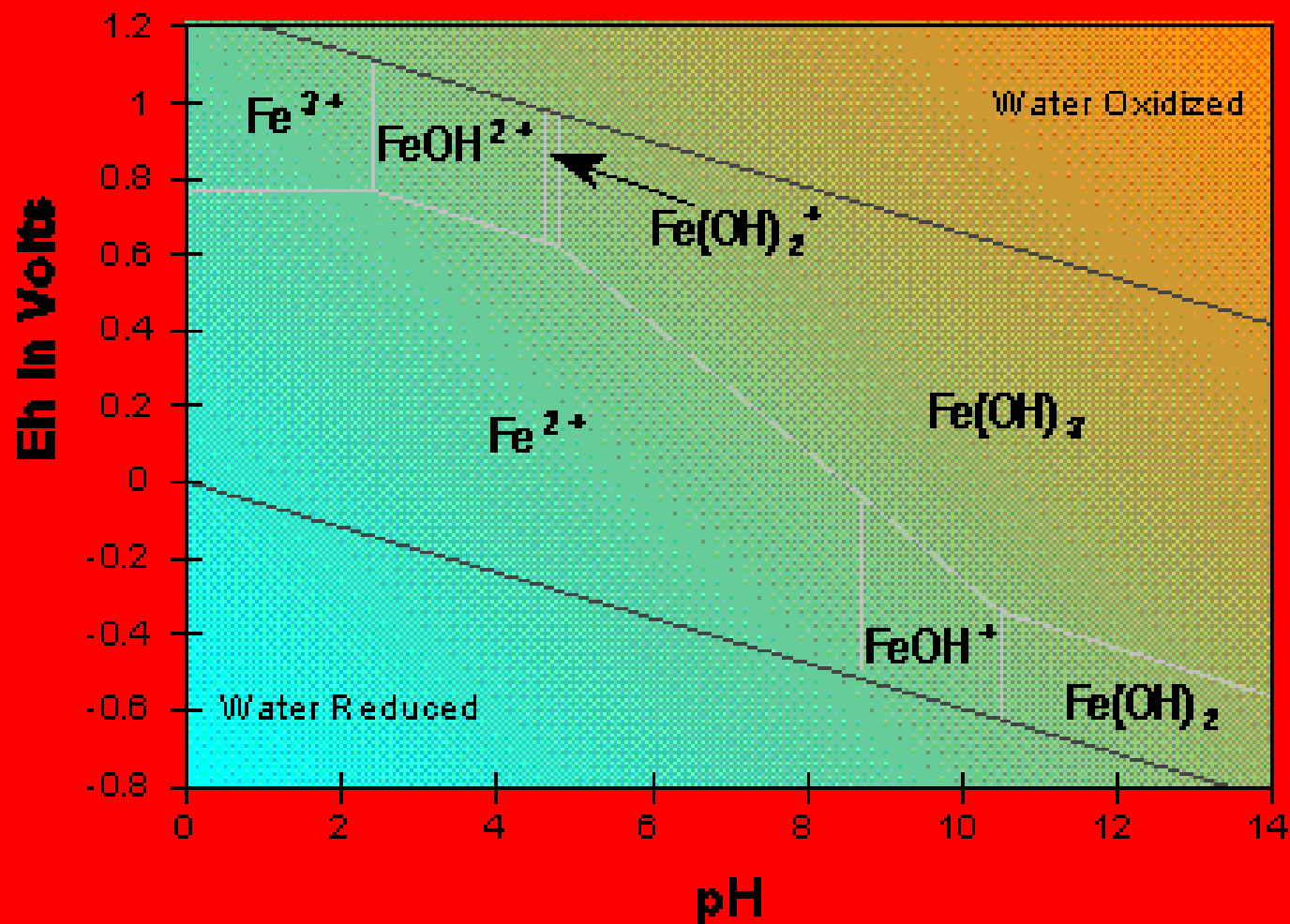
- Iron and Manganese (big controllers of other elements) Depends on pH:
  - Charge is negative under neutral and alkaline pH
  - Charge is positive under acidic pH
- Acid: iron is a big absorber of  $\text{PO}_4^-$  As

# REDOX Conditions

- Oxidized species vs reduced species (+ Eh vs – Eh)
- Redox controls, along with pH, the availability of most TRANSITION or trace metals (middle of the periodic table).
  - a) Gleyed soils more reduced → bioavailable metals; those normally sorbed to iron-manganese can be desorbed (change in valence as electrons become available or not)
  - b) Oxidic soils (red); less mobility – here pH may dominate and sulphides become important especially if cyclic (periods of wet and dry) Result: the metals are less available.



