



Economic Geology: Lecture Notes

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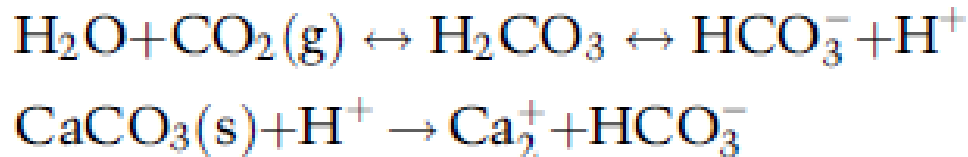
- Uranium infiltration mineralization
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Supergene Ore Formation Systems

Weathering of rocks and soil formation is the origin of many important ore deposits. Raw materials that are predominantly produced from **supergene (secondary) mineral deposits** include a diverse range of metals and minerals such as **copper, gold, aluminum, iron, manganese, gallium, niobium and kaolin**.

Chemical weathering is dominated by reactions between **minerals and rocks** with **meteoric water** containing **dissolved oxygen** and **carbon dioxide**. The **first reaction causes oxidation**, for example **Fe(II) to Fe(III)**, while **the second reaction induces moderate acidity**, especially after passage through **a humic soil horizon that multiplies CO₂ concentration in seepage water**.



Chemical weathering removes mobile cations (e.g. Ca²⁺, Na¹⁺, K¹⁺) relative to **stable residual components (Al³⁺, Ti⁴⁺)**.



pH and Eh are the main controls on reaction products between rocks and meteoric water. **Weathering rates are a function of climate**. **Highest rates occurred when high CO₂ is available in the atmosphere with consequent warm and humid climate**.

I. Principle of Supergene ore System

The principle of **supergene ore deposit** formation is the **concentration of some dilute** but valuable component of the primary rock. Two basically different process types may lead to **concentration**:

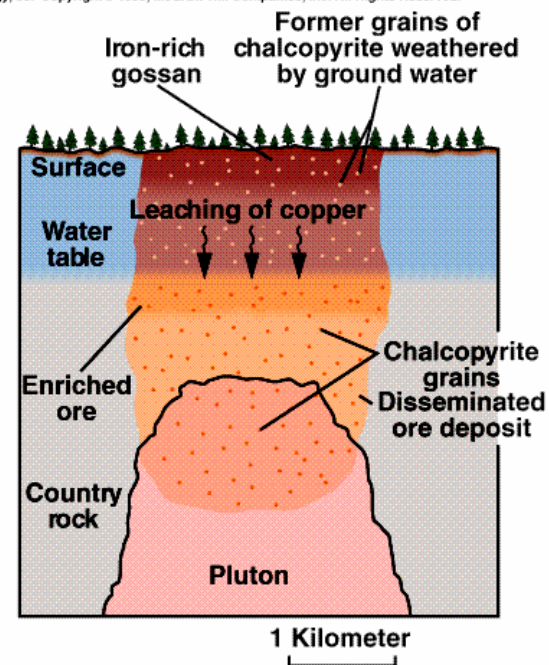
1. **The valued component is enriched in a residuum, while much of the rock mass is dissolved and carried away.**
2. **The valued component is dissolved, transported and concentrated on re-precipitation.**

In the latter case, the **transport distance is commonly very short (meters to tens of meters)**. Some ore deposits, however, originate after long-distance transport dissolved in surface and groundwater.

Examples of long-distance transport include **uranium in calcrete and in sandstone**, **iron in Tertiary river valleys of Western Australia** and **manganese in limestone karst caves**.

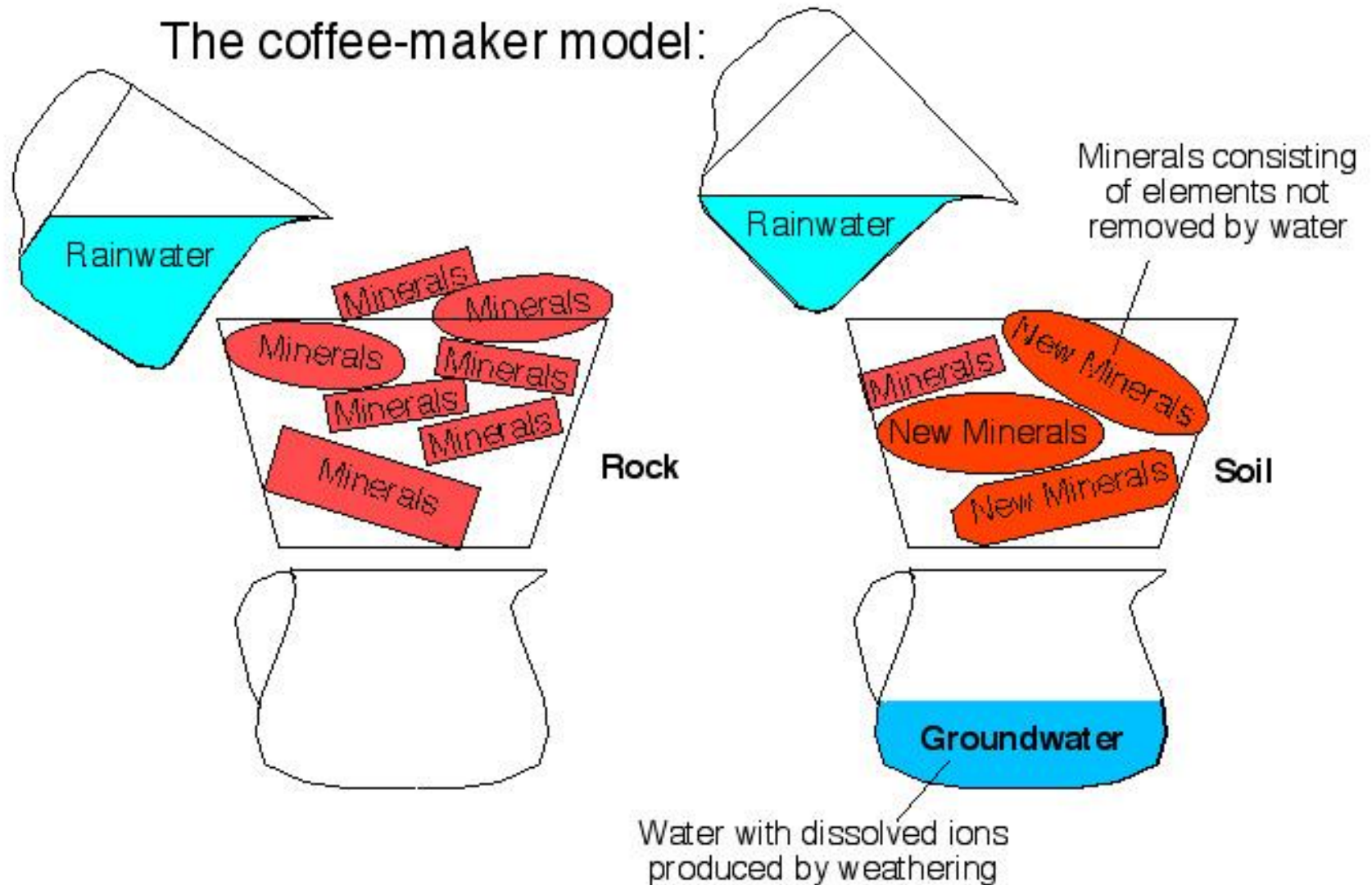
Supergene Enrichment

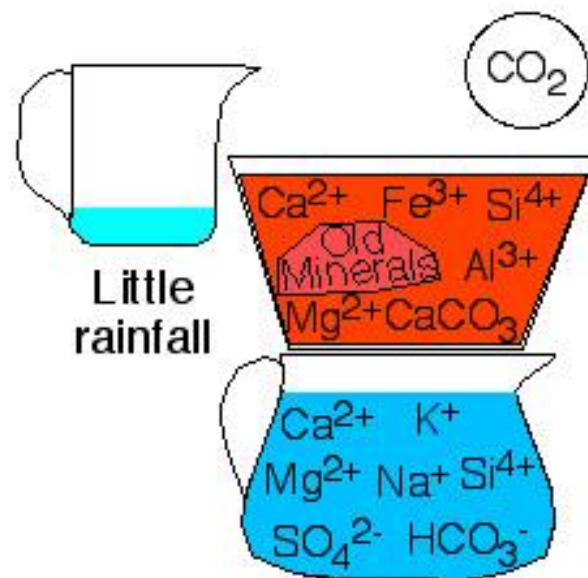
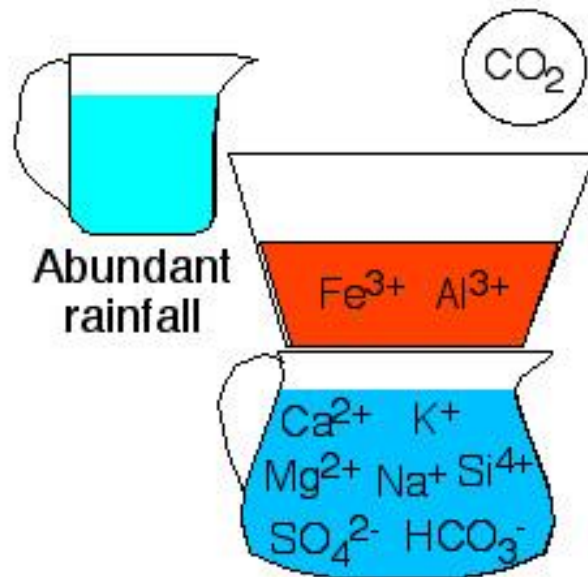
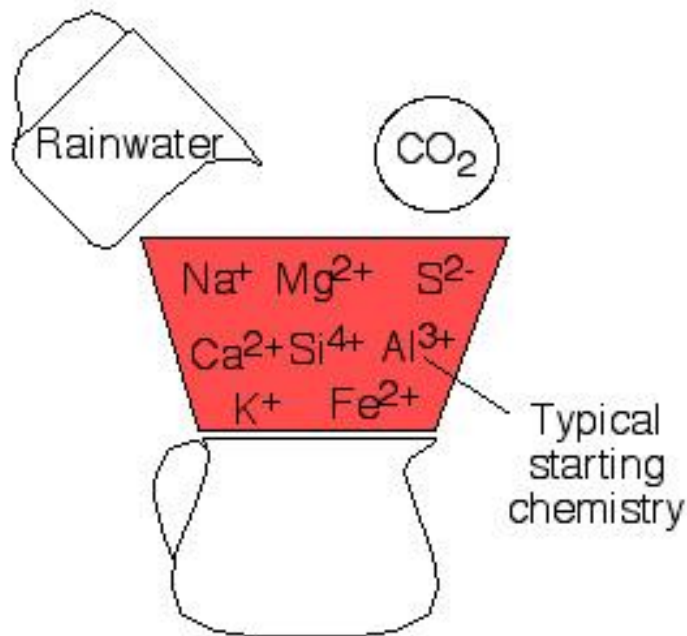
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Chemical weathering -
Removal of chemical constituents from rock
Generation of new minerals

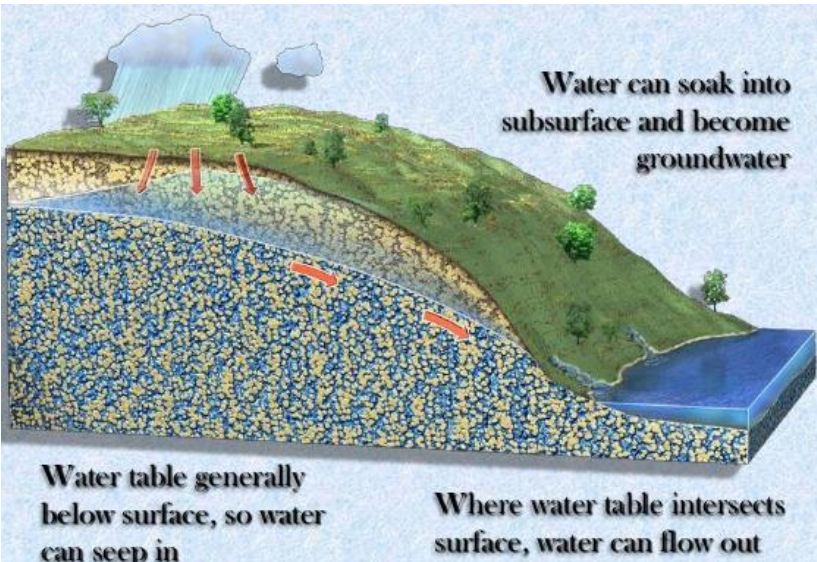
The coffee-maker model:



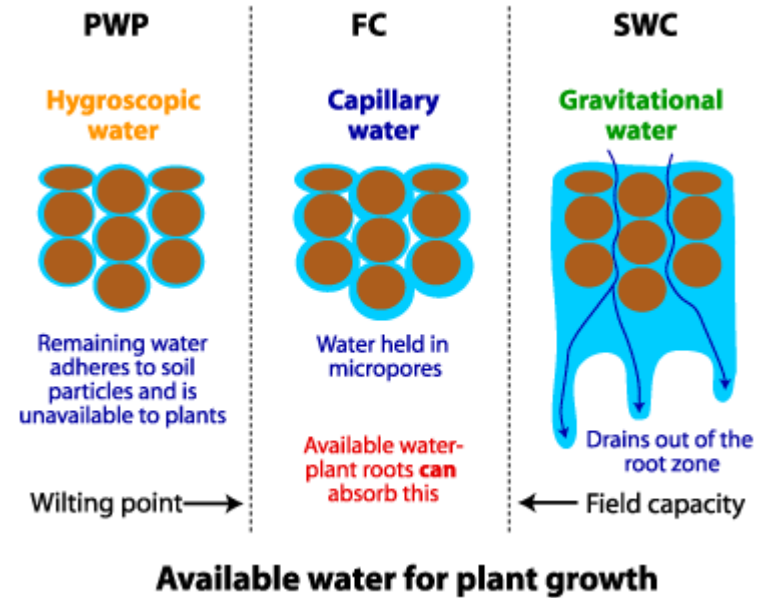


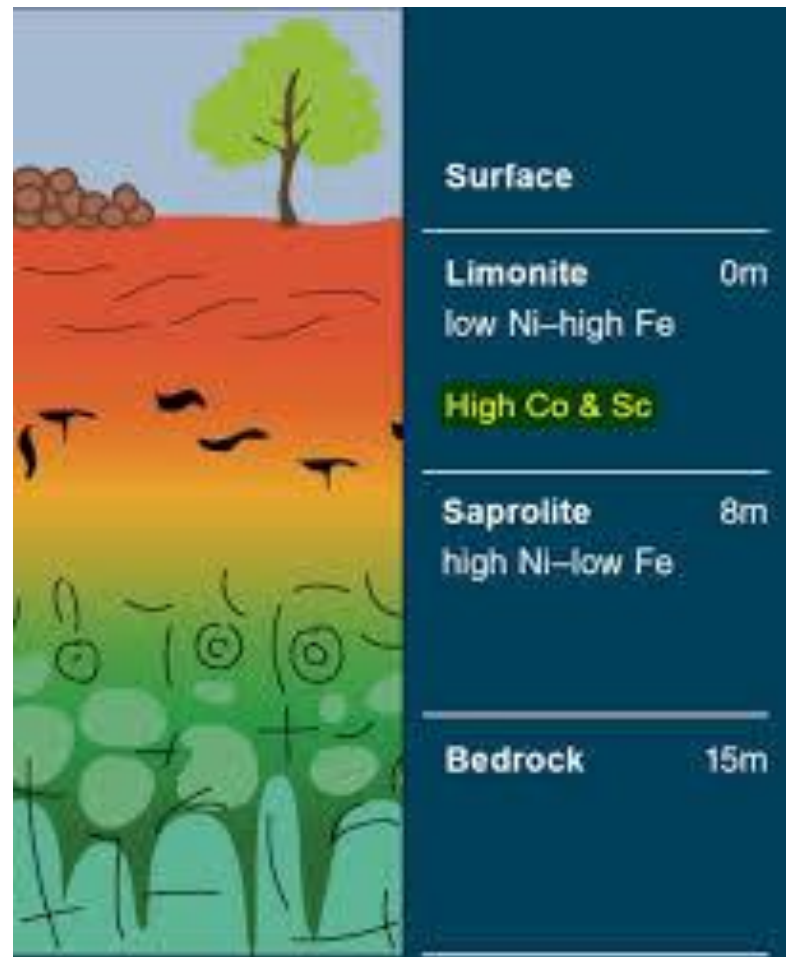
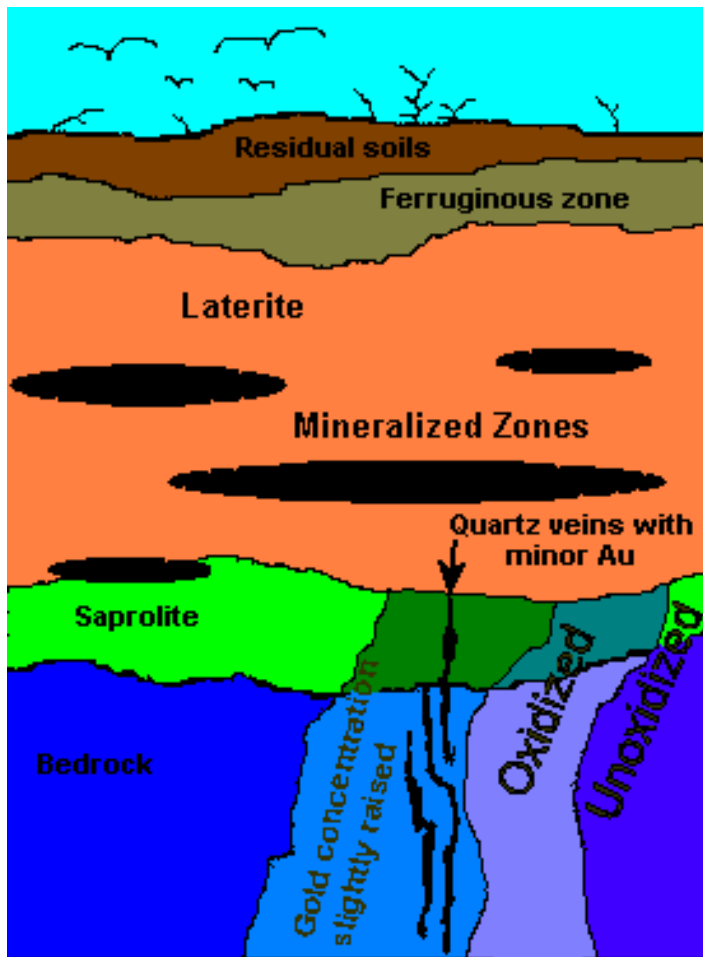
An important ore formation by weathering with metal transfer by **meteoric seepage water** is **the supergene enrichment of un-exploitable low-grade primary mineralizations "protore"**. Many copper, iron, manganese and silver deposits owe an economic ore grade to **supergene enrichment processes**.

Supergene ore deposits form in regions where weathering is favored by **a humid and hot climate that promotes the profuse growth of vegetation**. **Vegetation and organic matter** affect **supergene alteration** by two mechanisms. **Vegetation is the direct influence of plants on the soil water (e.g. retention)**. **Organic matter induces the abundance of organic acids in addition to the microbial activity that promote dissolution of primary minerals**.



In the supergene environment, iron and aluminium have a very low solubility compared to **alkalis and SiO₂**. Therefore, they are, **iron and aluminium**, enriched in the red, clayey-sandy soils **of the tropics and subtropics** that are generally called **laterites**. **Ordinary laterites** have little value except for making bricks and building roads.





II. Lateritic ore

Lateritic ore (of Al, Ni, Co, Fe, Mn, Cr, Au, etc.) is formed when exposure of suitable rocks coincides with favourable morphological, hydrogeological and geochemical conditions that enhance dissolution, transport and precipitation.

Time also has a role: long lasting weathering under stable conditions results in more mature and higher-grade ores.

