Radionuclides in the ecosystems :

sources, ecodynamics and impacts

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EJC 2019, 22-27 september 2019, Oléron

INTRODUCTORY PART

WEATHERING & SOIL CHEMISTRY
ENVIRONMENTAL RN CHEMISTRY
LL RADIOACTIVE WASTES & TENORM
IN FRANCE

INTRODUCTORY PART

THE CRITICAL ZONE

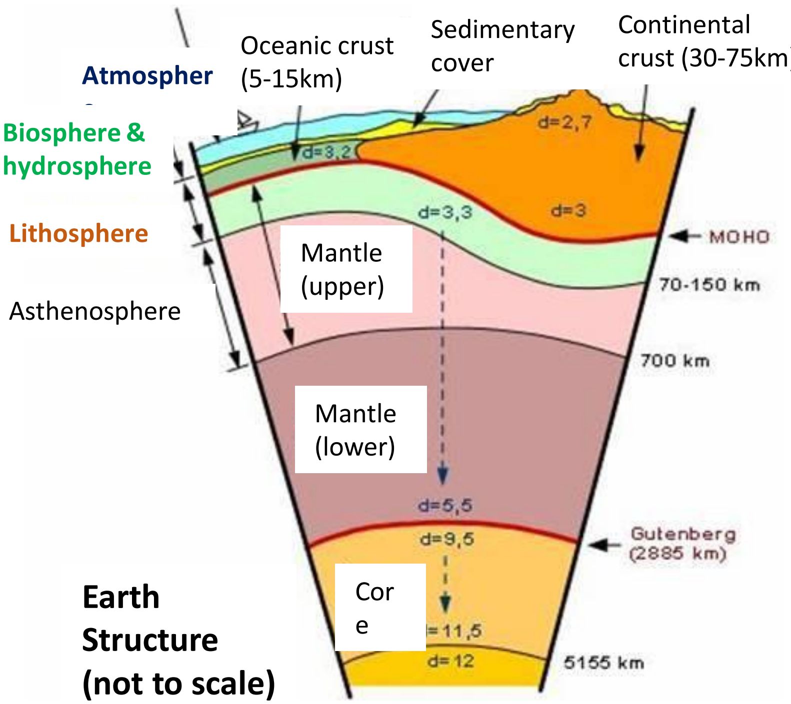
SOURCES OF RN

CHALLENGES : FATE OF RN

What is the Environment ?

A very thin pellicle at Earth's surface

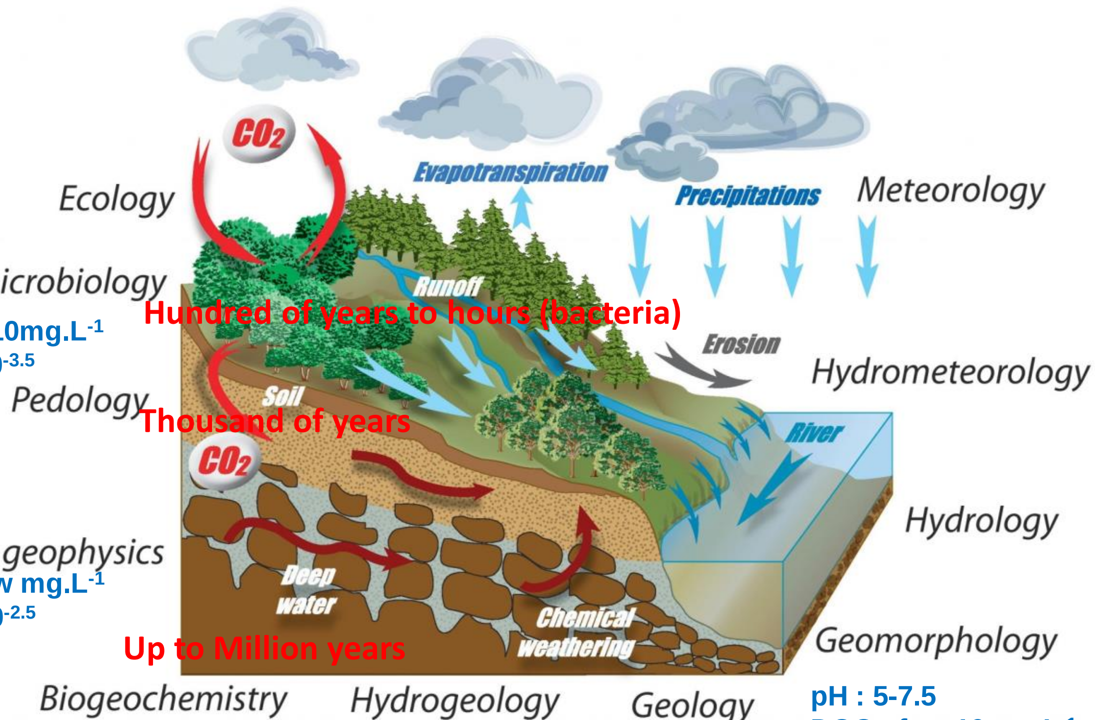
At the interface between lithosphere, hydrosphere, biosphere and atmosphere