## Eh/pH Conditions and Iron Speciation



**Figure 3.** Iron Speciation as Controlled by Eh/pH Conditions

# Cation Exchange Capacity

Several definitions:

- a) Number of positive charges (cations) a soil can hold.  
e.g. #H<sup>+</sup> ions needed to fill the holding sites per 100g of soil.
- b) In soil science and geology is often measured by (and hence defined as) uptake and release of ammonium ions (NH<sub>4</sub><sup>+</sup>) from 1M ammonium acetate solution at pH 7.0

# Cation Exchange Capacity

1. Positively charged ions – cations ( $\text{Ca}^{2+}$ ) attracted to negatively charged surfaces (clays or feroxides)  
pH  $\uparrow$  Fe vs. clays are favoured
2. Negatively charged ions – anions ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ) attracted to positively charged surfaces (ferrasols at low pH)
3. Table II and III – CEC and replacement (also Pauling)
  - a) Ranges from 3 to 60 centimoles of charge/kg
  - b) Organics – rise to 200

# Cation Exchange Capacity

Base Cations (Ca, Mg, K, Na)

The more of these that are available; the more ***acidity*** can be neutralized.

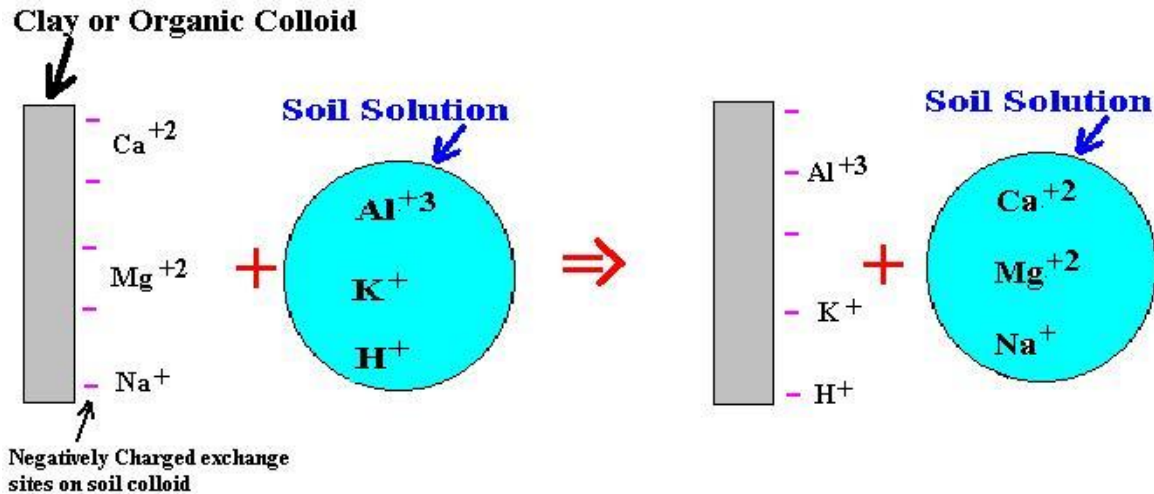
Example:

- high CEC ---add acid rain: result-- buffers or neutralizes
- lower the base → stays acidic (e.g. Amazon soils)



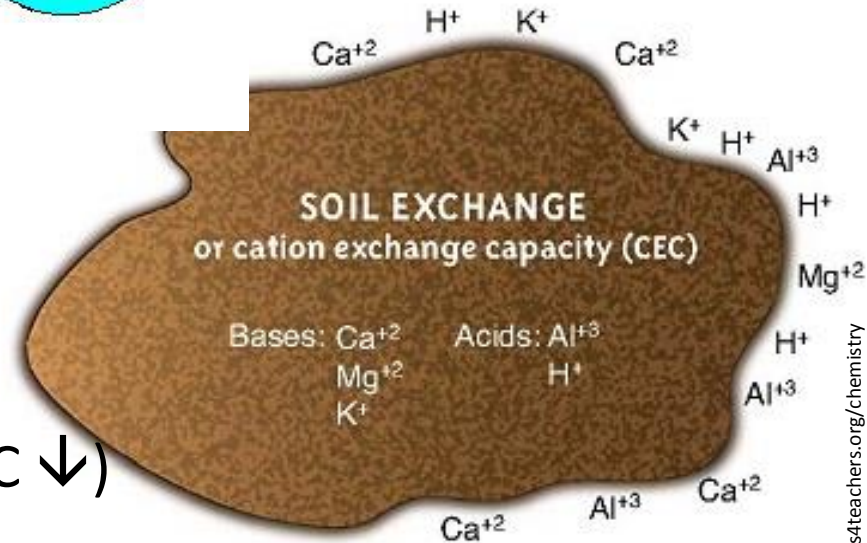
# Cation Exchange Capacity

## Cation Exchange Illustrated



## CEC & pH

- Add acidity pH ↓
- More  $\text{H}^{+}$  ions attach to colloids (CEC ↓)
- PUSH other ions into solution
- pH ↑ cations in solution decreases (CEC increases)