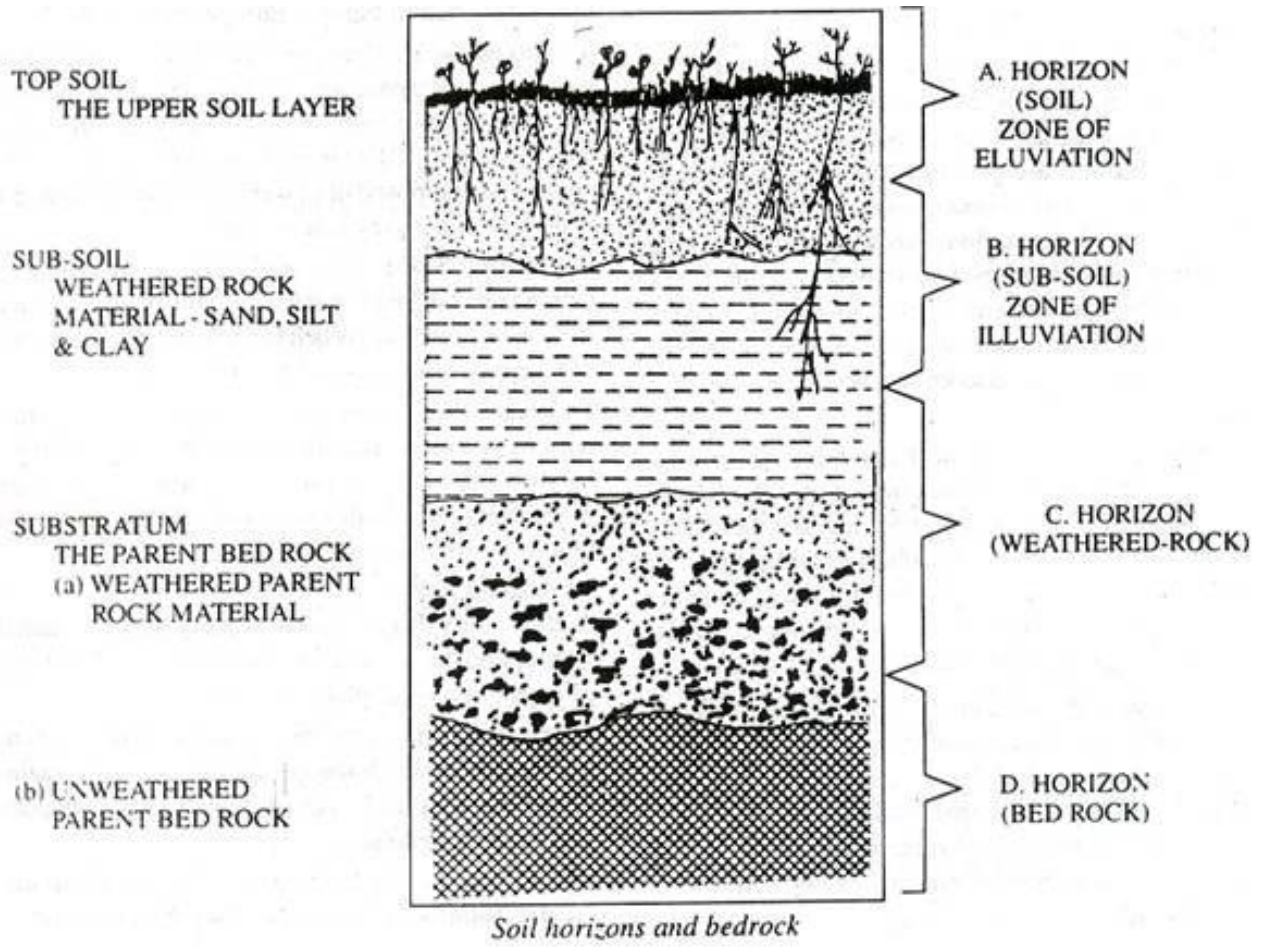
Laterite *sensu stricto* designates the upper leached and oxidized part of certain soil profiles with a well-developed vertical zonation.



Lateritic regolith* reaches more than 100m in thickness. Principally, the lateritic regolith profile comprises **an uppermost eluvial horizon (leached/bleached horizon) (A)**, **underlain by an illuvial zone (accumulation of leached element) (B)** and the altered but still recognizable precursor rock in situ (C) (saprolite zone) that rests on **un-weathered fresh rock (R)**.

In the eluvial zone, the ore minerals are leached/bleached - such as Fe - by organic acids derived from decaying vegetation.

Depending on the groundwater table, **zone (B)** is often divided into an **upper kaolinitic and haematite mottled layer** and **a greenish-grey smectitic material below the groundwater table.**



***(Regolith is a layer of broken and partly decomposed rock particles that covers bedrock; its upper part is soli).**

O horizon
Loose and partly decayed organic matter

A horizon
Mineral matter mixed with some humus

E horizon
Zone of eluviation and leaching

B horizon
Accumulation of clay, iron and aluminum from above

C horizon
Partially altered parent material

R horizon
Unweathered parent material



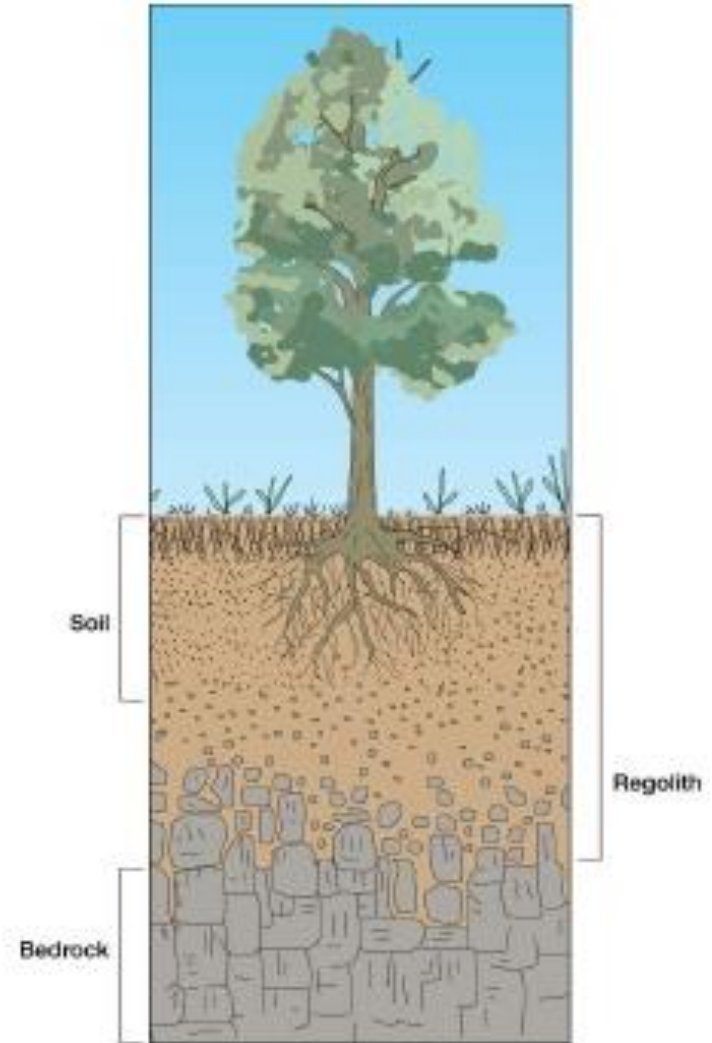
Soil

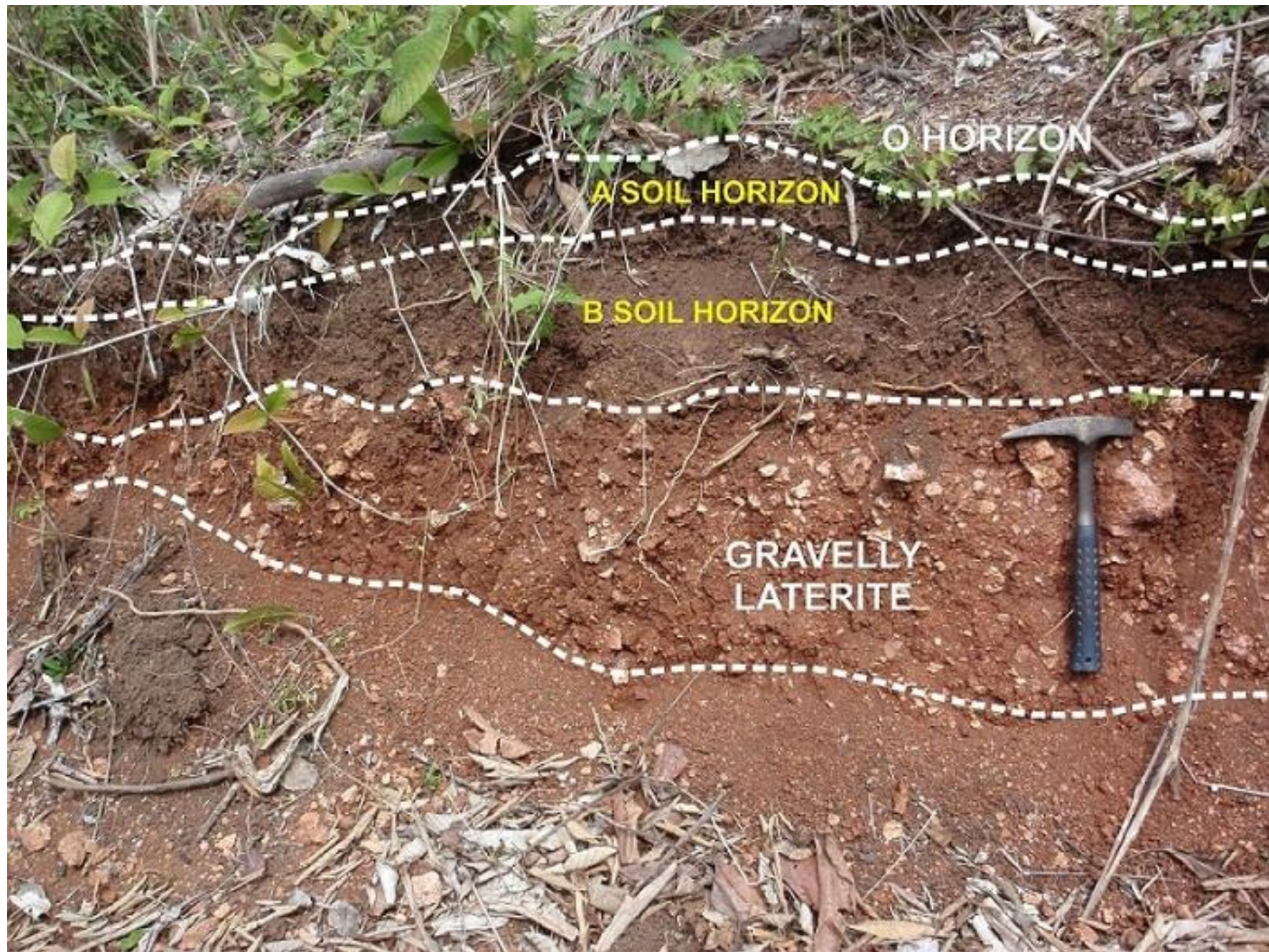
Regolith

Bedrock

***(Regolith is a layer of broken and partly decomposed rock particles that covers bedrock; its upper part is soli).**

- **Soil**—zone of plant growth.
 - The upper portion of lithosphere characterized by its ability to produce and store plant nutrients.
 - Average depth is about 15 centimeters (6 inches).
 - An infinitely varying mixture of weathered mineral particles, decaying organic matter, living organisms, gases, and liquid solutions.
 - Stage in a never-ending continuum of physical–chemical–biotic activities.
- **Regolith**—a layer of broken and partly decomposed rock particles that covers bedrock; its upper part is soil.





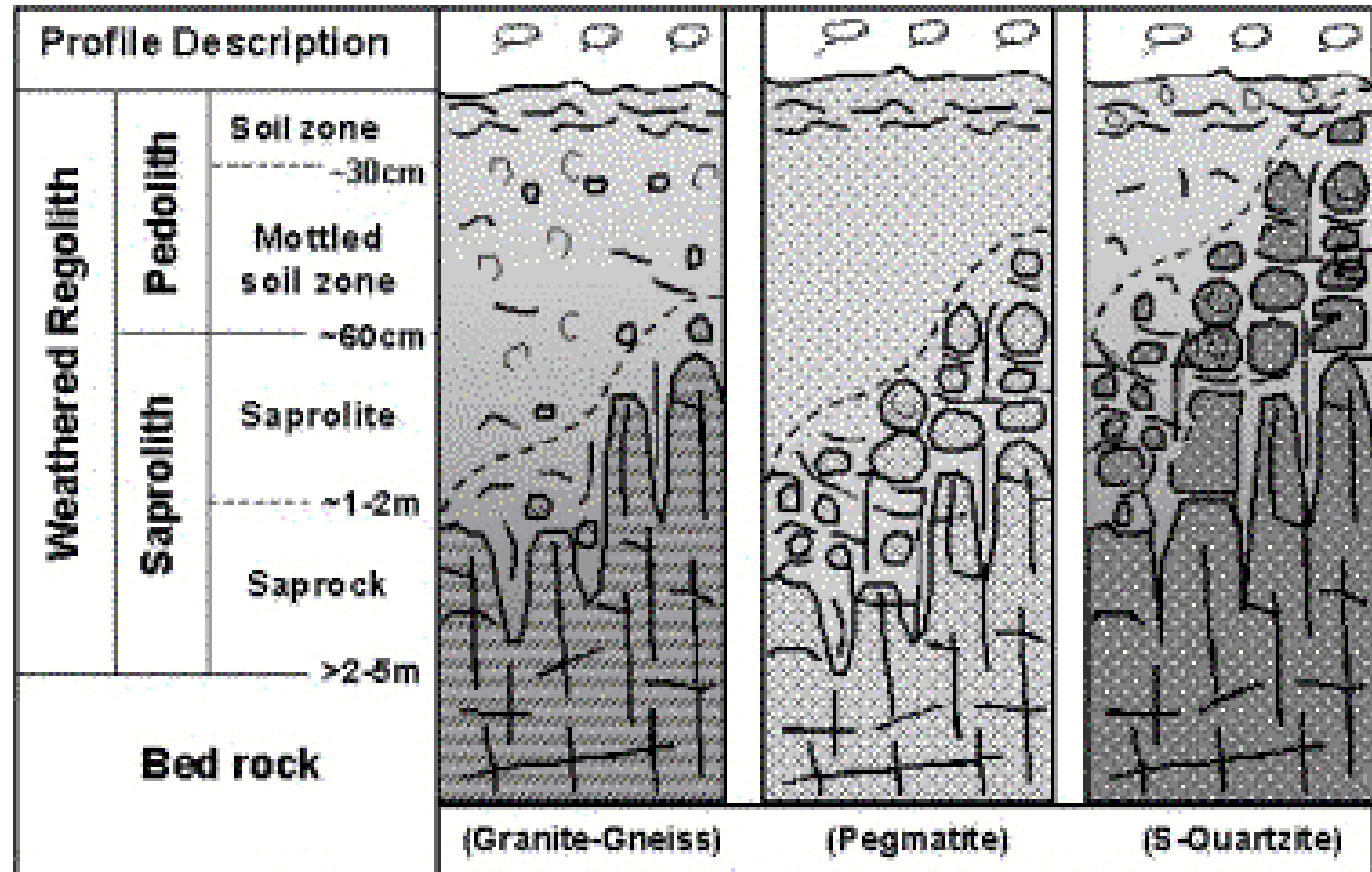
O HORIZON

A SOIL HORIZON

B SOIL HORIZON

GRAVELLY
LATERITE

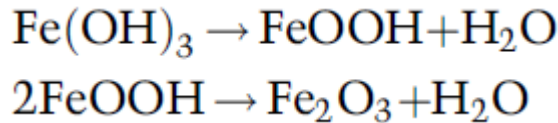
In (A) or in (B), many **laterites** have hard crusts (duricrust) that are composed of **SiO₂ (silcrete), iron (ferricrete) or manganese (mangcrete) oxides and oxyhydroxides**. Zone (C) is weathered rock and can be crumbled by hand but often displays an upper clay horizon (feldspars are argillized) (saprolite sub-zone) and a lower sandy horizon with intact feldspars but vermiculized biotite (saprock sub-zone).



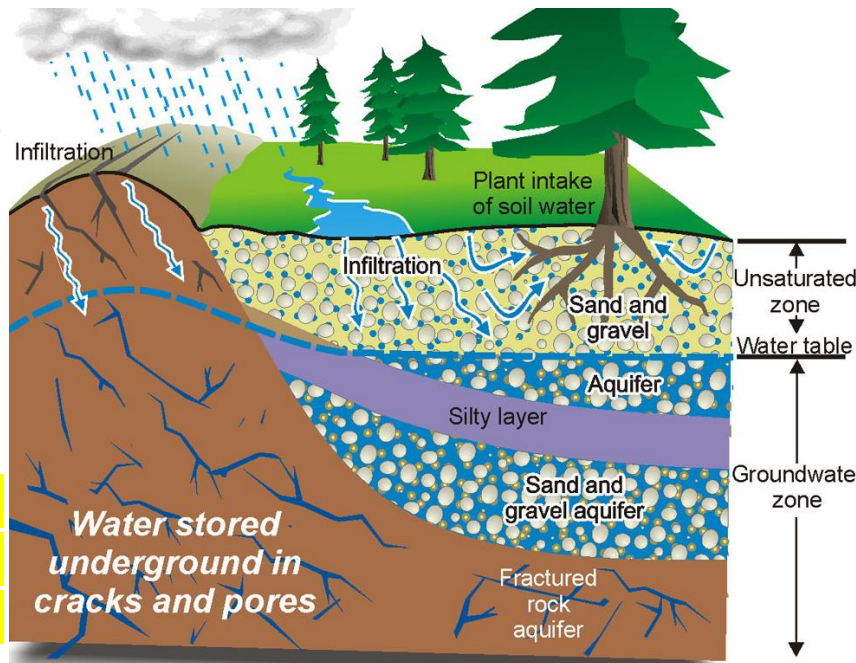
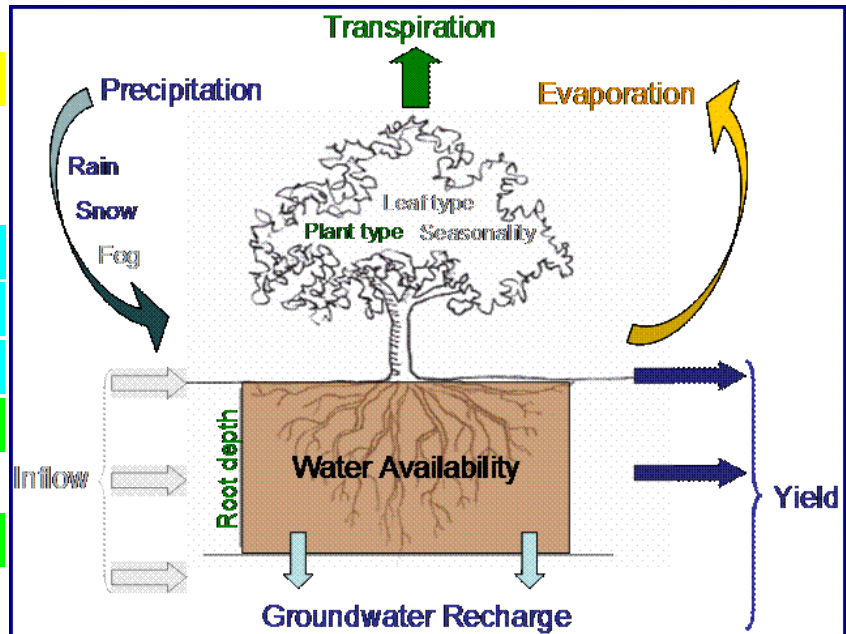
Laterite zonation is due to the effect of seasonal changes between dry and wet periods.

During dry seasons, soil water moves towards the surface and evaporates, inducing alkalic conditions that promote silica solubility. In wet seasons, acidic rain water seeps downward, dissolves and re-precipitates matter or takes it out of the system.

Textures of lateritic soils include banded crusts, shrinking fissures, concretions, pisolites and oolites, small vertical tubular structures, and many more. Newly formed solids are often amorphous and colloform, but diagenetically aging into minerals. An example is the transformation of iron hydroxide gel into goethite and haematite.



The crucial factor for effective leaching is water, modulated by hydraulic properties of soil and bedrock that influence the contact time between water and minerals.