Earth Structure (not to scale)

The Critical Zone

"A zone where interactions between rock, soil, water, air and living organisms control habitats and life-sustaining resources"



pH : 4-6
DOC : > 10mg.L^{-1}
pCO_2 : $10^{-3.5}$

pH > 7
DOC : few mg.L^{-1}
pCO_2 : $10^{-2.5}$

pH : 5-7.5
DOC : few-10 mg.L^{-1}
pCO_2 : $10^{-3.5}$

Natural processes & transformations

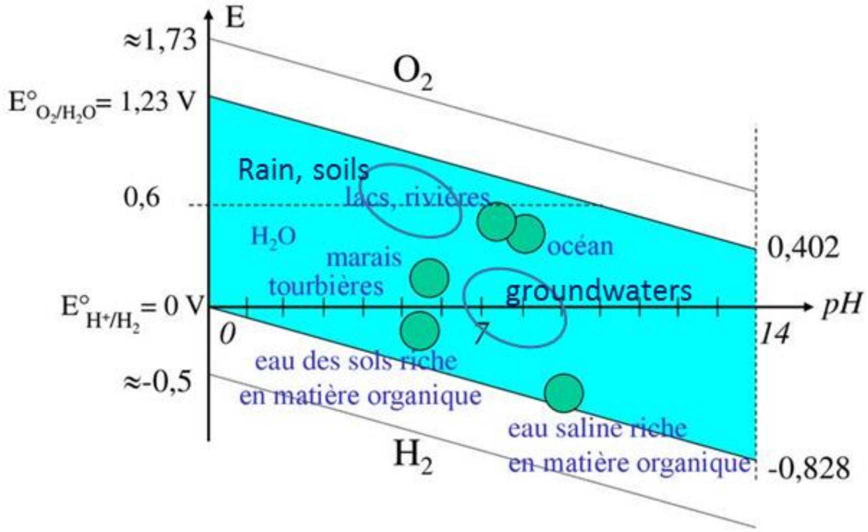
Rock alteration, soil formation, water and carbon cycle, life growth, biogeochemical cycles

- Time-scale variations
- Spatial variations
- Chemical variations

The Critical Zone

"A zone where interactions between rock, soil, water, air and living organisms control habitats and life-sustaining resources"

Domains of natural waters



Natural processes & transformations

Rock alteration, soil formation, water and carbon cycle, life growth, biogeochemical cycles

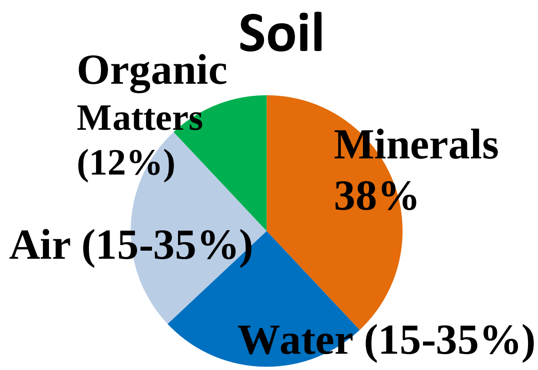
- Time-scale variations
- Spatial variations
- Chemical variations