**Table 15.2** Typical cation exchange capacity values for soil constituents

Soil constituent	CEC ( $\text{cmols}_c\text{kg}^{-1}$ )
Soil organic matter	150–300
Kaolinite (clay)	2–5
Illite (clay)	15–40
Montmorillonite (clay)	80–100
Vermiculite (clay)	150
Hydrous oxides of iron, manganese and aluminum	4

From Ross (1989)

Selinus *et al.* 2013

**Table 15.3** Typical orders of replacement of trace element cations on various soil constituents

Soil constituent	Selectivity order	Ref.
Montmorillonite	Ca > Pb > Cu > Mg > Cd > Zn	Bittel and Miller (1974)
Illite	Pb > Cu > Zn > Ca > Cd > Mg	Bittel and Miller (1974)
Kaolinite	Pb > Ca > Cu > Mg > Zn > Cd	Bittel and Miller (1974)
Smectite, vermiculite and kaolinite	Zn > Mn > Cd > Hg	Stuanes (1976)
(ferrihydrite)	Pb > Cu > Zn > Ni > Co > Sr > Mg	Kinniburgh et al. (1976)
Fe oxides- (hematite)	Pb > Cu > Zn > Co > Ni	MaKenzie (1980)
(goethite)	Cu > Pb > Zn > Co > Cd	Forbes et al. (1976)
Peat	Pb > Cu > Cd = Zn > Ca	Bunzl et al. (1976)
Fulvic acid	Fe <sup>3+</sup> > Cu > Zn > Mn > Ca > Mg	Murray and Lindler (1983)
Humic substances	Cu > Pb > Zn = Ni > Co > Cd > Mn > Ca > Mg	Tipping and Hurley (1992)

Selinus et al. 2013

**Table 15.5** Concentrations of selected trace and major elements in the lithosphere, agricultural soils, and food crops (mgkg<sup>-1</sup> dry matter)

Element	Content in lithosphere	Common range for agricultural soils	Selected average for soils	Typical range in food crops
Silver (Ag)	0.10	0.03–0.9	0.05	0.03–2.9
Arsenic (As)	5	<1–95	5.8	0.009–1.5
Barium (Ba)	430	19–2,368	500	1–198
Boron (B)	10	1–467	9.5–85	1.3–16
Calcium (Ca)	36,000	7,000–500,000	13,700	1,000–50,000
Cadmium (Cd)	0.2	0.01–2.5	0.06–1.1	0.13–0.28
Cobalt (Co)	40	0.1–70	7.9	8–100
Chromium (Cr)	200	1.4–1,300	54	0.013–4.2
Copper (Cu)	70	1–205	13–24	1–10
Fluorine (F)	625	10–1,360	329	0.2–28.3
Iron (Fe)	51,000	5,000–50,000	38,000	25–130
Mercury (Hg)	0.1	0.05–0.3	0.03	0.0026–0.086
Iodine (I)	0.3	0.1–10	2.8	0.005–10.4
Potassium (K)	26,000	400–30,000	8,300	20,000–50,000
Magnesium (Mg)	21,000	20–10,000	5,000	1,500–3,500
Manganese (Mn)	900	270–525	437	15–133
Molybdenum (Mo)	2.3	0.013–17	1.8	0.07–1.75
Sodium (Na)	28,000	750–7,500	6,300	–
Nickel (Ni)	100	0.2–450	20	0.3–3.8
Phosphorus (P)	1,200	200–5,000	600	3,000–5,000
Lead (Pb)	16	3–189	32	0.05–3.0
Sulfur (S)	600	30–10,000	700	1,000–5,000
Selenium (Se)	0.09	0.005–3.5	0.33	0.001–18.0
Tin (Sn)	40	1–11	–	0.2–7.9
Titanium (Ti)	6,000	1,000–9,000	3,500	0.15–80
Vanadium (V)	150	18–115	58	0.5–280
Zinc (Zn)	80	17–125	64	1.2–73.0

Compiled from Lindsay (1979), Kabata-Pendias and Pendias (1992), Adriano (2001), and Marschner (1995)

Note: The typical plant concentrations for the macronutrients calcium, potassium, phosphorus, and sulfur are those for optimum growth and not the full range that may be actually found in crops around the world