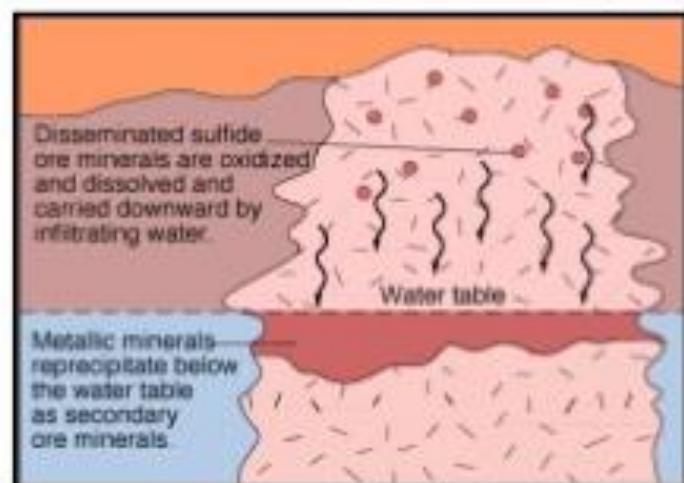
Weathering processes and Supergene ore Deposits

- ❑ Sulfide ore bodies have been subjected to weathering at or near the surface of the Earth after eons of erosion removed overlying rocks.
- ❑ Sulfide minerals are **not stable at the earth's surface** and **breakdown during weathering liberating** metallic ions (e.g., Cu^{2+} , Pb^{2+} , Zn^{2+} , Ag^{2+}).
- ❑ The surface waters oxidize many ore minerals and yield solvents that dissolve other minerals.
- ❑ An ore deposit thus becomes oxidised and generally **leached** of many of its valuable materials down to the groundwater table, or to a depth where oxidation cannot take place.
- ❑ These ions may **precipitate** as **oxides, carbonates and sulfates above the water table** to form the secondary copper, lead, zinc and silver deposits.
- ❑ Where **copper ions reach the water table** and **react with primary sulphides, supergene copper deposits form that are dominated by copper sulphides.**

1) Oxidation and reduction enrichment go hand in hand.
2) Without oxidation there can be no supply of solvents from which minerals may later be precipitated in the zones of oxidation or of supergene sulfides.

- 3) The process resolves itself into three stages:
- (i) Oxidation and solution in the zone of oxidation,
 - (ii) Deposition in the zone of oxidation, and
 - (iii) Supergene sulfide deposition.

Each is considered separately



4) Ideal starting material

For this to happen, the rock (starting material) needs to be:

- Porous and permeable.
 - ***Contains abundant pyrite.***
 - Contains acid soluble ore-metal-minerals.
 - Underlain by precipitative environment.
- ❑ Can apply to many transition metals but Cu is the outstanding example.
 - ❑ Acidic oxidizing solutions will dissolve many minerals.
 - ❑ Basic reducing conditions at or below groundwater table will precipitate.

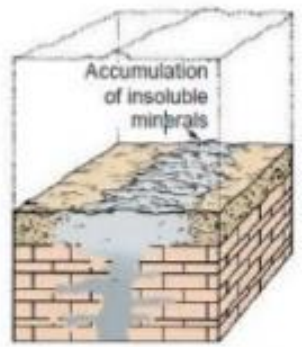
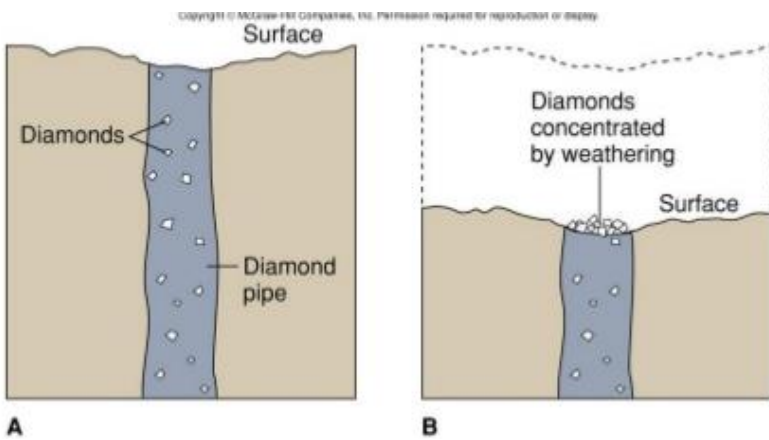
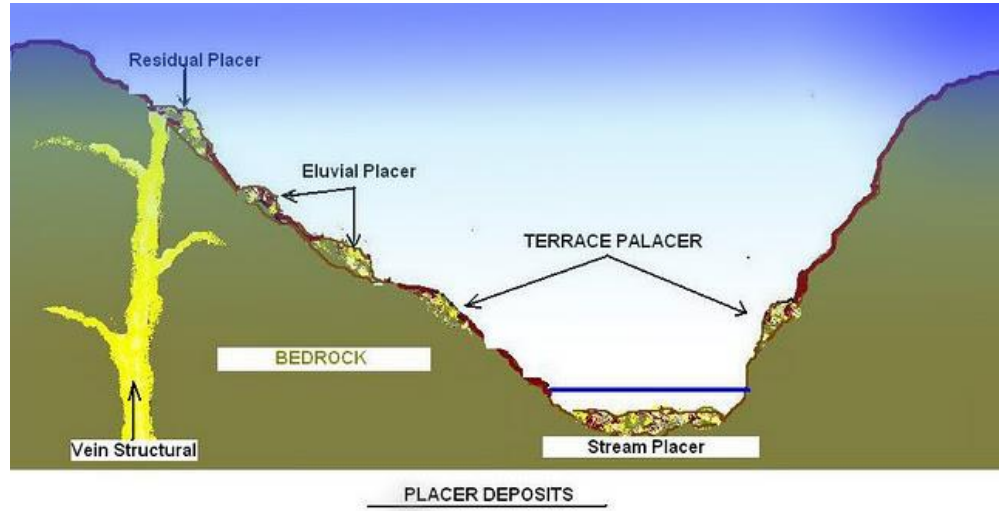
Conditions that influence supergene enrichment

- Active chemical weathering with ground level lowered by erosion.
- Weathering under ***acidic (carbonated water) and oxidizing conditions.***
- Permeability and Porous
- Composition of the ore from the standpoint of chemistry of the solution, chemical environment;
 - ✓ ***Contains abundant pyrite.***
 - ✓ Contains acid soluble ore-metal-minerals.
- Time.
- Deep water table imposing reducing conditions.
- Latitude and altitude, and depth of water level
- Climate and physiographic development
- Restricted to non-glacial terranes.

III. Residual ore deposits

In residual ore deposits, the economically interesting component is concentrated in situ, while weathering removes diluting parts of the rock. Examples are residual and eluvial placers, bauxite, lateritic gold, platinum, iron (Ni, Co) and nickel ores, residual enrichment of sub-economic protore iron and manganese, and industrial minerals such as phosphate, magnesite and kaolin.

The fundamental geochemical principle of the enrichment is the steady activity of a reaction front in soil (the valuable component is immobilized), while the land surface is lowered by weathering and erosion.

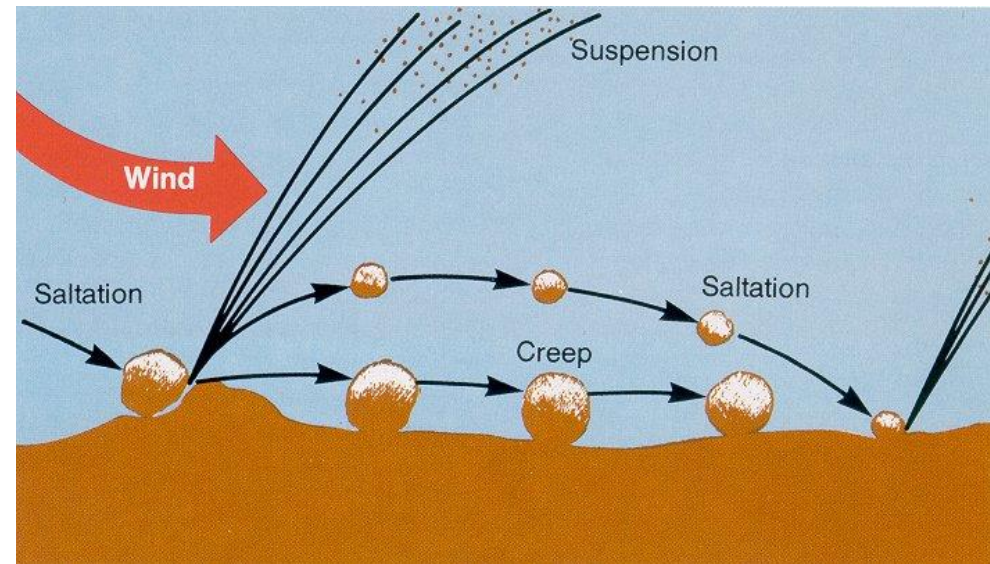
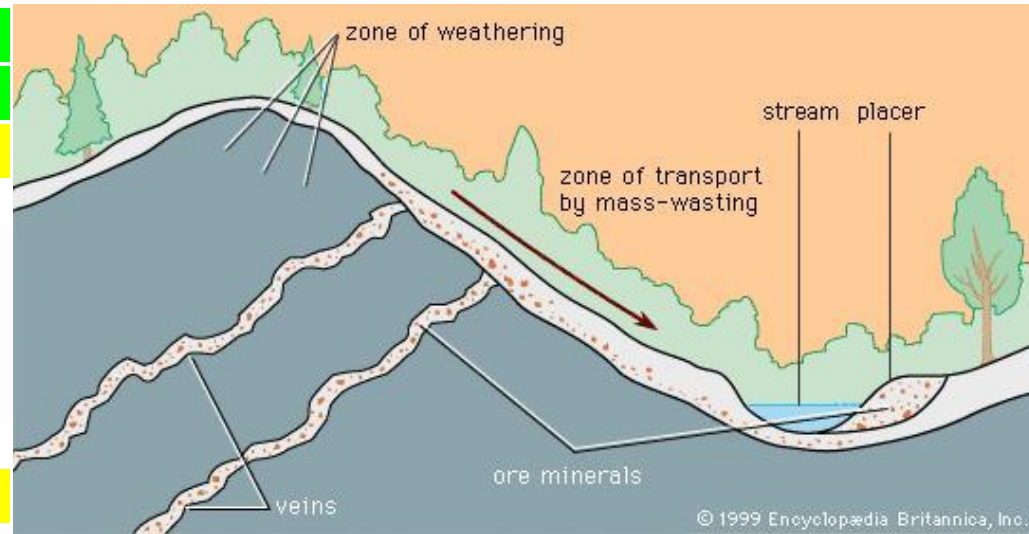


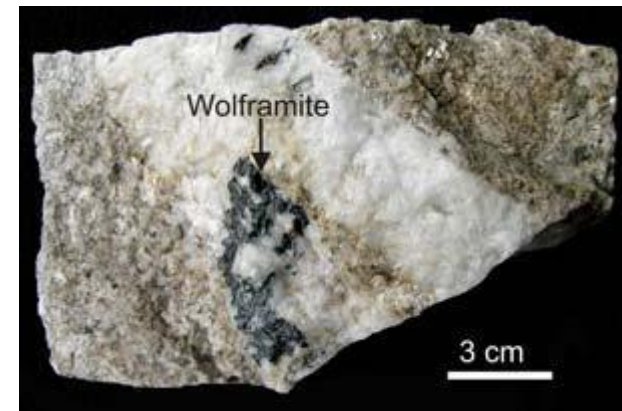
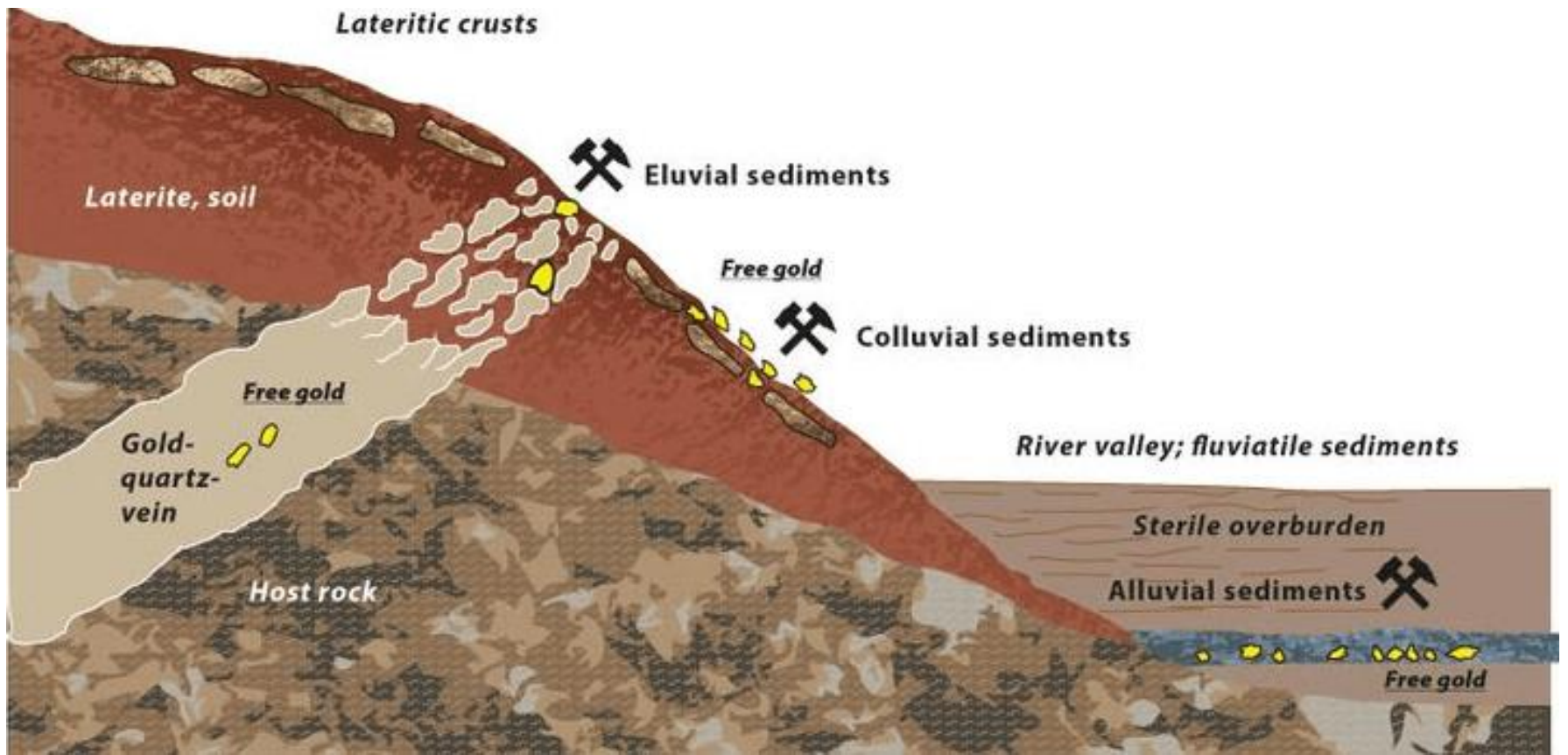
The concentration of ore deposits by weathering processes occurs as soluble rock, such as limestone, is removed in solution, leaving insoluble minerals concentrated as a residue.

□ Residual/eluvial placers (gold, cassiterite and wolframite)

Residual placers are concentrations of weathering resistant ore minerals that are due to supergene abstraction of non-ore material. The term eluvial (outwash) describes the same result, i.e., residual although with more emphasis on physical removal of barren gangue. Many ore deposits, such as native gold, cassiterite and wolframite, contain heavy minerals that resist dissolution. In this case, physical weathering is the main agent.

Residual placers are only stable in flat morphologies, because steeper slopes induce soil creep and with it a down-slope displacement of ore fragments (resulting in colluvial placers). Residual placers often occur at the “stone-line” level of a soil profile, where quartz and durable ore minerals are concentrated.





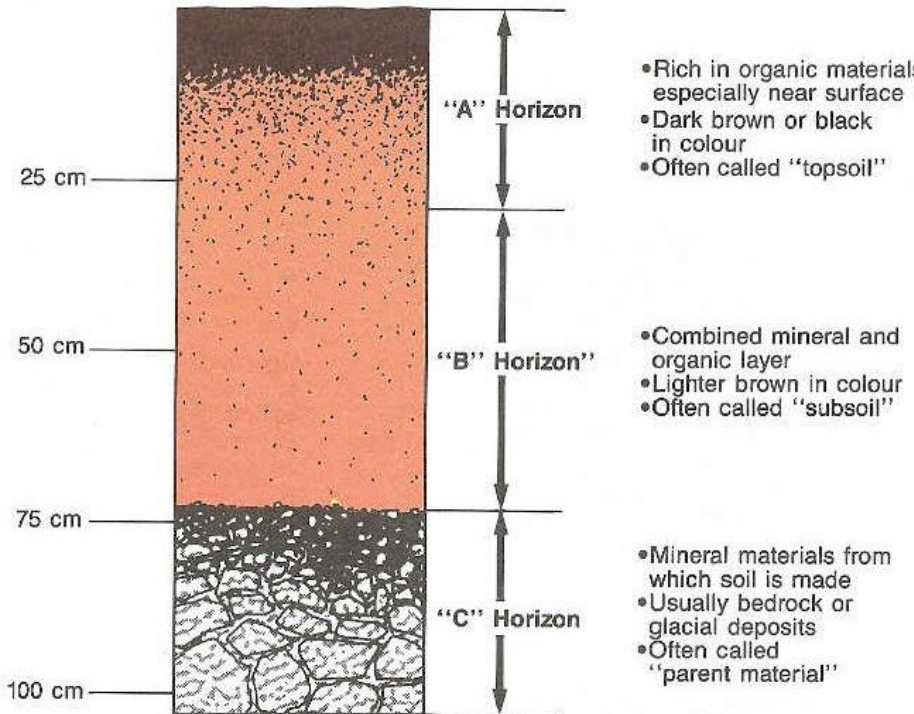
Lateritic gold deposits

Lateritic gold deposits as a class are a relatively recent discovery. One of the largest representatives of this group was the **Boddington bauxite mine in Western Australia**, which until closure in 2001 was the **biggest gold mine in Australia with an annual gold production of 2500 kg**. Pre-mining resources amounted to 60Mt of ore at 1.6ppm Au, apart from **bauxite with gold contents of less than 1 ppm**.



Exploitable gold was located in near-surface, Fe-Al hard crusts that reached a thickness of 5m and in additional 8m thick lumpy Fe-Al laterite of the B horizon. **Sources of the lateritic gold in soil at Boddington are quartz veins and hydrothermally altered bodies.**

Lateritic gold deposits are worked. They are attractive because exploration, extraction and processing of soil is less costly compared with hard rock mining.

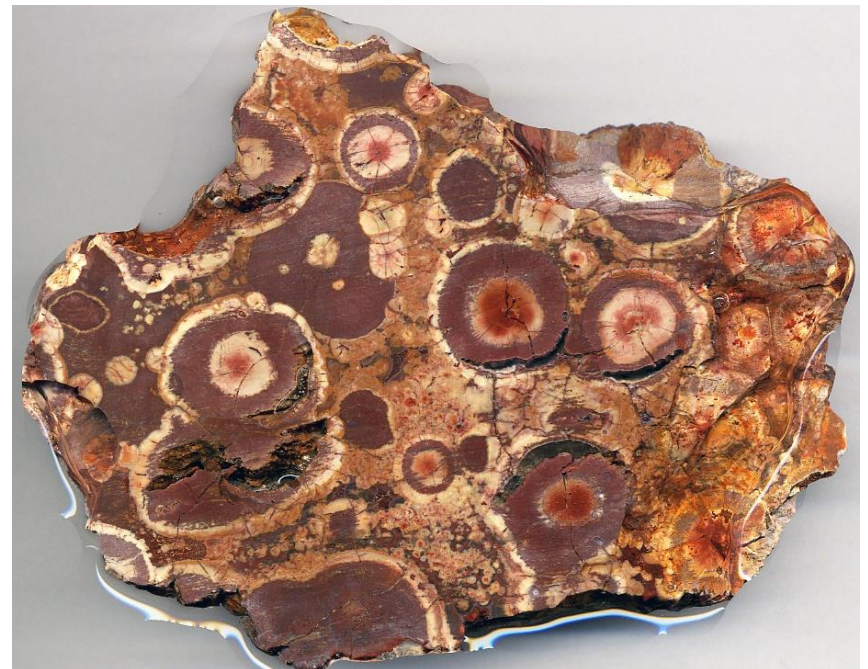


□ Bauxite laterite/Residual bauxite

Bauxite is the main source of Al in the world. Bauxite ore deposits originate either by **autochthonous/in-situ weathering of aluminium silicate rocks (e.g. basalt; nepheline syenite)**, or by **allochthonous sedimentation after erosion of bauxite soil blankets.**

Autochthonous upland bauxites are discerned from **lowland bauxites** that include **detrital (sedimentary) deposits.**

Residual bauxite horizons often extend over large areas and mark regional unconformities that are related to favorable tectonic and climatic conditions. **Many aluminium silicate rocks contain an average of 15% Al_2O_3 that must be upgraded by weathering to at least 35% Al_2O_3 to be economically exploitable.** **Alumina enrichment is caused by leaching of SiO_2 and iron, two substances that are not easily dissolved.**



Constitution of Bauxite

Mineralogy:

- ❑ Bauxite is an aluminum ore and is not actually a mineral.
- ❑ The present usage of the term, both mineralogically and in commerce *is to designate a commonly occurring substance that is a mixture of several hydrated aluminium oxides with considerable variation in alumina content.*
- ❑ It is a hardened and partly crystallised hydrogel that consists of variable proportions of the minerals **gibbsite** ($\text{Al}(\text{OH})_3$) or **hydrargillite**, and **boehmite** ($\text{AlO}(\text{OH})$) and its dimorphous form (i.e. **diaspore** $\alpha\text{AlO}(\text{OH})$), together with hematite, the clay mineral kaolinite and small amounts of anatase (TiO_2).
- ❑ Impurities are invariably present in the form of **halloysite**, **kaolinite**, **nontronite**, and **iron oxides**; rarely, bauxite contains **octahedrite**.