The Critical Zone

Environmental soil chemistry

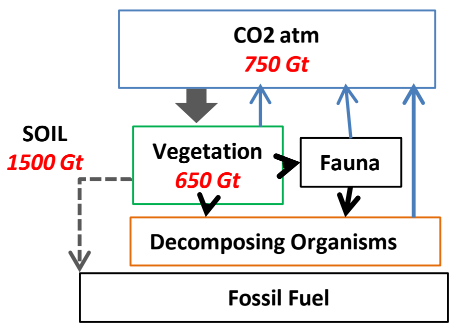
Soil takes thousands of years to form…

Recycling of organic matters

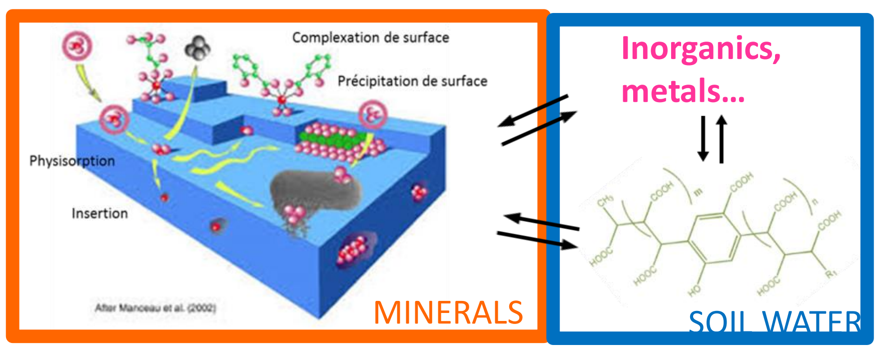


→ Supply of elements to biosphere

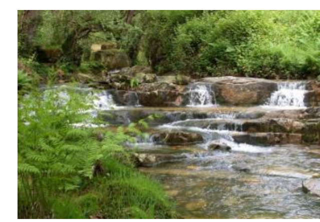
Storage of Carbon



Source INRA 2002



→ Control of water composition



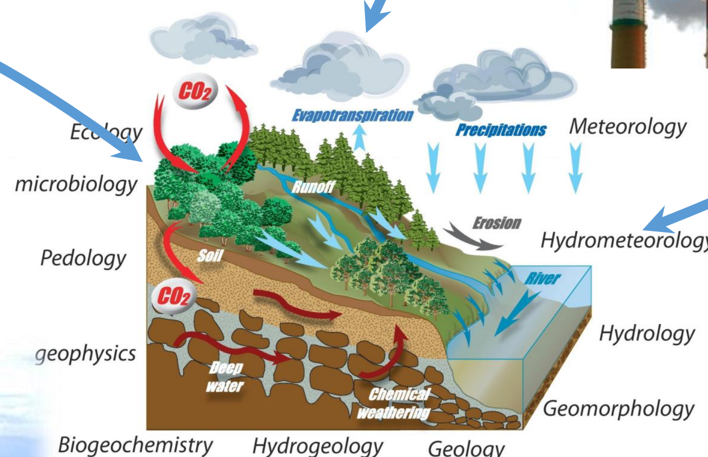
An element transfer depends on its speciation