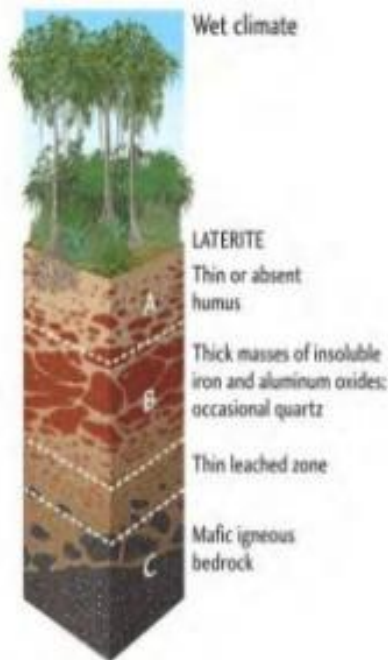
- Gibbsite: $\text{Al}(\text{OH})_3$
- Diaspore : $\alpha\text{AlO}(\text{OH})$
- Boehmite: $\text{AlO}(\text{OH})$
- Kaolinite: $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$
- Halloysite: $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$
- Montmorillonite: $(\text{Na}, \text{Ca})_{0.33}(\text{Al}, \text{Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$

- ❑ Typical bauxite contains:
 - ✓ 35 to 65% Al_2O_3
 - ✓ 2 to 10 % SiO_2
 - ✓ 2 to 20% Fe_2O_3
 - ✓ 1 to 3 % TiO_2
 - ✓ 10 to 30% combined water.
- ❑ **For aluminium ore:** bauxite should contain preferably at least 35% Al_2O_3 and less than 5% SiO_2 , 6% Fe_2O_3 and 3% TiO_2 .
- ❑ **For the chemical industry:** the percentage of silica is less important, but iron and titanium oxides should not exceed 3% each; and
- ❑ **For abrasive use:** SiO_2 and Fe_2O_3 should be less than 6% each.
- ❑ Commercial bauxite occurs in three forms:
 - ✓ Pisolitic or oolitic, in which the **kernels** are much as a centimeter in diameter and consist principally of amorphous trihydrate;
- ❑ Sponge ore (**Arkansas**), which is porous, commonly retains the texture of the source rock, and is composed, mainly of gibbsite; and amorphous or clay ore. All three may be intermingled

Origin and Mode of formation

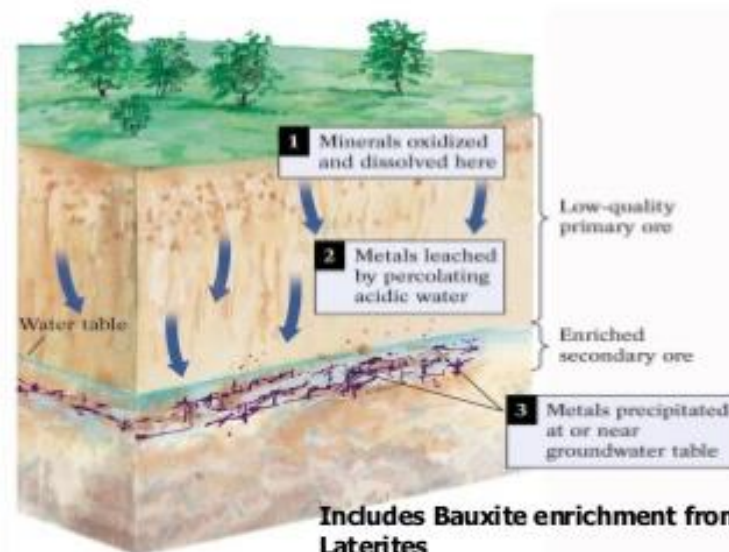
Formation of Bauxite deposit is formed by lateritization (intense chemical weathering in hot, wet, tropical areas) of various silicate rocks such as granite, gneiss, basalt, and shale.

Conditions necessary for bauxite formation	Mode of formation
<ol style="list-style-type: none"> 1) favorable parent rock. 2) porosity. 3) high rainfall with intermittent dry spells. 4) good drainage. 5) tropical warm climate. 6) low relief. 7) long period of exposure. 8) vegetation. 9) Low Fe, Ti, alkalis, and alkali earths 	<ol style="list-style-type: none"> 1) Weathering. 2) In situ leaching of elements and enrichment of residue in Al. 3) Possible erosion and redeposition? 4) Addition of eolian dust.



In situ leaching of elements and enrichment of residue in Al.

Laterite



Mode of Formation (Cont.)

Steps:

- Al is abundant in earth (after O and Si). But, binds very strongly to O, poorly soluble = difficult to process.
- Bauxite is an accumulated product of peculiar weathering of aluminium silicate rocks lacking in much free quartz, silicates are broken down; silica is removed; iron is partly removed; water is added; and alumina, along with titanium and ferric oxide (and perhaps manganese oxide), becomes concentrated in the residuum.
- leaching in tropical/subtropical where abundant rainfall (leaching), near neutral pH where Al least soluble.
- Highly soluble materials like Na, K, Ca leach first.
- Then Mg and others.
- Formation of kaolinite from K-feldspar, also production of gibbsite (bauxite) as H_2SiO_4 drops as SiO_2 is leached (Kaolinite \leftrightarrow Gibbsite + Silicic Acid).



Al converted mainly to kaolinite (often from feldspars: see phase diagrams and reactions, compare phase diagram to le Chatelier principle).

- Formation of kaolinite from K-feldspar, also production of gibbsite (bauxite) as H_2SiO_4 drops as SiO_2 is leached (**Kaolinite \leftrightarrow Gibbsite + Silicic Acid**)
- Progressive dissolution of silica from clays in wet soils will eventually turn the:



- Basic reaction:



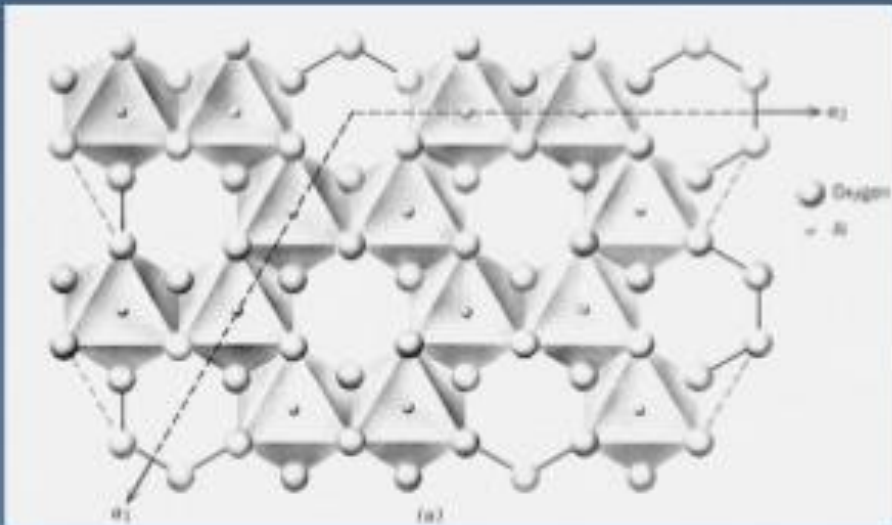
- Eventually, Si in kaolinite can leach out, leaving Al oxides and hydroxides (gibbsite= $Al(OH)_3$, boehmite= $AlO(OH)$).
- Where conditions are slightly more acidic, Fe may also leach (narrow zone), or, more likely, if rocks are initially low in Fe.
- Can be redeposited
- these soils become *bauxite*, a major ore of aluminum.
- This produces more pure Al ore.
- low relief = slow erosion compared to rate of chemical leaching common pisolitic texture, consequence of insitu process of phase transformation.

Gibbsite $\text{Al}(\text{OH})_3$

Gibbsite-type – dioctahedral sheets (only two of three octahedral sites are filled). $(\text{OH})^-$ main anionic group forming octahedrally coordinated sheets with weak bonds between



Diaspore $\alpha\text{AlO}(\text{OH})$



Bauxite Al-hydroxide*



*hybrid mix of diaspore, gibbsite, and boehmite

Characteristics:

☐ *Shape and Form:*

- 1) *Pocket Deposit* : pocket; hole (ex. Jamaica & South Europe)
- 2) *Blanket deposits*: Irregular *blankets* several meters to tens of meters thick on top of their parent rock (usually but not always){ ex. Australia, Guyana, Surinam}.
- 3) *Detrital Deposits* : Accumulate in high slope land and inclined bed
- 4) *Mixed 1, 2 and 3* (ex.Blanket & Detrital Deposits ; Arkansas)

☐ *Age:* mostly post-Mesozoic.

- ✓ More than 90 % of all known bauxite deposits **formed during the last 60 million years,**
- ✓ All of the very large bauxite deposits **formed less than 25 million years ago.**

☐ *Mined by open pit method.*

☐ *Main producers:* Australia, Guinea, Jamaica, Brazil, India, Surinam and Balkan Republics.

- Largest producers are Australia, Jamaica and Guinea.

Types of deposits:

High level/upland bauxite

- Directly on volcanic or plutonic rocks, no clay body in between.
- < 30 m in thickness
- In tropical and subtropical climates
- Porous and friable, often with relict textures
- Predominated by Gibbsite
- Weathering controlled by structures in parent rocks
- *Examples:* Ghana and Guinea

Low level/peneplain bauxite

- Somewhat transported, separated from their parent rock by kaolinitic under clay.
- ~ 9 m thick.
- Along tropical coastlines
- Pisolitic textures.
- Associated with *detrital bauxites* produced by fluvial and marine activity.
- *Examples:* South America, Australia, and Malaysia.

Karst bauxite

- Oldest known.
- In Eastern Europe.
- On top of karst surfaces in limestone and dolomite.
- Structureless, earthy, concretions, variable textures!
- Predominated by Boehemite.

□ Iron Laterite/Residual iron

Lateritic iron ore deposits are not an important source of iron, because both deposit size and iron grades are rather low. The ore consists of oolitic, red, yellow or brown haematite and goethite with elevated contents of H_2O , SiO_2 and Al_2O_3 . Most deposits take the form of autochthonous or locally transported hard crusts (ferricrete) that reach a thickness of only a few meters.

Lateritic iron ore is derived from ultramafic source rocks and is exploited in several countries (Albania, Greece, Moa Bay, Cuba and in the Philippines) as a high-iron limonite nickel ore (also termed “oxide nickel ore”) for pig-iron blast furnaces.

In Fe-oxide nickel ore, nickel is absorbed in amorphous iron-hydroxides or occurs as inclusions in goethite.



Residual supergene enrichment of iron pre-concentrations is the last upgrading event in the multistage evolution of high-grade haematite ore deposits with 60–68 wt.% Fe, which could be derived from alteration of Precambrian BIF (Banded Iron Formation) by diagenetic brines.

□ Manganese laterite/Residual manganese

Residual manganese ore deposits are derived from rocks with **above-average manganese contents**. Laterites developed from such rocks include **hard crusts (mangcrete)** or **earthy manganese ore that may blanket considerable areas**. In contrast to iron that tends to concentrate in the upper soil horizons (ferricrete), **the slightly more mobile manganese is typically enriched in lower parts of the laterite profile**.

Lateritic manganese ores are often high-grade and of superior quality.

Sources (protore) are **manganese quartzites, carbonates and volcano-sedimentary rocks that contain exhalative-sedimentary pre enriched horizons**.



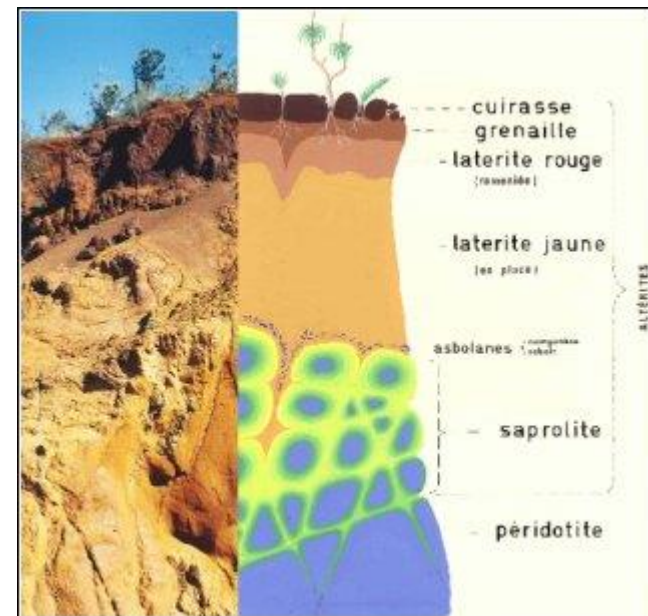
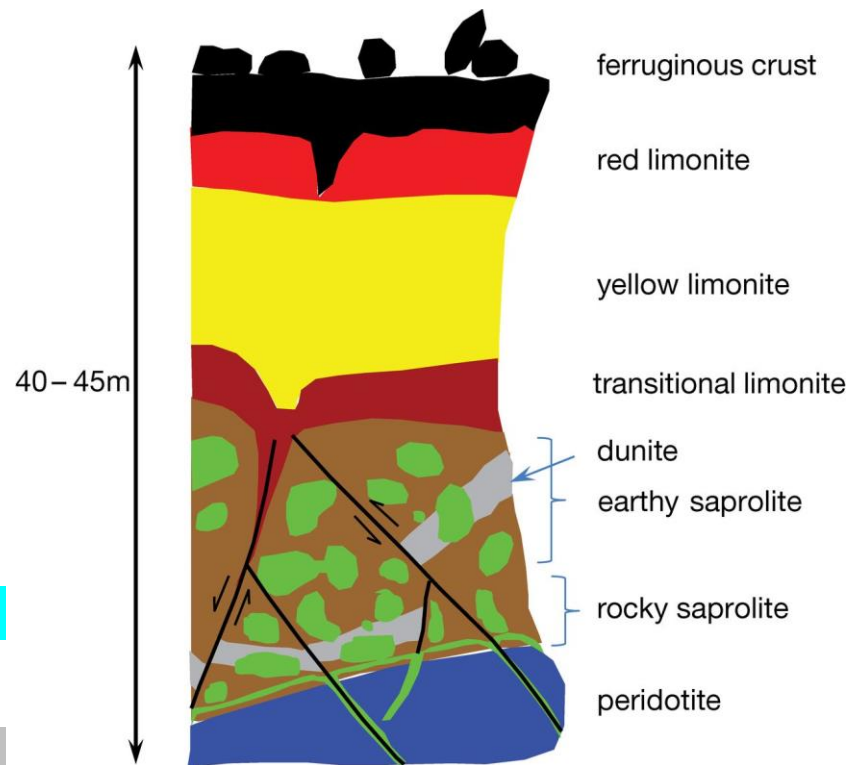
□ Nickel Laterite

Lateritic nickel ore deposits are of major economic importance. They form by intensive and long-lived tropical weathering of ordinary ultramafic rocks, which enriches nickel (and cobalt).

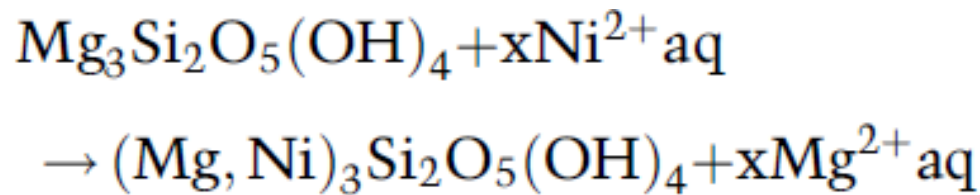
Two types of nickel laterite are distinguished:

- i. the oxide type in the upper, oxidized iron-rich part of the laterite; (Ni as hydroxide in the ferruginous zone) and
- ii. the silicate type in the lower, reduced saprolitic section of the regolith (Ni as hydrous silicates in saprolite) (above the parent rock).

Laterite regolith zonation and the redistribution of nickel are the result of meteoric water percolating through the soil. Olivine, pyroxene and serpentine are rapidly decomposed by acidic rain and soil water. From a surface value of 6, the pH of deeper soil water turns alkaline (pH 8.5).

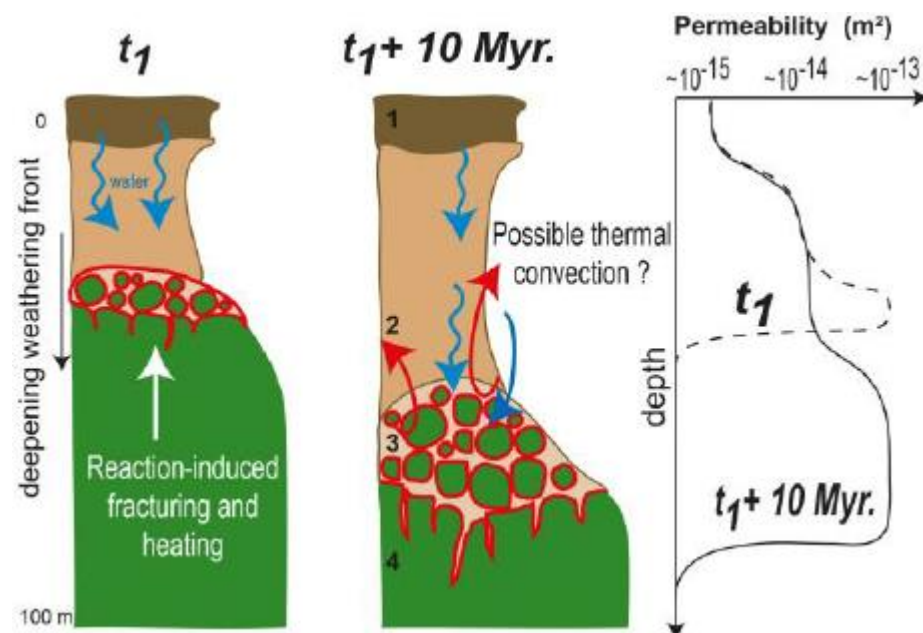
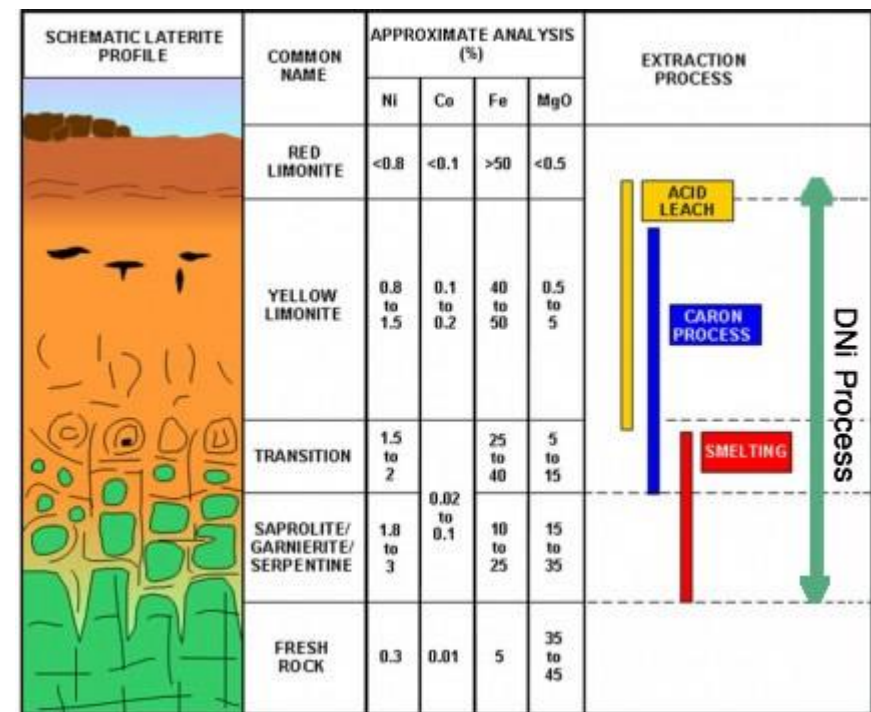


Nickel is dissolved and flushed downward, where it is immobilized by ion exchange with Mg in newly forming magnesium hydrosilicates. A schematic example of this reaction (neogenesis of the Ni-serpentine from serpentine) is given in equation. **Neogenesis of Ni-silicate in the saprolite zone:**



Normally, groundwater removes the dissolved magnesium from the system. Some is precipitated as a carbonate (magnesite) in joints.

New Caledonia is the largest ore province of Ni-laterites. The serpentinized and unaltered harzburgite-dunite displays an average 0.25% Ni (mainly in olivine) and 0.02% Co. Lateritization of the exposed ophiolite resulted in a mature profile:



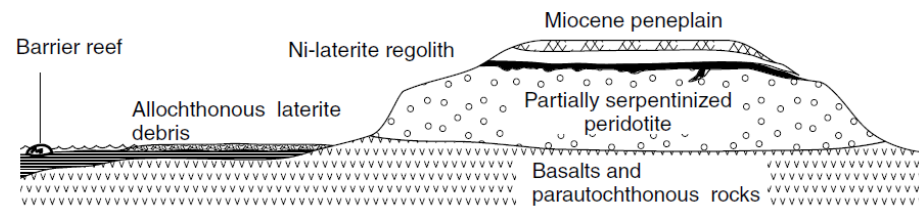
1. **Top:** Massive goethitic (ferricrete); with low residual nickel concentration;

2. **Limonite zone:** with residual manganese, chromium, haematite and aluminium. Nickel, cobalt, magnesium, calcium and silica are leached and strongly depleted; in rare cases, residual nickel is exploitable;

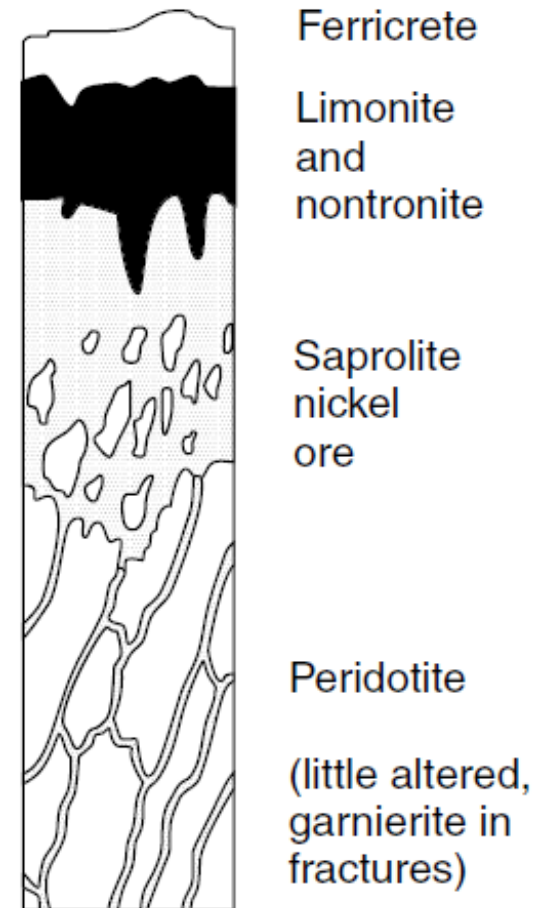
3. **Nontronite zone:** Ferrallitic, earthy, red and yellow clays are the norm. Nickel and manganese are enriched to exploitable grades.

4. **Saprolite zone:** It is the main nickel ore horizon. Olivine and pyroxene are altered to colloform magnesium silicates that age into the minerals antigorite (serpentine), talc and smectitic clays; nickel is taken up by these minerals in their lattice by cation exchange of Mg^{2+} .

5. **Bottom:** Unaltered hard rock (protore) with rare garnierite in joints and fractures.



Schematic profile of laterite blanket with nickel ore (black, garnierite-saprolite horizon) above peridotitic rocks such as the New Caledonian ophiolite (not to scale).



Regolith profile of exploitable nickel laterite in New Caledonia. Note the control of garnierite by joints and fractures of peridotite.



Surface

Limonite 0m
low Ni-high Fe

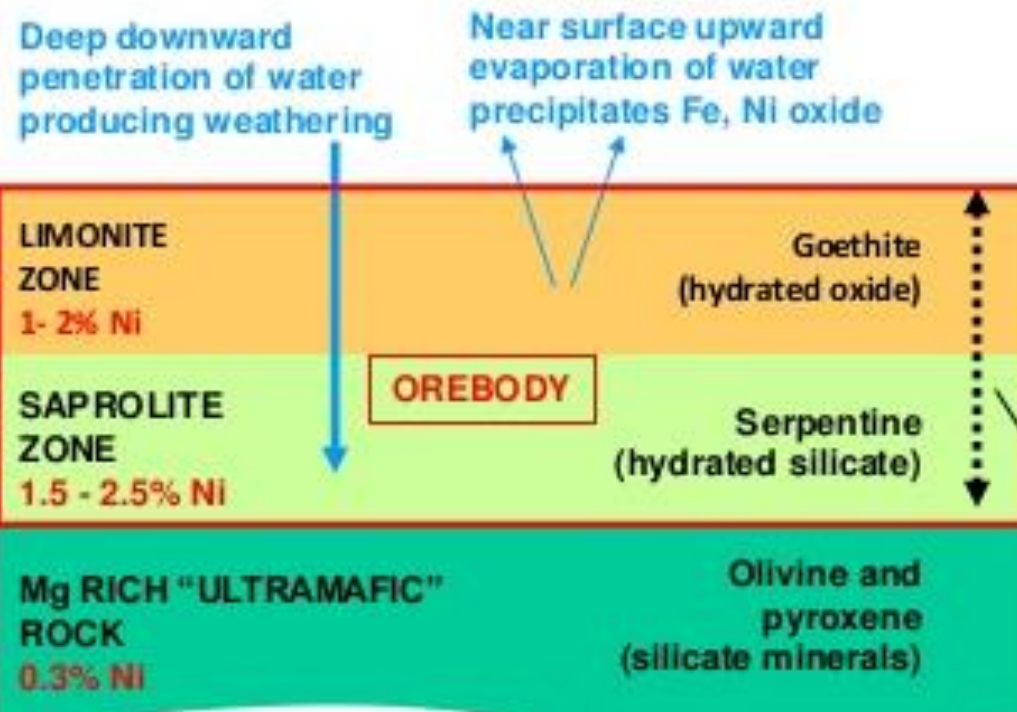
High Co & Sc

Saprolite 8m
high Ni-low Fe

Bedrock 15m

❑ **Ultramafic rock** - igneous rocks formed from magma with very low concentrations of quartz (SiO_2). **Peridotite** is a common ultramafic rock type which contains **olivine**, a greenish-gray mineral, with *magnesium and nickel*.

- Rocks containing nickel are broken down by intense weathering to form a soil layer :
 - ✓ Weathering begins on joints and fractures in the rock to form large blocks or boulders with a thin soil layer.
 - ✓ Further weathering and biological processes thicken the soil layer.
 - ✓ Water flowing through the soil leaches nickel, iron, and magnesium (and other metals) from the soil.
 - ✓ The metals (nickel, iron, magnesium and other) then precipitate from water as oxides, hydroxides and silicates in different parts of the soil layer as laterite.



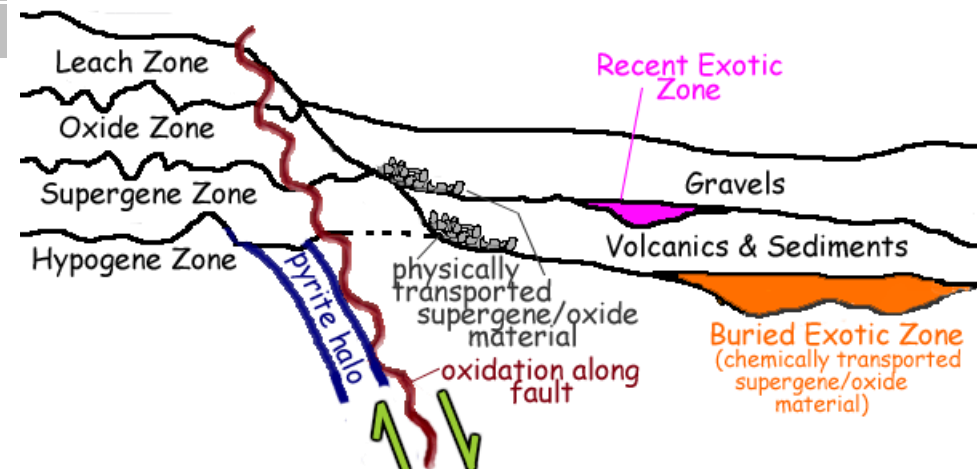
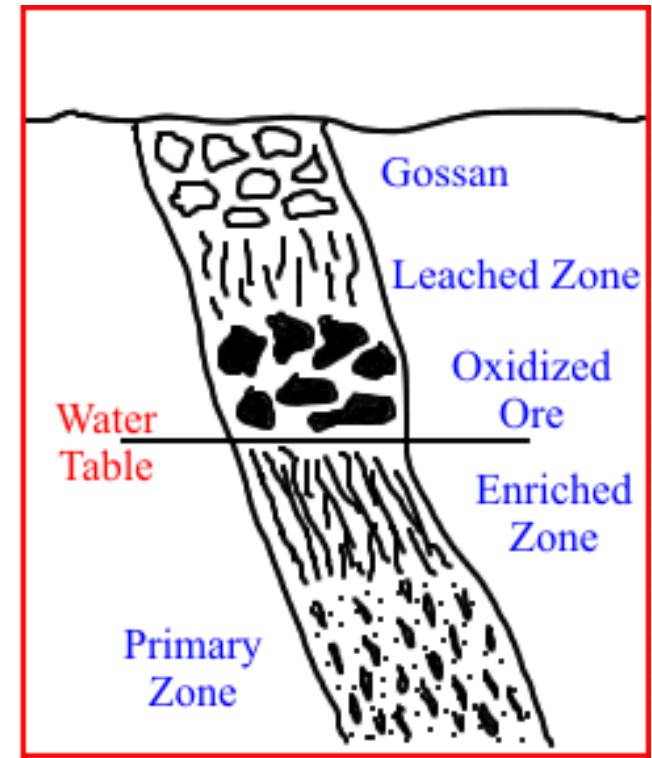
The process of oxidation and weathering depletes the original mafic rock of Mg and Si, and concentrates Fe and Ni in the weathered zone.

Supergene metal deposits form when common rock types or deeply buried primary ore bodies are exposed at or near the Earth's surface and undergo oxidation, dissolution and re-concentration of the metals. **Supergene metal deposits** are economically interesting because of their accessibility for extraction and increased grades. Scientifically they are attractive because of their mineralogical diversity and what they reveal about surficial history.

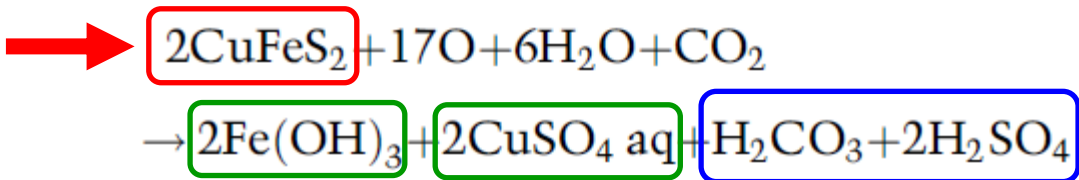
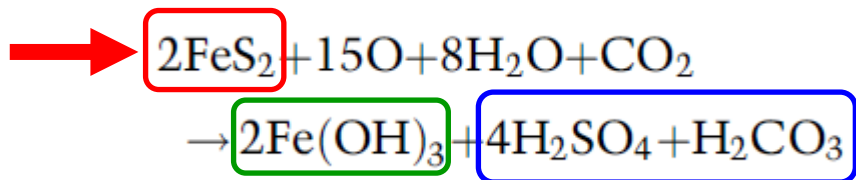
Supergene enrichment of pre-existing mineralization (chemical weathering)

Supergene, descendent alteration, may be exceptionally beneficial where pre-existing uneconomic mineralization or low-grade orebodies are affected. Primary ore (protore) in deeper parts of the weathering profile is upgraded by seepage solutions. For sulphide copper and silver ores, iron oxides and certain uranium ore deposits, the supergene enrichment process is of economic significance.

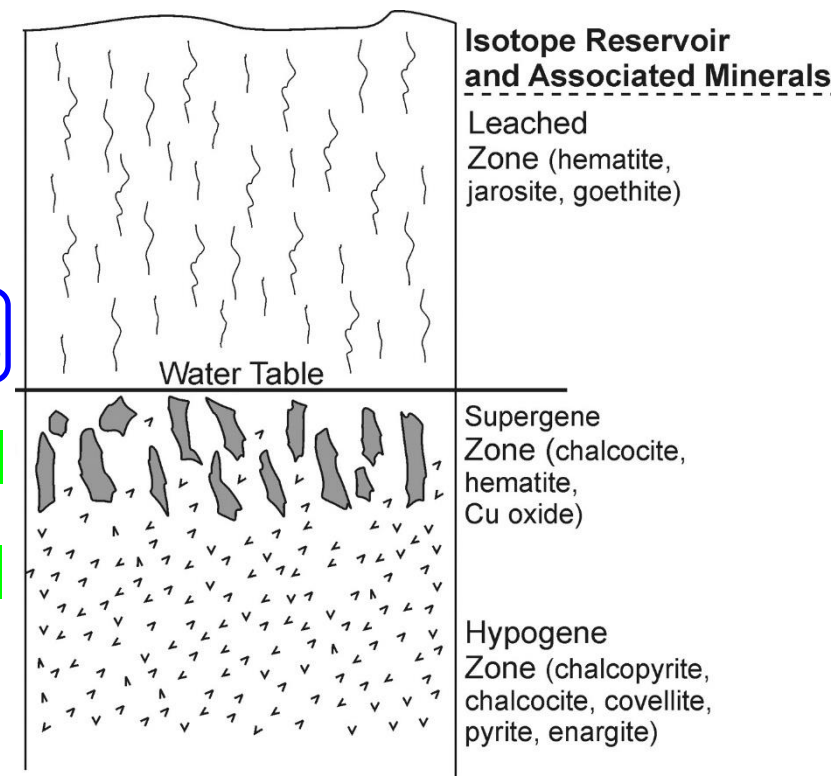
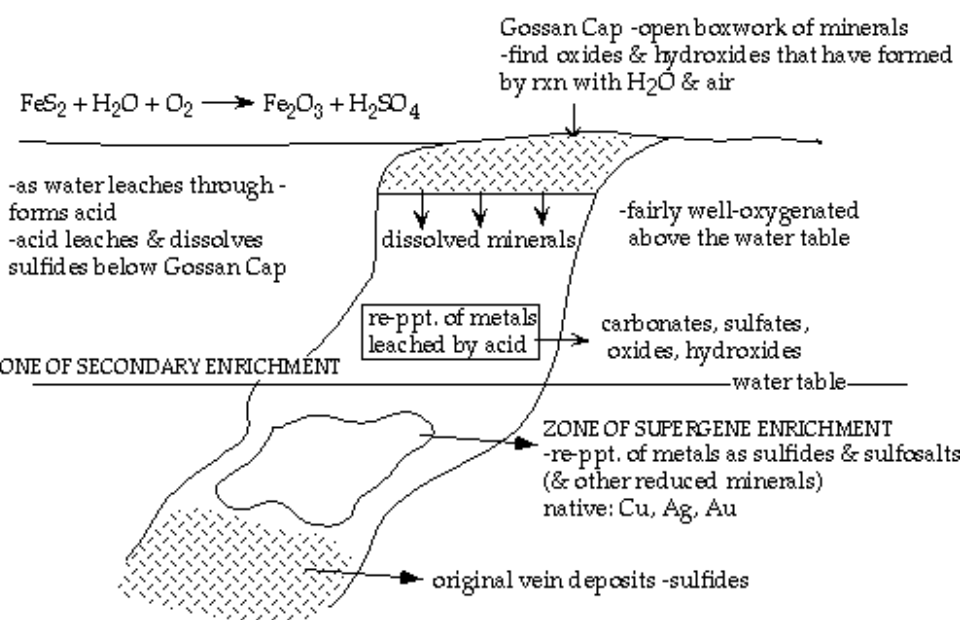
□ The supergene enrichment of sulphide ore is a consequence of near-surface oxidation of sulphides caused by meteoric water seeping downwards. Other agents include dissolved oxygen and microbes that have a role as “self-replicating catalysts”. Sulphide-oxidizing microbes are cultivated in leach pads or large vats in order to decompose sulphide ores of, for example, gold, copper, nickel and cobalt.



1- The oxidation of sulphur and iron pyrite (FeS_2) (or marcasite) produces acidic water/solution. Consequently, weathering of pyrite bearing rock (and other sulphides) is a natural or anthropogenic (due to industry) source of extremely acidic solutions causing acid rock drainage (ARD), or acid mine drainage (AMD). Supergene oxidation of pyrite-rich copper ore (pyrite and chalcopyrite) is illustrated by equations:

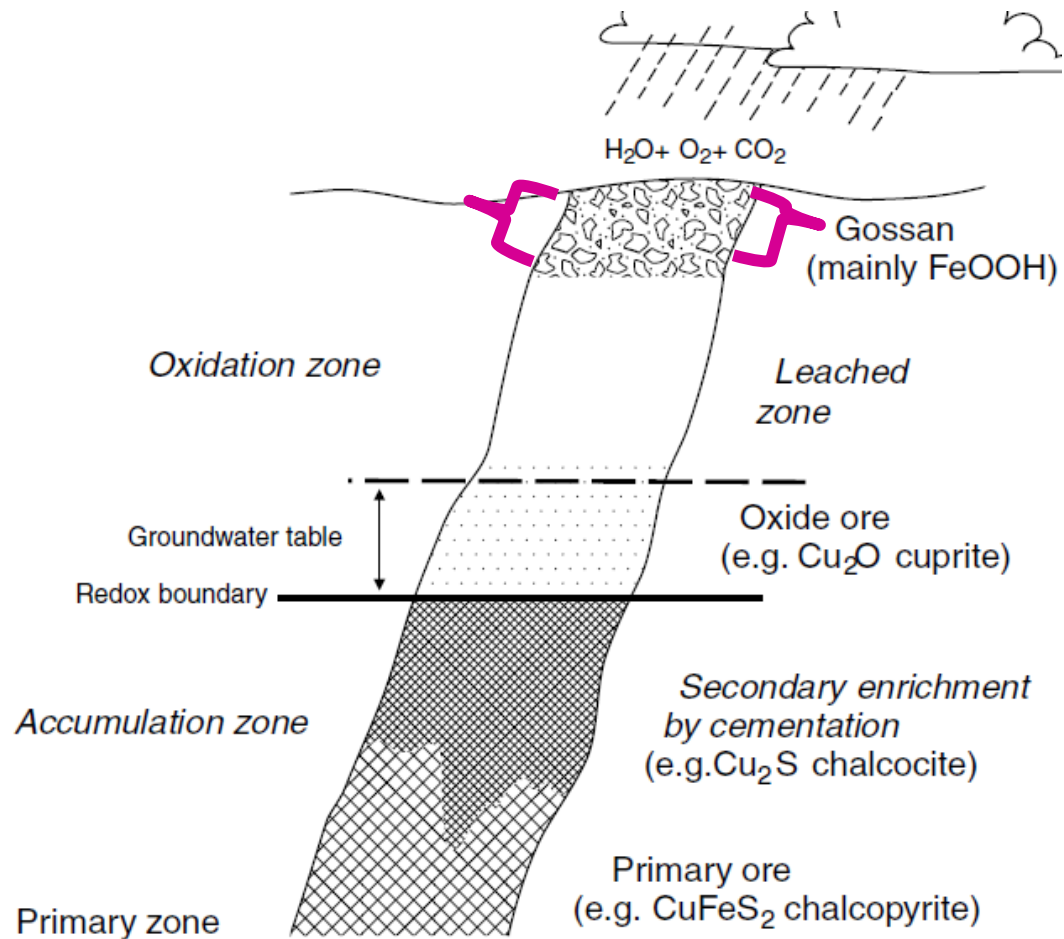


The results are acidic solutions, which move dissolved copper, but also silver, zinc and other metals through unsaturated soil down towards the groundwater.