The Critical Zone

Agriculture

Urban, domestic

Industry



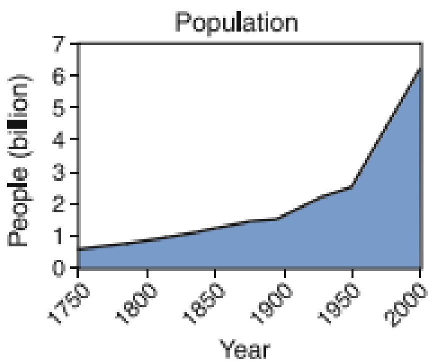
Anthropogenic pressures

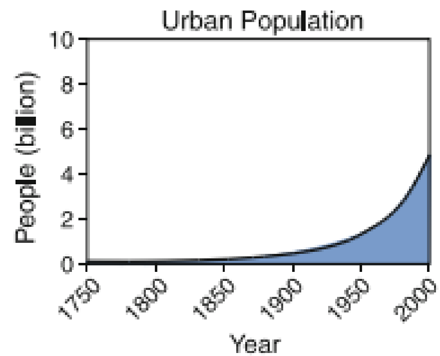
- Recent
- Cycles of water, soil, C

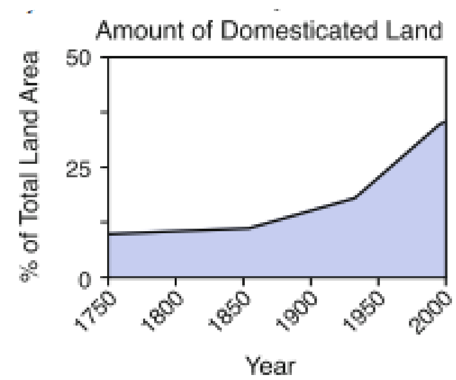
The Critical Zone

Anthropogenic pressures

Population growth, urbanization, industrialization, intensive agriculture, deforestation…





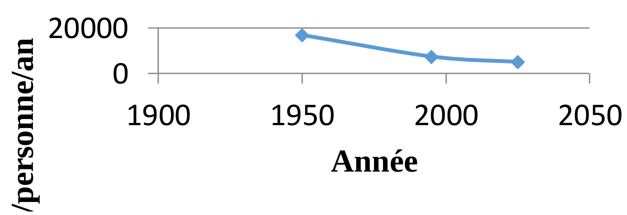


Steffen et al. (2011). "The Anthropocene: From Global Change to Planetary Stewardship". AMBIO, 40:739–761

Consequences :

Decrease of the world's resource in drinkable and available waters

Eurostat Source 2002



Decrease of soil resource

- 12 % of the world's land are farmed.
- Circa 50% of world soils are degradated (source FAO)

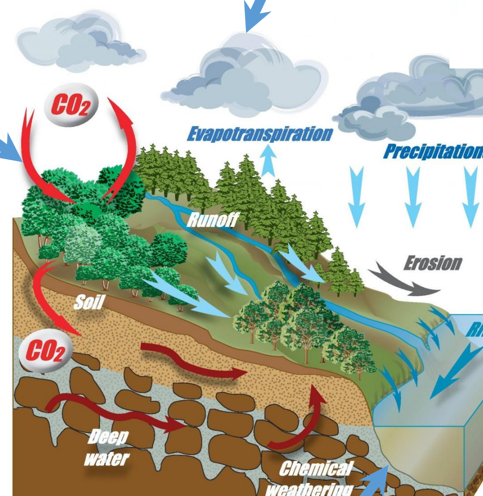
The Critical Zone

Agriculture

- Alkylphénols
- Pesticides
- Metals

Industry

- Alkylphénols
- Chloroalkanes
- PAH
- VOC
- Heavy Metals



Urban, domestic

PAH, VOC, Chloroalkanes,
Alkylphenols, Parabens, Phtalates
- Pharmaceutical residues
- Heavy metals

Anthropogenic pressures

- Recent
- Cycles of water, soil, C
- Micropollutants
- All compartments

INTRODUCTORY PART

THE CRITICAL ZONE

SOURCES OF RN

CHALLENGES : FATE OF RN

Sources of radionuclides

Cosmogenic radionuclides
Tritium, Carbon 14, Krypton 85...