2- Because of their low solubility in oxic environments, iron hydroxides remain near the surface and form the characteristic botryoidal and cellular limonite-haematite masses of the "Gossan". In addition to iron, manganese and gold are enriched in gossans. Traces of minor metals in the primary sulphides may be preserved, such as Ag, Pb, Cu, Zn, Cd, Mo, Ni, As and Sb. Gossans are often "collapse breccias", because a large mass of the original ore rock was abstracted. Gossans are conspicuous indicators for the possible presence of hidden sulphide ore and therefore, are prime prospecting guides.

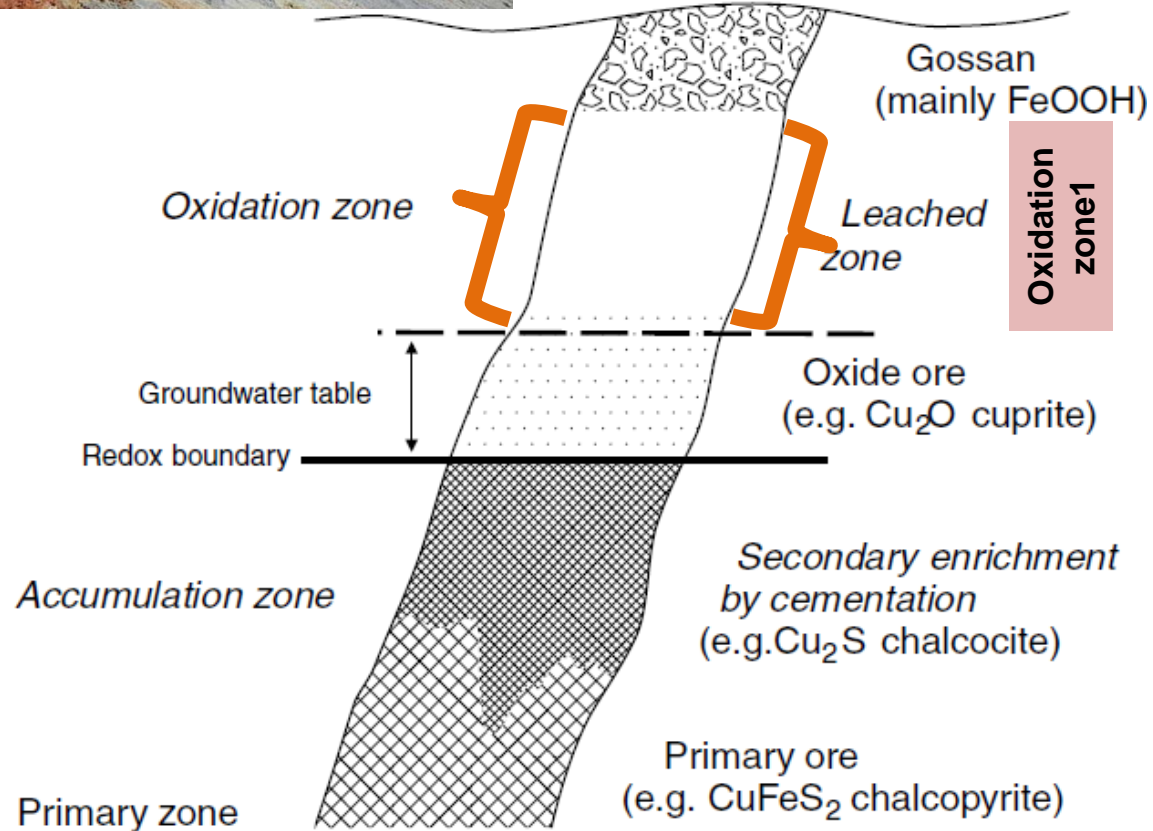
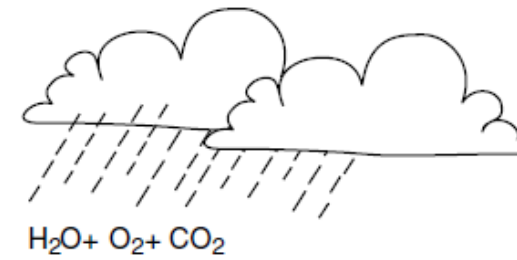
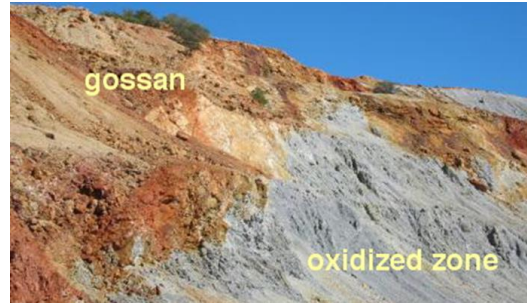
Gossans can be orebodies in their own right, mainly of gold. Of course, not all supergene limonite-haematite masses "gossans" are connected with valuable ore "false gossans". The distinction is possible by mineralogical and geochemical investigations.



Schematic profile of a deeply weathered copper sulphide ore deposit, displaying the supergene "secondary" zonation resulting from redistribution of elements.

3- The zone below the gossan is known as the first oxidation zone, at which the ore is leached reflecting the former passage of strong acidic water. Native copper and copper oxides (cuprite, tenorite), carbonates (malachite, azurite), chlorides (atacamite), silicates (chrysocolla) and sulphates (chalcocite), display a strikingly varicolored paragenesis.

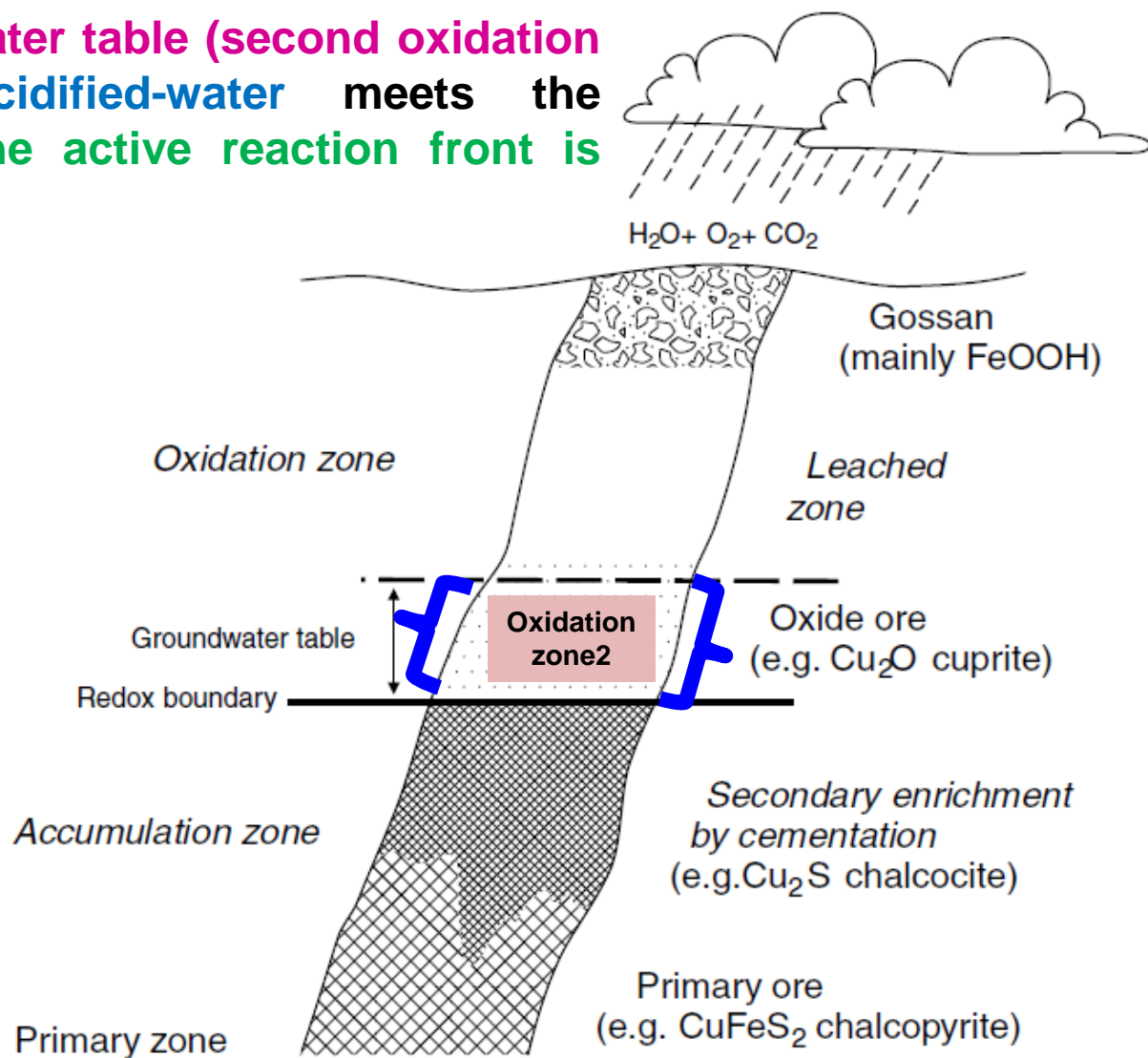
This zone (the leached zone/oxidation zone1) could be enriched to an exploitable volume and grade. Prominent examples are several Chilean copper porphyry deposits that have important “exotic oxide” outliers.



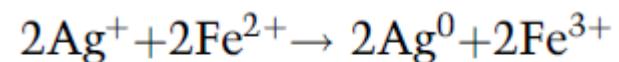
Schematic profile of a deeply weathered copper sulphide ore deposit, displaying the supergene “secondary” zonation resulting from redistribution of elements.

4- In the groundwater area/water table (second oxidation zone), the percolating acidified-water meets the groundwater table, where the active reaction front is reached.

Here, extensive exothermic oxidation of primary sulphides takes place, as well as the secondary enrichment by the aid of thermophilic microbes. The secondary enrichment is referred to the possible oxidation of the CuSO_4 carried by the acidic solution and the deposition of CuO and Cu_2O as a cementing oxides. The efficiency of secondary enrichment depends mainly on conservation of the acidic environment, but also on favourable hydraulic conditions (e.g. permeability).



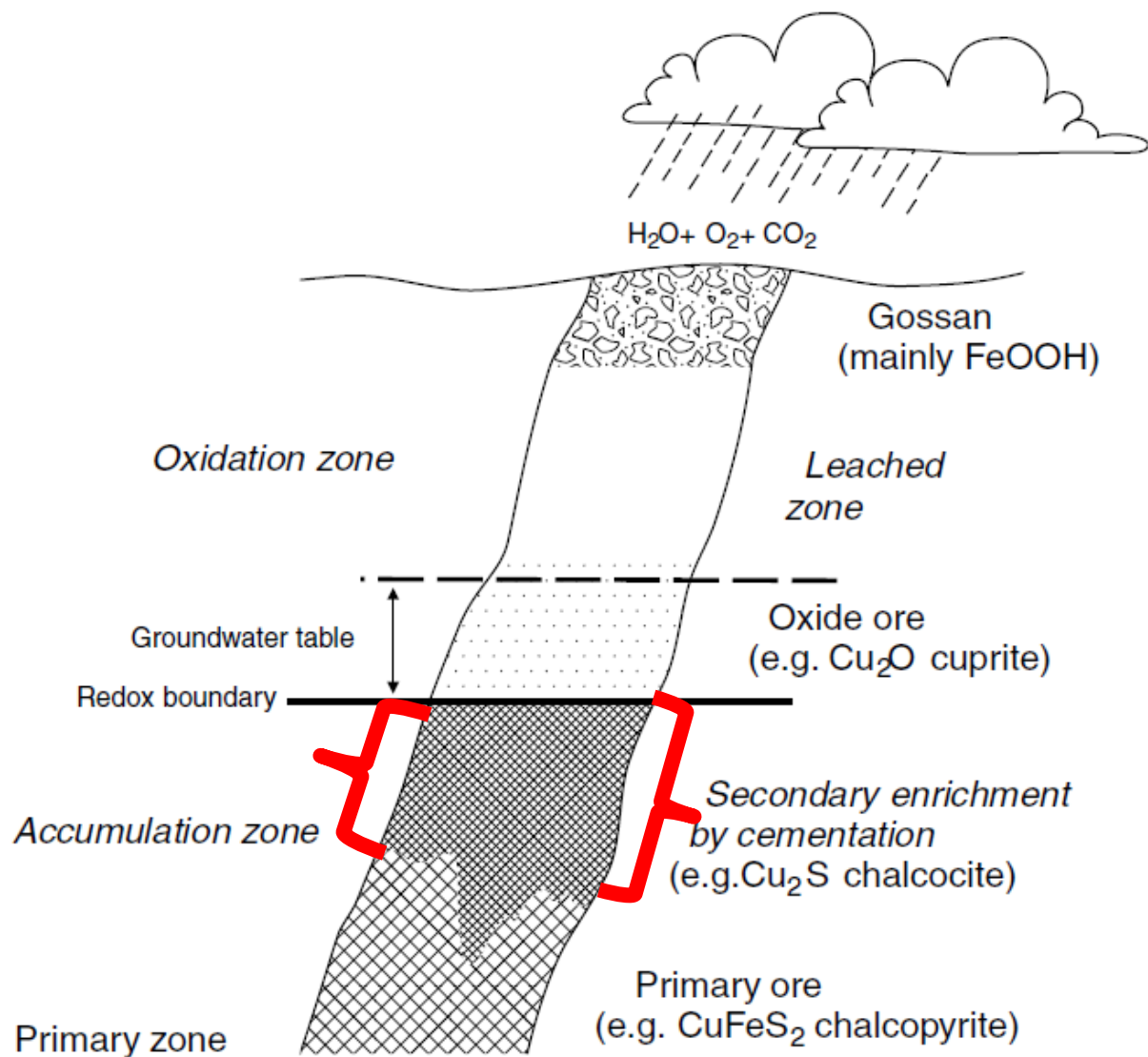
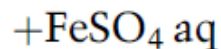
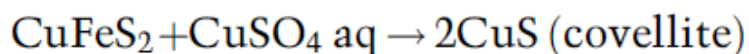
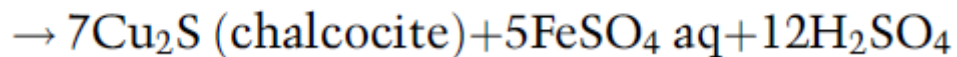
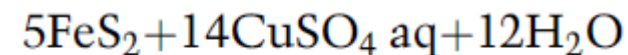
In the second oxidation zone as well, more noble metals (copper, silver, gold) could occur in the native form, which may be explained by a redox reaction:



(in water with dissolved SO_4^{2-})

5- Below the water table, (actually below the Redox boundary), a secondary supergene enrichment zone (accumulation zone) is developed. This is achieved when the enriched CuSO_4 acidic solution is reduced – aided by the microbe actions – and the supergene sulfide phases – chalcocite (Cu_2S), covellite (CuS) and bornite (Cu_5FeS_4) – are deposited as cementing phases.

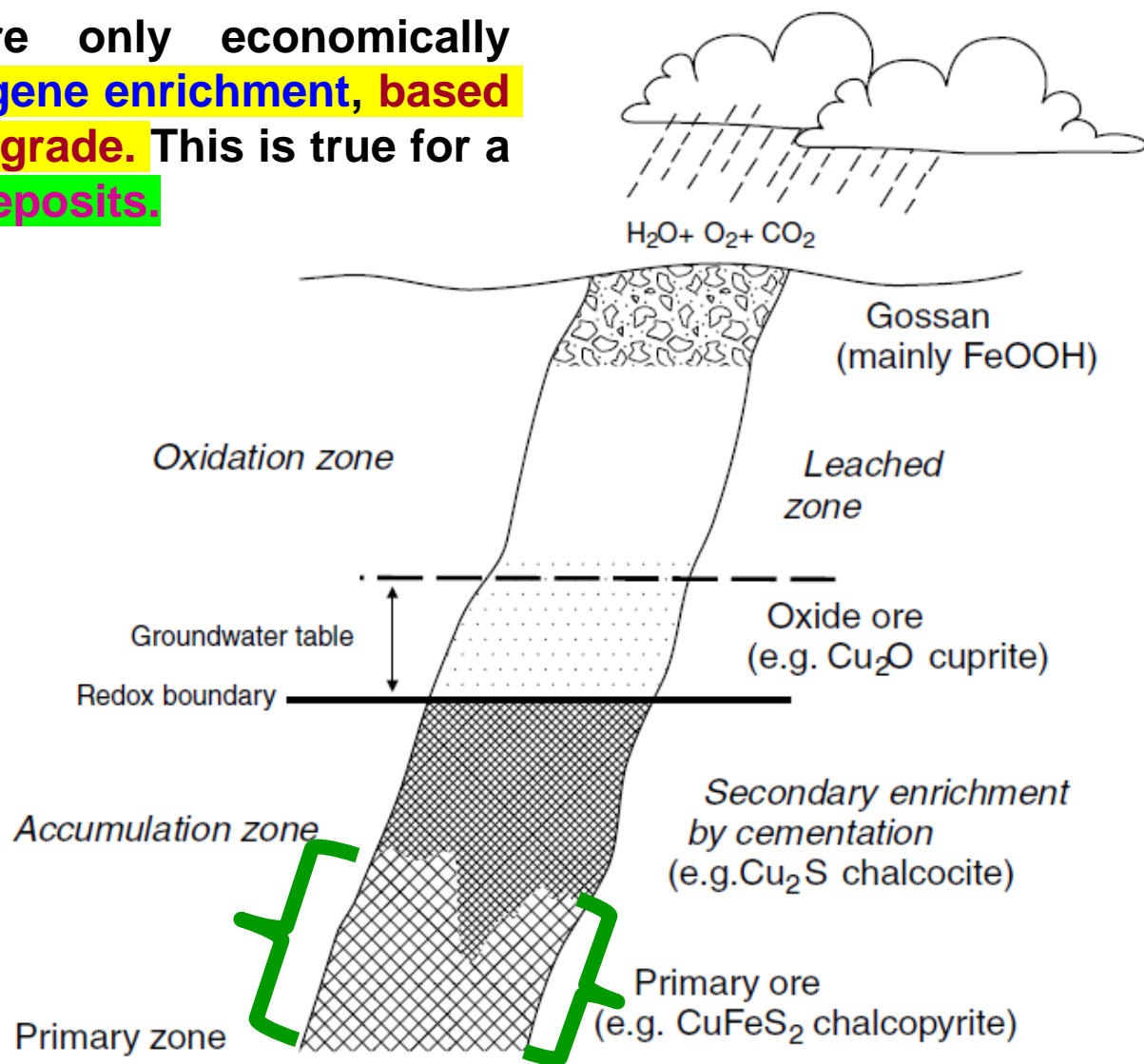
Precipitation of enriched phases can be schematized as a cation-exchange reactions:



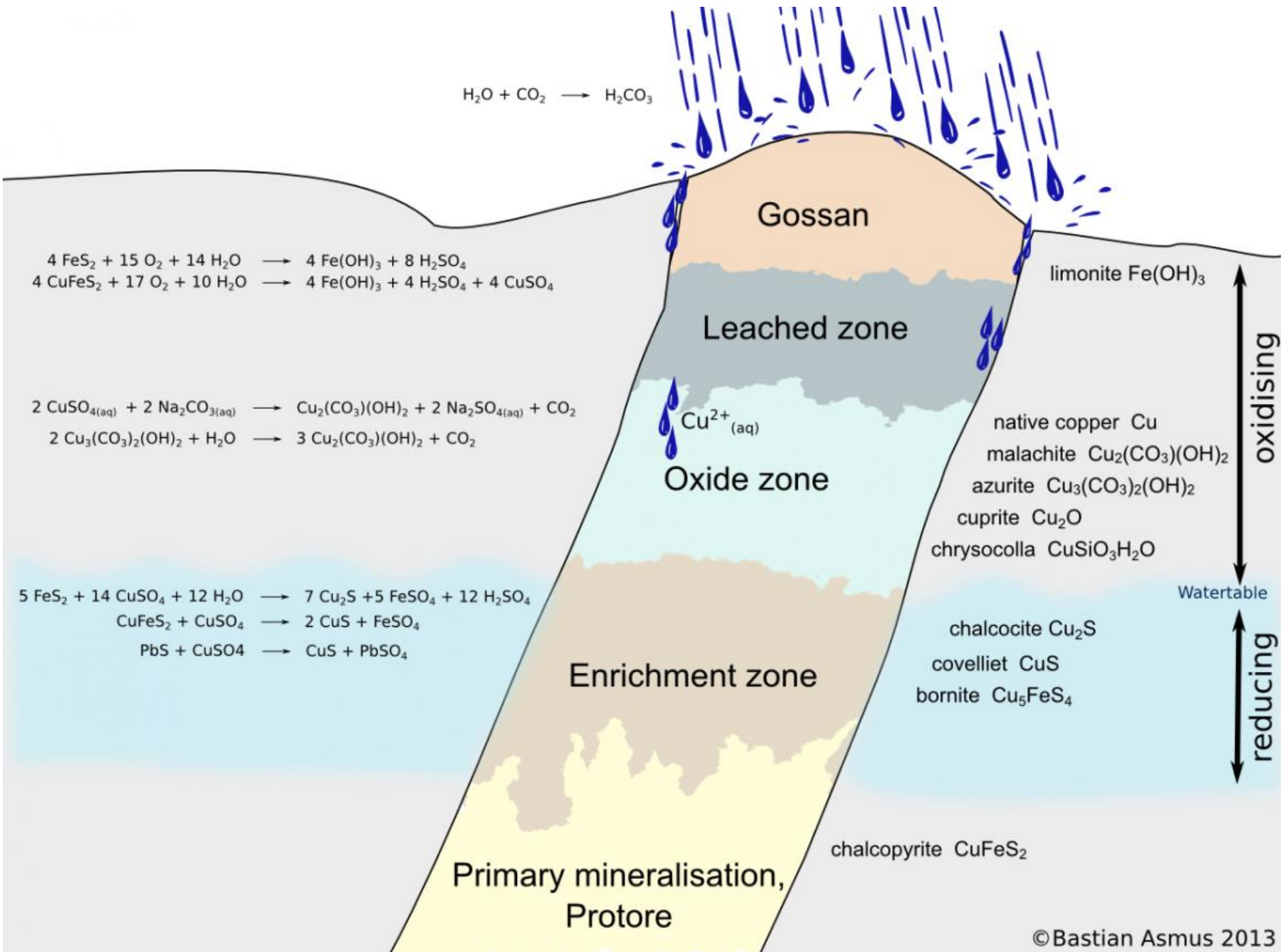
Schematic profile of a deeply weathered copper sulphide ore deposit, displaying the supergene "secondary" zonation resulting from redistribution of elements.

6- Many ore deposits are only economically exploitable because of **supergene enrichment, based on primary sulphides of poor grade.** This is true for a number of **porphyry copper deposits.**

Prolonged weathering of a sulphide ore deposit results in a vertical zonation that comprises a **leached/oxidation zone** and a **metal-rich cementation zone (supergene blanket)**, grading into **unaltered mineralized rock of the primary zone (parent) (protore) (Hypogene zone).**



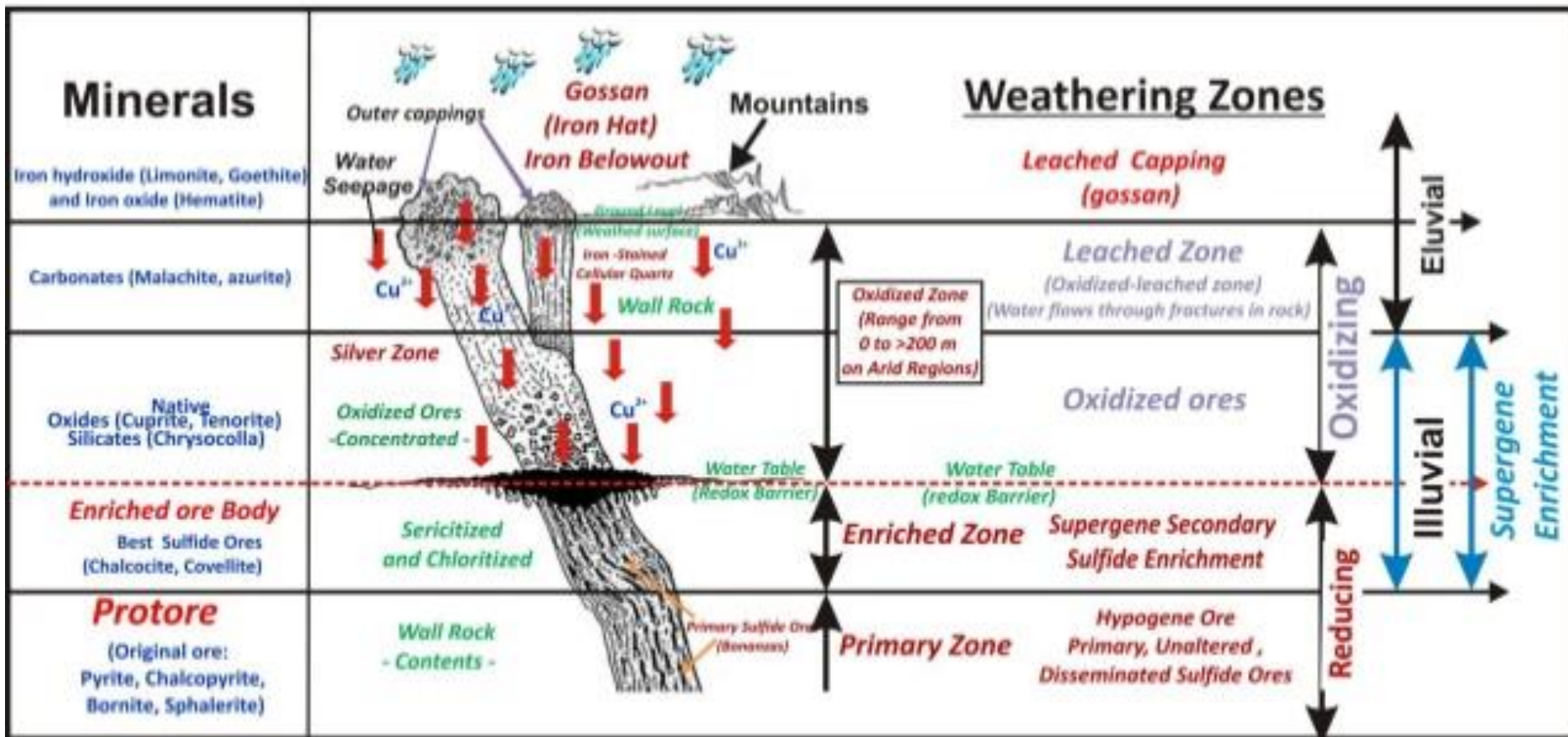
Schematic profile of a deeply weathered copper sulphide ore deposit, displaying the supergene "secondary" zonation resulting from redistribution of elements.



Zones:

Ideally, them, there are three fundamental zones:

- 1) Oxidized zone → leached
- 2) Supergene zone → enriched + Gossans and Cappings
- 3) Hypogene zone {or Protore (parent)}

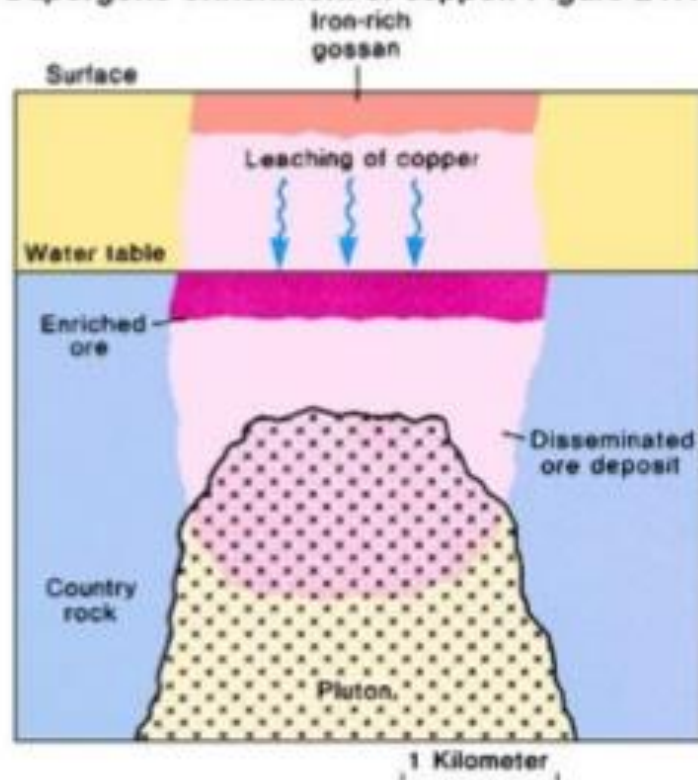


Formation of Copper Oxides

- ❑ Copper ore bodies have been subjected to weathering at or near the surface of the Earth after eons of erosion removed overlying rocks.
- ❑ Oxygenated groundwater, derived from rainwater, trickles through fractures in the rock and forms a **leaching zone** where chalcopyrite, a primary sulfide mineral, is dissolved and oxidized.

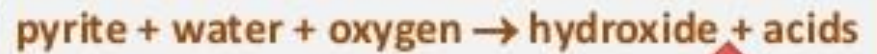
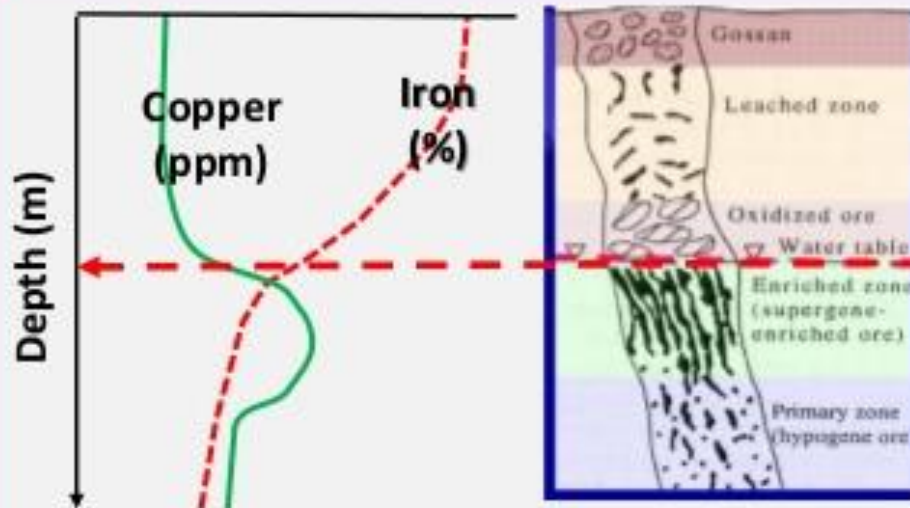
Plummer and McGeary, PHYSICAL GEOLOGY, 7th ed. © 1995 Times Mirror Higher Education Group, Inc., Dubuque, Iowa.

Supergene enrichment of copper. Figure 21.19

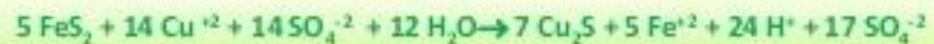
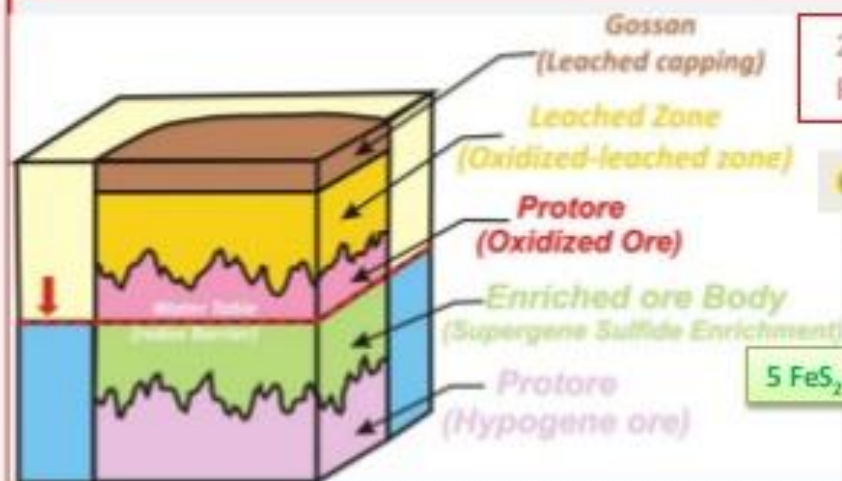
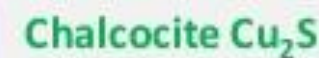


Formation of Copper Oxides





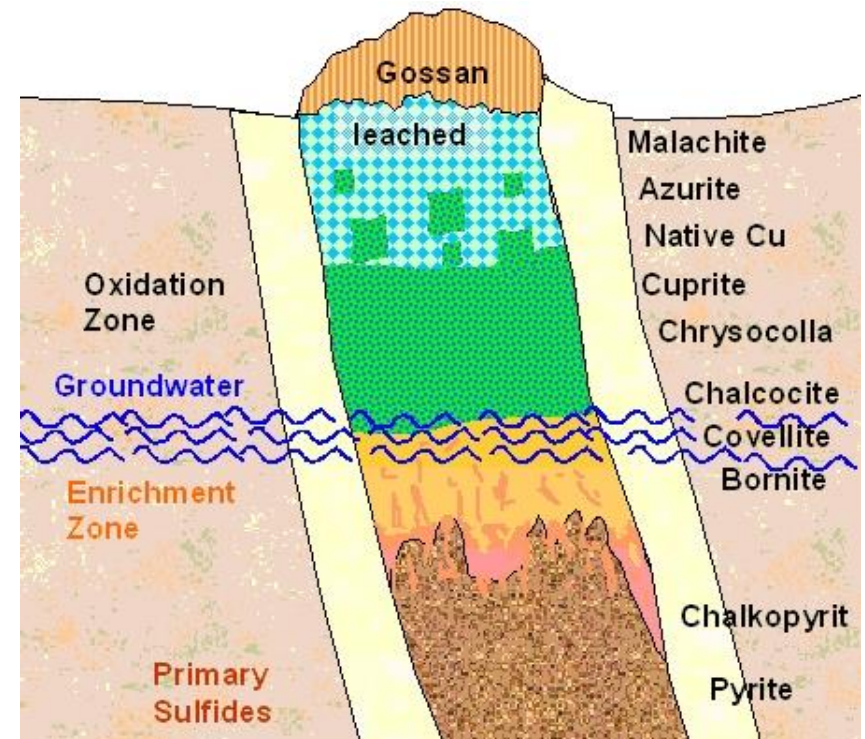
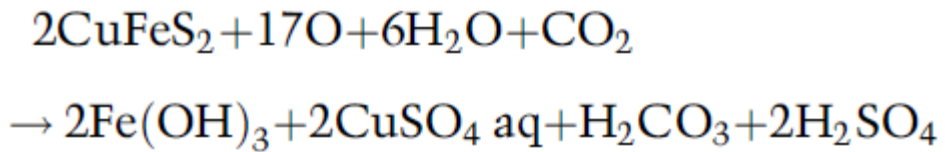
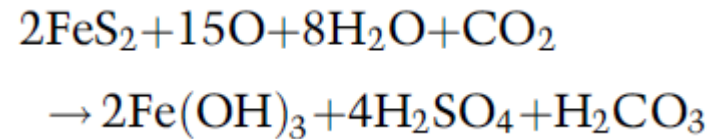
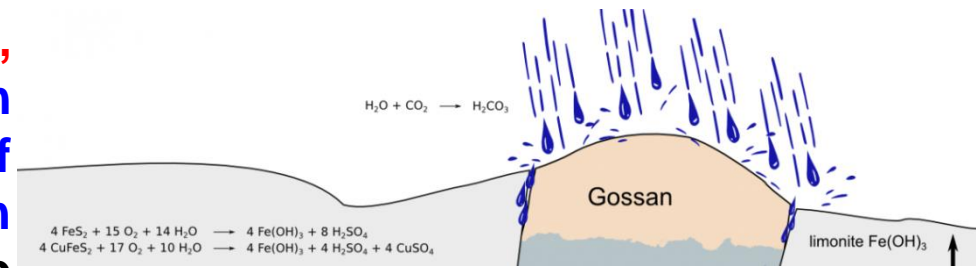
--- → **Water Table**



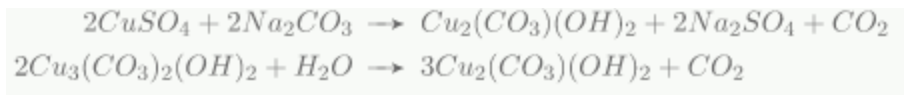
The **gossan** can be called **iron cap**, because it denotes a **concretion of iron hydroxides** that has formed on top of **sulphide mineral vein**, when the vein reaches the surface. It is the very top weathered deposit with only useless stuff. **The gossan** forms during the **supergene sulphide ore enrichment**, when **weakly acid surface water percolates through the mineral deposit**. Many sulphide ores are oxidized in this process and brought into solution:



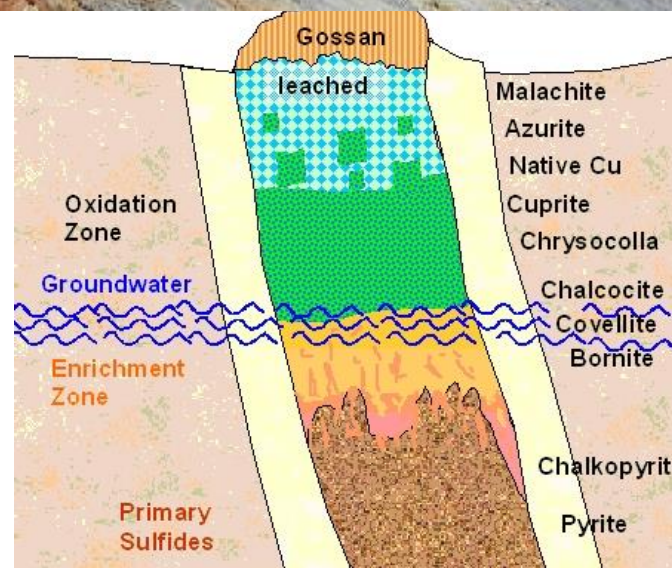
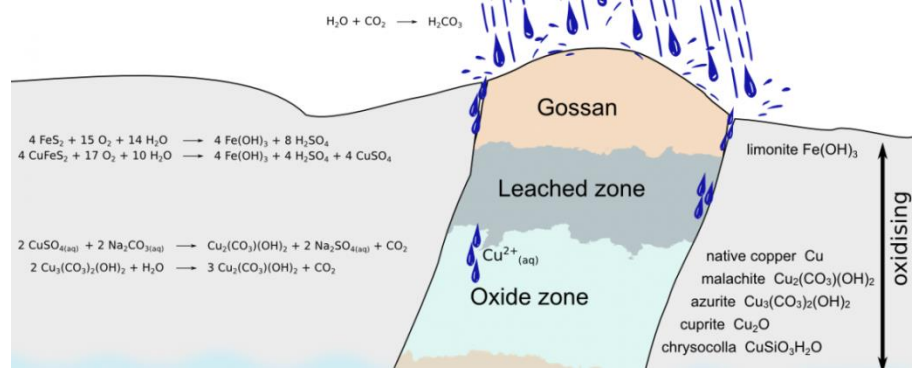
The resulting solution dissolves further minerals. In sulphide ore bodies, **pyrite (Fe_2S)** breaks down to **sulphuric acid** and **limonite ($\text{Fe}(\text{OH})_3$)**. **Limonite is insoluble in water** and remains in the **upper zones of the oxidised ore body**. Since the formation of **limonite** is accompanied by an **increase in volume**, it is easily recognized by prospectors and indicated **the presence of an ore body to below**.