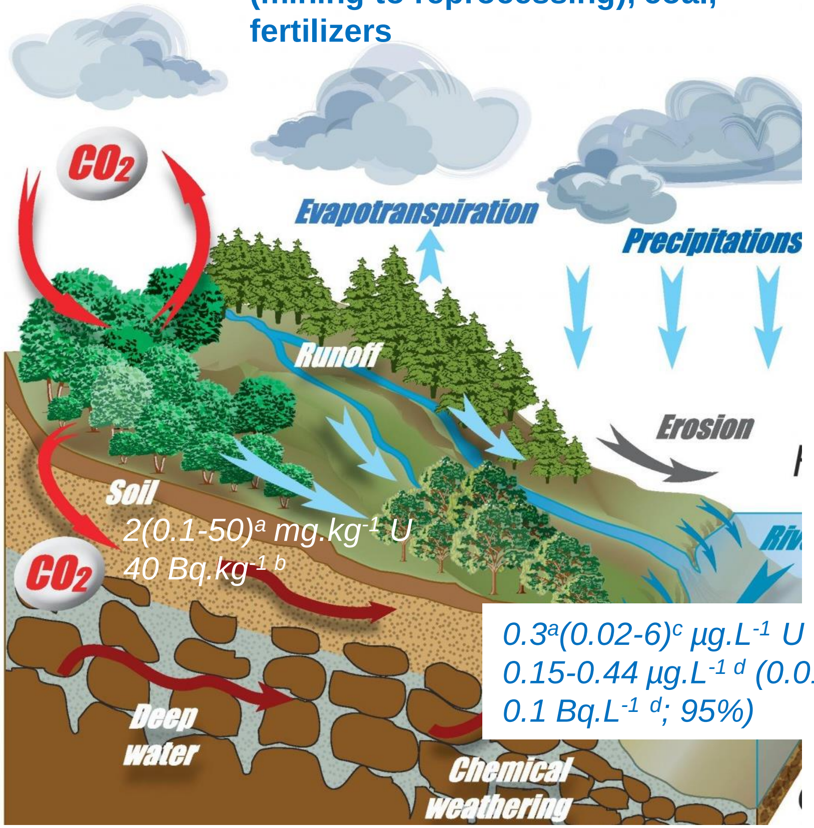
Natural RN – NORM

TENORM : nuclear industry (mining to reprocessing), coal, fertilizers

Air radionuclides
Radon 219, 220, 222

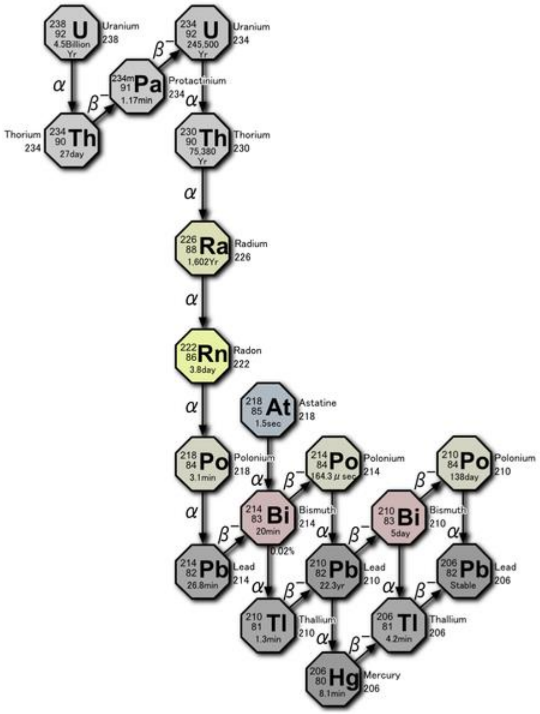
0-150 Bq/m^3 in habitats in France[e]

Telluric radionuclides:
potassium 40, and decay series of Uranium 238, Uranium 235, Thorium 232
Black shales, granites
300-5 mg.kg^{-1}



0.3[a]*(0.02-6)*[c] *µg.L^{-1} U*
0.15-0.44 µg.L^{-1}[d] *(0.01-0.1 Bq.L^{-1}*[d]*; 95%)*

Radioactive decay chain of ^{238}U



[a]De Vos & Tarvainen, 2006 (Europe); [b]Le Roux (France); [c]Bonin & Blanc, 2001 (Europe); [d]Salpeteur & Angel, 2010 (France); [e]IRSN (France)

Sources of radionuclides

Artificial RN

Nuclear weapon test

Carbone 14, Strontium 90, Iodine 129 (410 GBq)[a], Cesium 137(948 PBq)[a], Americium 241, Plutonium 238 (0.3 PBq)[a], 239, 240, (13 PBq)[a], 241 (170 PBq)[a]…

Reprocessing & Nuclear PP

Tritium, Carbon 14, Cesium 137 (6.24 TBq in 2004, Sellafield)[b], Cobalt 60, Iodine 129, 131 (520GBq in 1997, Sellafield)[c] Technitium 99 (1 000 TBq,1984, RP)[d]

Radionucléide	Half life	Emissions
^{3}H	12.32 yr	β
^{14}C	**5 730 yr**	β
^{60}Co	5.27 yr	β, γ
^{90}Sr	28.78 yr	β
$^{129,\ 131}I$	**1.57 million yr** 8 d	β, γ
^{137}Cs	30.07 yr	β, γ
^{238}Pu	87.7 yr	α
$^{239,240,241}Pu$	**24 100** **6 560** **14290 yr**	α α β, α
^{241}Am	**242 yr**	α, γ

[a] UNSCEAR, 1982; [b] CEFAS, 2004, [c] BNFL, 1997, [d]Luykx, 1986

Sources of radionuclides

Nuclear accidents

UO2, Iodine 129, Cesium 137 (85 PBq)[a], Americium 241, Plutonium 241 (6 000 TBq)[a]…

ACCIDENTS
MANUFACTURING (e.g. U : ORNL, Pu :Rocky Flats, USA)
DISPOSAL HLW WASTES (Pu, SRS USA)
IMMERSION OF WASTES
MILL TAILING STORAGE (e.g. Fry Canyon, UT, USA

Radionucléide	Half life	Emissions
^{3}H	12.32 yr	β
^{14}C	**5 730 yr**	β
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[a] UNSCEAR, 1982; [b] CEFAS, 2004, [c] BNFL, 1997, [d]Luykx, 1986

Sources of radionuclides

Skipperud and Salbu, 2018 : selected sources of artificial RN in environment

Maher et al. Inorg. Chem, 2013 (USA)

Thakur et al., Sci. Tot. Environ., 2013, (RN in northern hemisphere, Fukushima)

Sources of radionuclides

Main artificial RN present in the environment, France (IRSN source)

Radionucléide	Half life	Emissions	Descendant	Origin
^{3}H	12.32 yr	β	^{3}He	Cosmic, Nuclear tests, releases of nuclear and clock industry
^{14}C	5 730 yr	β	^{14}N	Cosmic, Nuclear tests, Nuclear and research industry
^{60}Co	5.27 yr	Β, γ	^{60}Ni	Nuclear industry
^{90}Sr	28.78 yr	β	^{90}Y	Nuclear tests, Nuclear industry
^{131}I	8 d	β, γ	^{131}Xe	Nuclear industry and medicine
^{137}Cs	30.07 yr	β, γ	^{137}Ba	Nuclear tests, Chernobyl, Nuclear industry
^{238}Pu	87.7 yr	α	^{234}U	Nuclear tests, Nuclear industry
$^{239+240}Pu$	24 100 & 6 560 yr	α	$^{235+236}U$	Nuclear tests, Nuclear industry

< 5 000 Bq.m-^{2} soils
(up to 40 000 in East)
<1 µBq.m^{3} air; 0.01-0.1 mBq.L^{-1}

Behavior and fate in the environment ?

Challenges : Fate of RN

Distribution coefficients water-soil Kd ($Bq.kg^{-1}$ dry soil / $Bq.L^{-1}$)

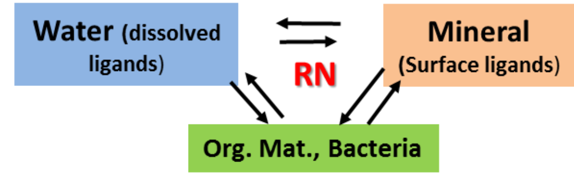
	^{238}U	^{241}Am	^{137}Cs
Sandy soil	33	2000 (11 – 2.6 10^5)	270
Clayey soil	1500	8100 (45 – 1.5 10^6)	1800
Silty soil	12	990 (600 – 1.6 10^5)	4400
Organic soil (> 30% organic matter)	400	1.1 10^5 (3.6 10^3 – 3.3 10^6)	270

IAEA, 1994

Need to rationalize knowledge on radionuclide fate and water-soil-plant transfers

INTRODUCTORY PART

THE CRITICAL ZONE
SOURCES OF RN
CHALLENGES : FATE OF RN

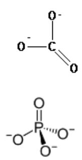


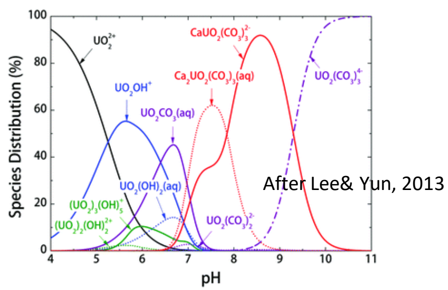
Challenges : Fate of RN

Speciation determines mobility, bioavailability (ecotoxicity) and transport of RN