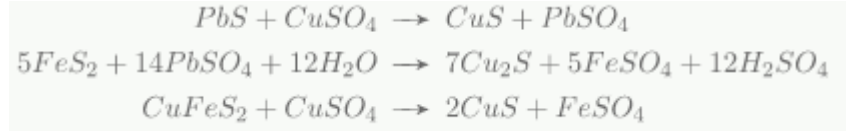
In the underlying **leached oxide zone** other ore minerals are dissolved by the sulphuric acid. The ore body is “leached” and the metal ions are transported down to where they may be partly precipitated as oxides again. A zone with oxidized ore remains. Carbonated, oxidizing water may form carbonates such as malachite or azurite, e.g.:



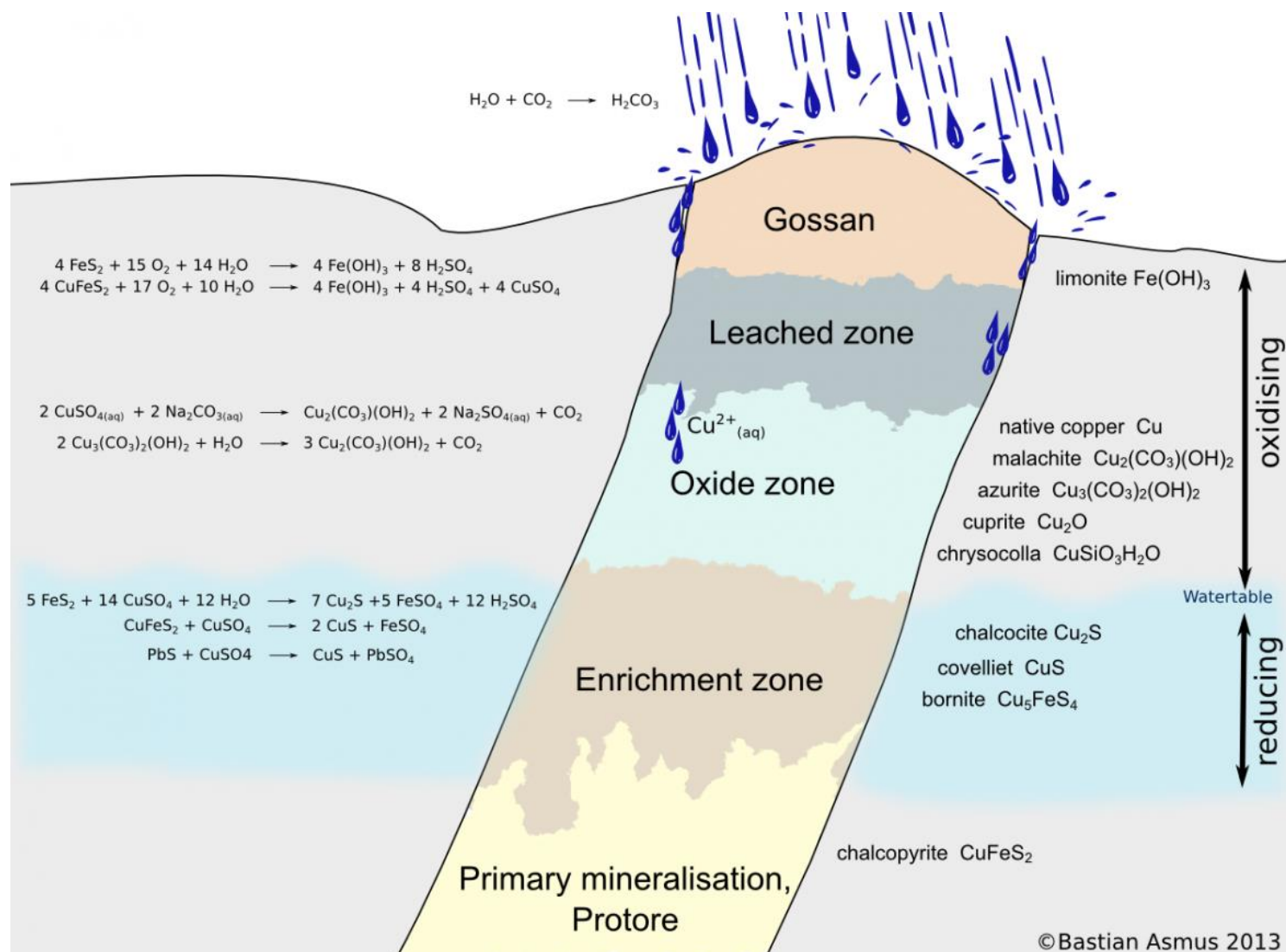
The copper ions of the dissolved copper sulphate CuSO_4 reacts with carbonates which are also easily dissolved in carbonated water. Malachite $\text{Cu}_2(\text{CO}_3)(\text{OH})_2$ or azurite $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$ are thereby precipitated. In contact with water azurite reacts to malachite. However, other ores like cuprite, chrysocolla, or even native copper can occur in this zone.



The greater part of the dissolved metal freight is re-precipitated in the reducing enrichment zone below the water table. Thus the ores of the enrichment zone may significantly surpass the metal content of the primary mineralisation. Typical reactions are:



Schematic view of a sulphide vein. The oxidation zone, consists of the gossan, the leached zone and the oxidised zone. The reducing zone consists of the enrichment zone and the area of primary mineralization.

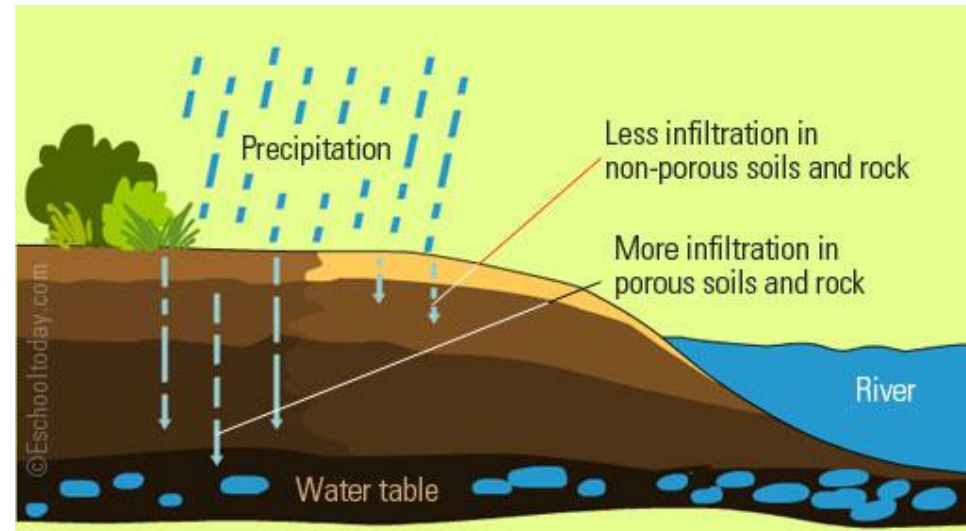


Supergene ore enrichment by Infiltration

Infiltration is used to describe the movement of surface water into soil, porous rock, or karst. **Infiltration ore deposits** are formed when **meteoric waters** take up a substance that is dissolved by weathering, and **concentrate it** after considerable transport **by infiltration** in a different geological setting.

Uranium is a good example, because during **surficial alteration** it is easily dissolved from **granite, gneiss and felsic tuff**, and is transported by creeks and rivers for kilometres, **until infiltrating into an aquifer** where **reduced conditions** cause precipitation and concentration.

Selective weathering of different minerals may produce a pattern of **spatial or temporal separation**, for example by **first leaching traces of uranium, copper and zinc** from plagioclase and Fe-Mn oxyhydroxides, followed by barium, lead and SiO_2 when the more stable K-feldspar is decomposed.

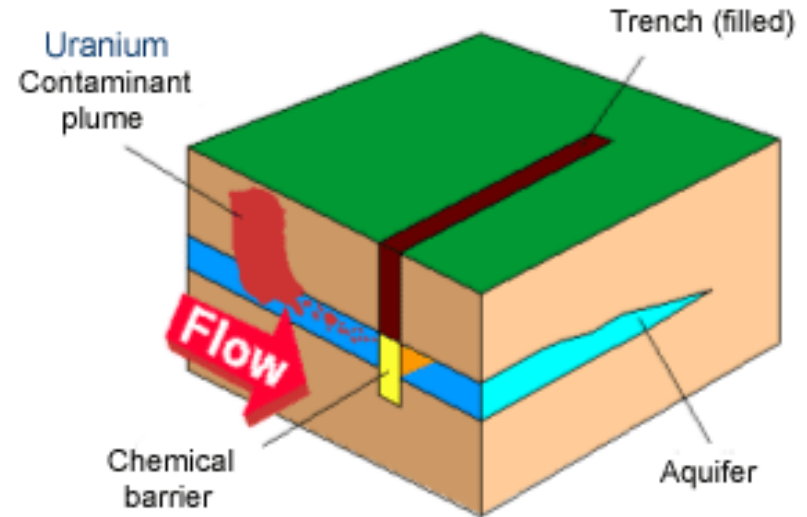


Copper, lead and silver ores embedded in haematitic sandstone suites "**red bed deposits**" may have originated in a way similar to infiltration deposits of uranium (e.g. the Transfiguration deposit in Quebec, Canada).

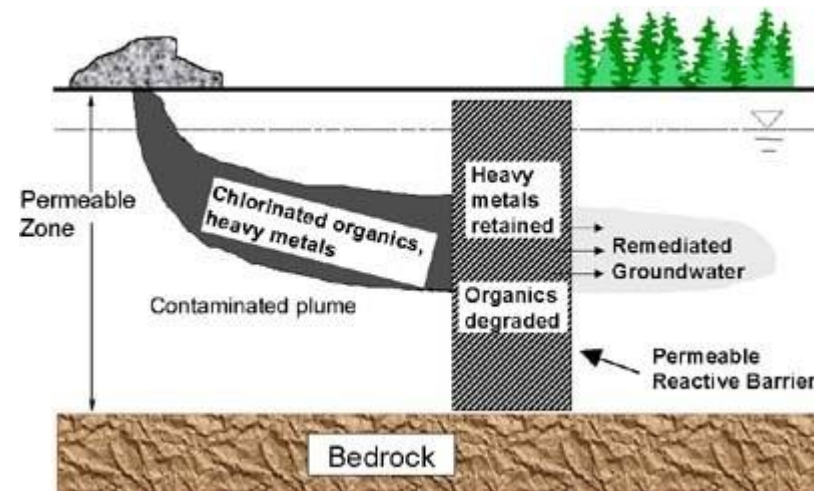
□ **Uranium infiltration mineralization** The concentration of solutes (solved material) in surface and groundwater is generally very low. Enrichment to **ore-grade** and an exploitable volume is only possible where a large mass flow is focused into a highly efficient filter.

Geochemical barriers are most effective, commonly in the form of a **rapid change of pH and Eh**. Geological actors include carbonates, H_2S or SO_4 in the pore waters, as well as **organic matter**. Because precipitation takes place in pre-existing rock, **infiltration mineralization** is clearly epigenetic process. **Infiltration deposits of uranium** are very common and economically important. **Oxidative chemical weathering** transforms uranium (IV) in rocks to uranium (VI), which forms complex ions with free SO_4 , CO_3 , OH , alkalis and humates.

Under oxic conditions (low oxygen) in surface and groundwater, these complexes are stable and allow long distance transport. Geochemical barriers for uranium are phosphates, arsenates, vanadates and carbonates in percolated rocks.



Schematic diagram of a reactive barrier.

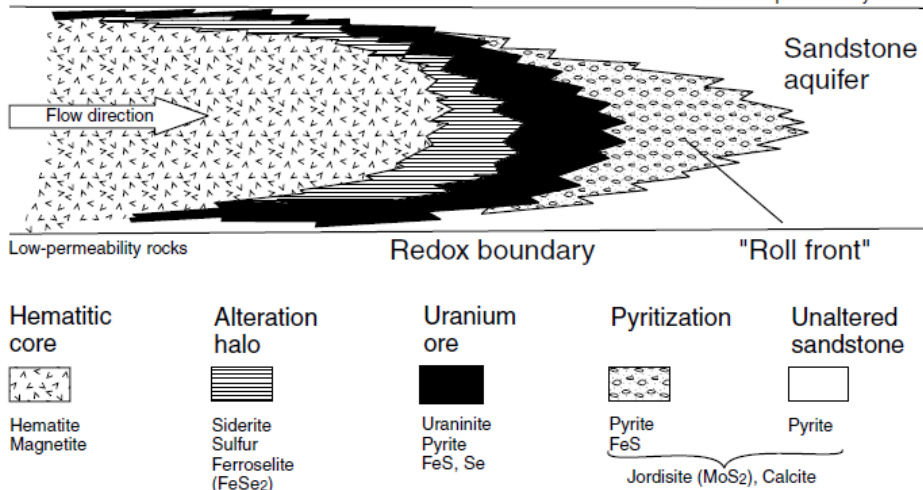


Uranium infiltration mineralization and ore deposits occur in permeable sandstone and conglomerate (Colorado Plateau, or "sandstone type"), in

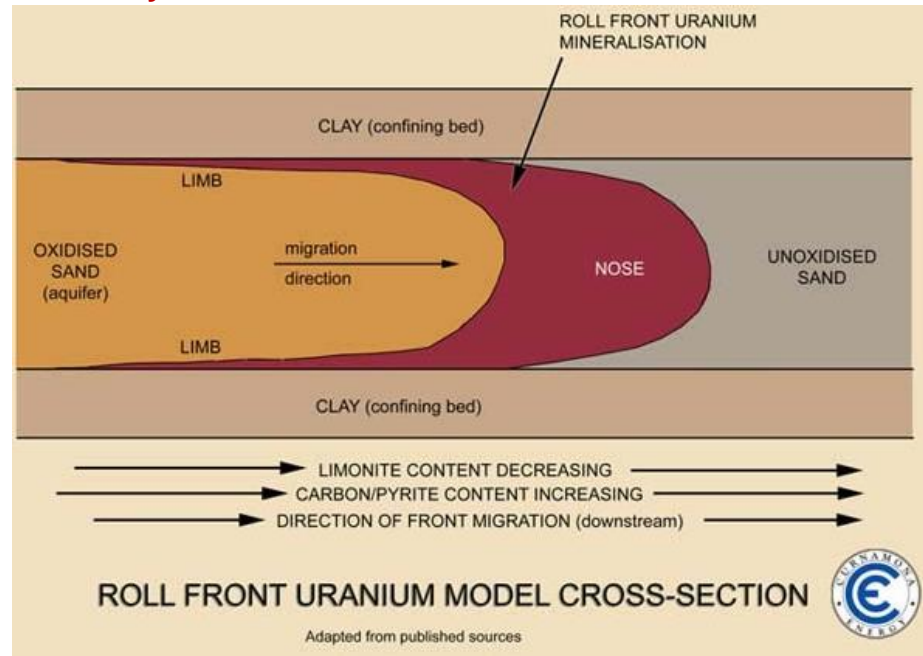
volcanic ash beds, in faults and breccia bodies, in peat, lignite and coal seams, in asphalt, and in terrestrial calcite crusts of semiarid lands (the "calcrete type"). The genesis of the last includes a pronounced component of evaporation.

The shape of orebodies varies widely, including tabular lenses, pockets and the characteristic "roll fronts", often in connection with buried river courses.

Roll fronts mark the redox boundary in space and time where the infiltrating meteoric water lost its capacity to oxidize the percolated sandstone and to retain – the sandstone – uranium in solution. Ore minerals include coffinite, uraninite, vanadium-rich clays and minor sulphides (of Fe, Mo, Cu, Pb, Zn, Se, etc.).



Roll front uranium orebodies develop, where infiltrating uraniferous meteoric water passes through a redox boundary.



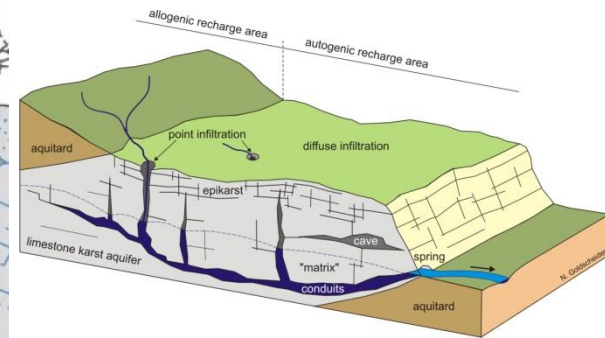
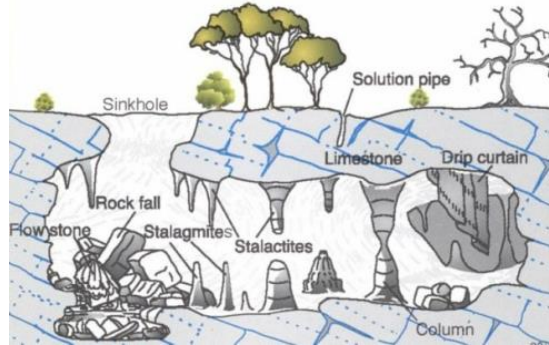
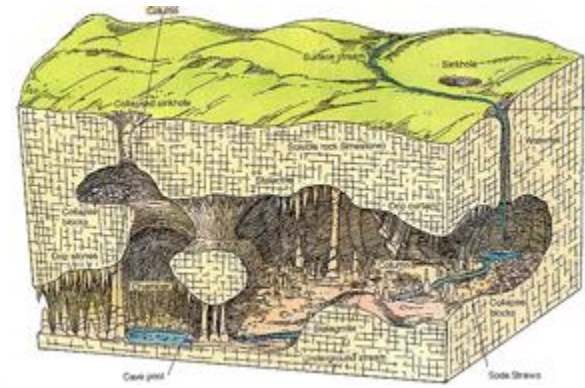
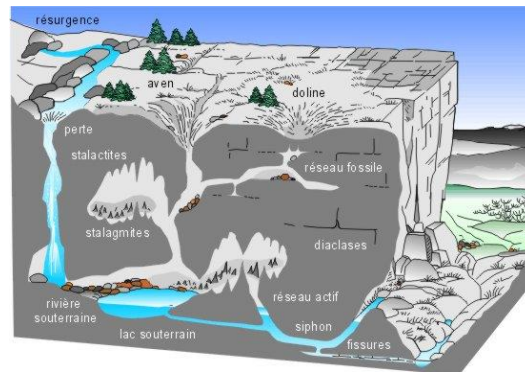
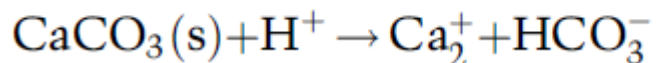
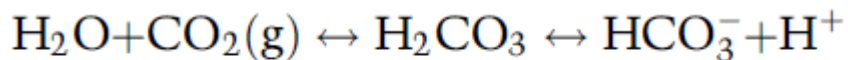
Roll-front deposits cut across bedding. Uranium-bearing ground waters precipitate uranium oxide minerals when they come in contact with reducing conditions.

□ Karst systems

Formation of **karst systems** in **carbonate rock bodies** and the **contemporaneous deposition of mineralization in the caves** may also be related to **infiltration processes**.

Karst formation is caused by **infiltration of meteoric water, which is enriched in CO₂**, for example by percolation through the organic soil horizon.

Dissociation of carbonic acid produces acidity (H) that is essential in limestone dissolution. Because of a much slower reaction rate, dolomite is less affected by **karstification**.

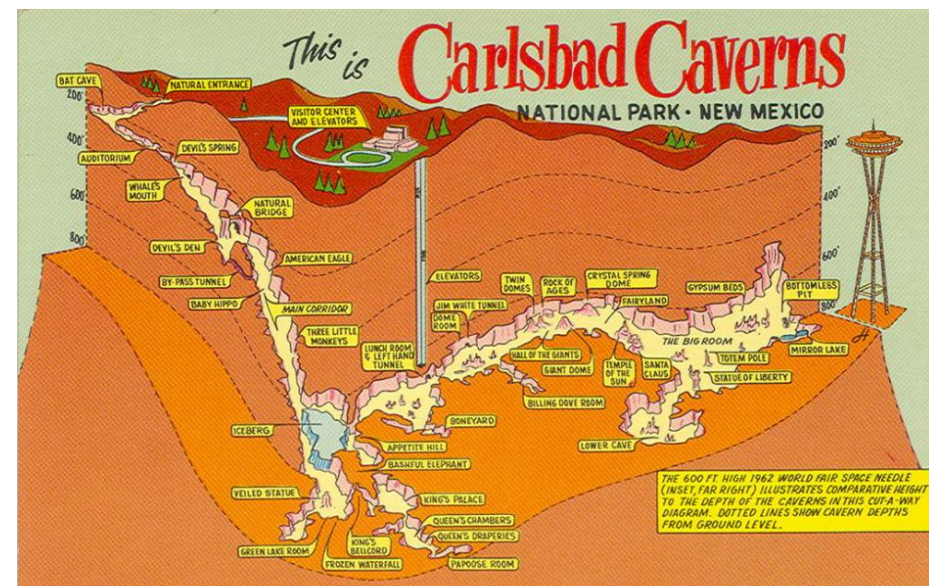


There are three possible modes of ore deposit formation in karst:

1. **Hydrothermal karst** originating from **hot ascending fluids**. Structural relations such as cementation of host rock karst breccia by **sulphides** reveal **simultaneous calcite dissolution and sulphide precipitation** (Carlsbad caves in New Mexico) (note the possible connection with metasomatic ore formation).

2. **Common meteoric karst**, formed by **downward percolating water with dissolved carbon dioxide**, which was later filled by ascending hydrothermal fluids with ore and gangue, independent of karstification.

3. **Common meteoric karst**, and synchronous supergene infiltration of ore elements.



End of Lecture