Key is speciation

Mobile species - - - - - - - -> **Mobile to immobile**

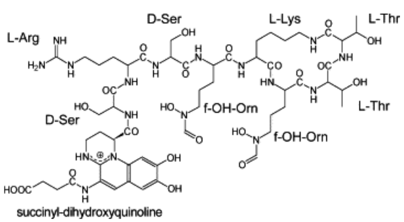


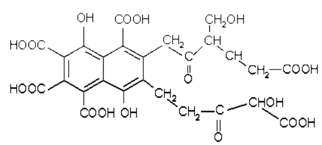


Potentially Ecotoxic

Aqueous complexation

Sorption/reduction at mineral surfaces





Bioaccumulation, bioreduction…

Bioavailable - - - - - - - -> **Potentially not bioavailable**

Challenges : Fate of RN

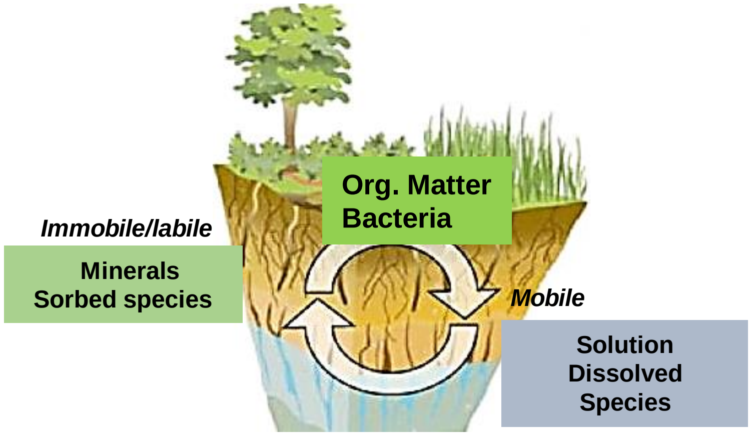
Environmental RN chemistry

→ Supply to plants & organisms

RN bioavailability

RN sources

Soil : storage / release of RN



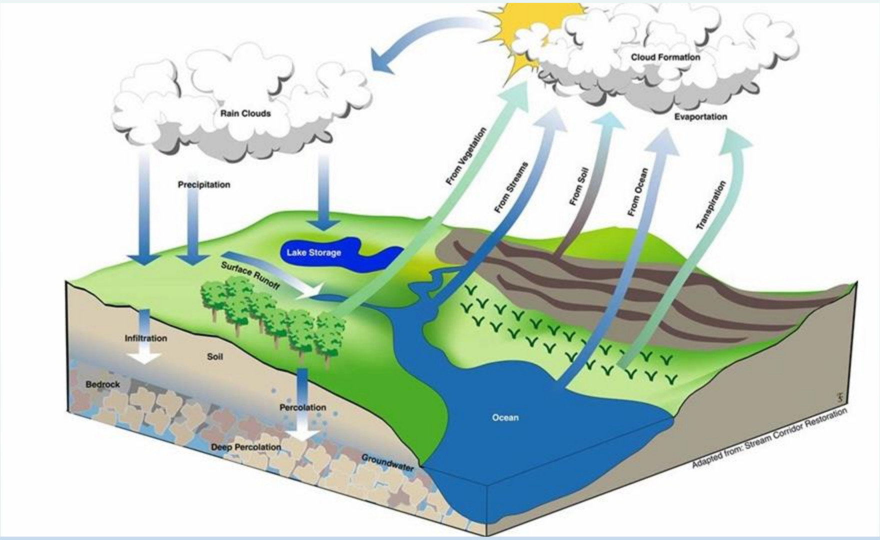
RN lability

RN speciation

→ Supply to waters

RN mobility & migration

Links between RN <u>speciation</u>, fate and impacts



INTRODUCTORY PART

WEATHERING & SOIL CHEMISTRY

ENVIRONMENTAL RN CHEMISTRY

LL RADIOACTIVE WASTES & TENORM

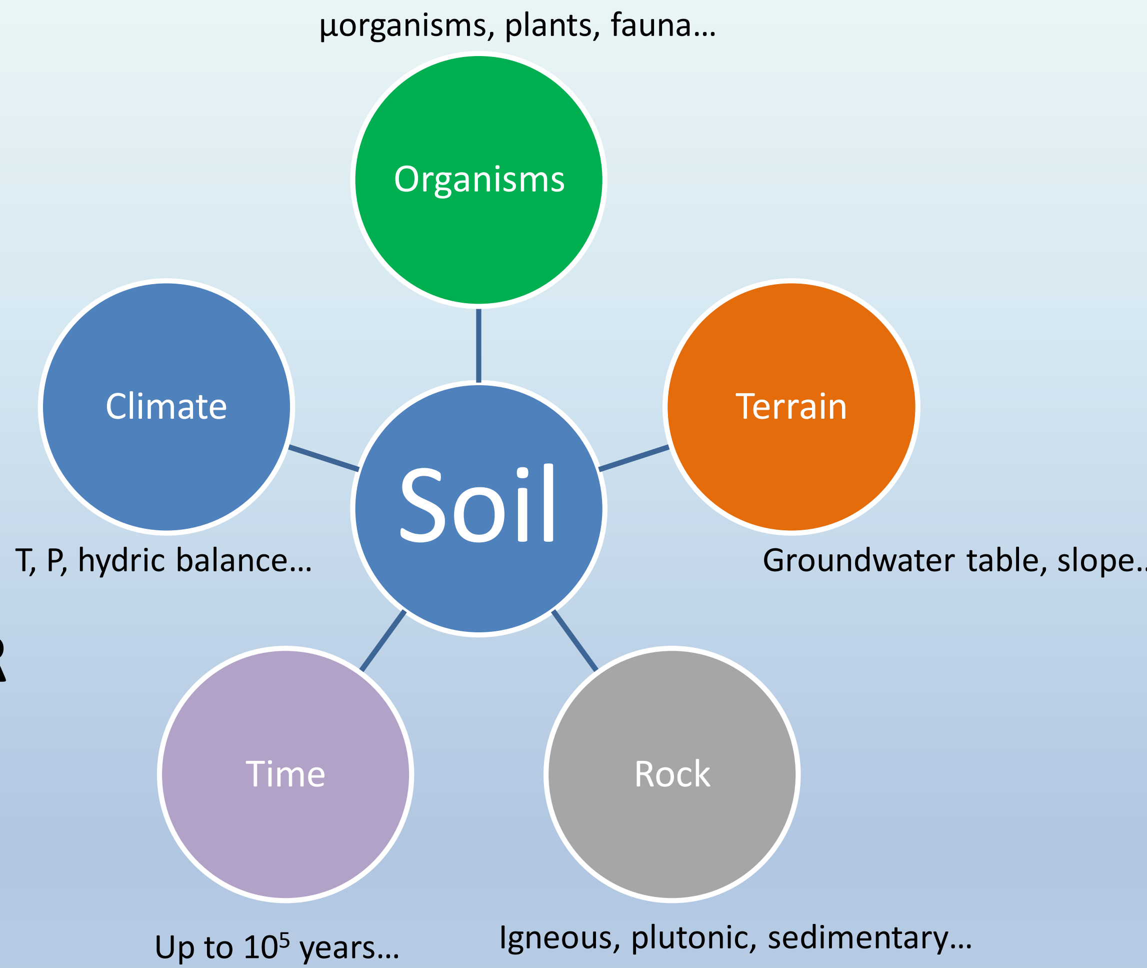
IN FRANCE

SOIL FORMATION

BIO&ORGANIC MATTER

SORPTION PROCESSES

CHALLENGES



Soil formation

Primary rock minerals

Quartz
Feldspars & plagioclases
(Framework silicates)
Pyroxenes, Amphiboles
(Chain silicates)
Olivines
(Orthosilicates)
Illite, Micas, Chlorite
(Phyllosilicates)
Apathite
Sulfides
Calcite
U minerals

Dissolution

Soil minerals

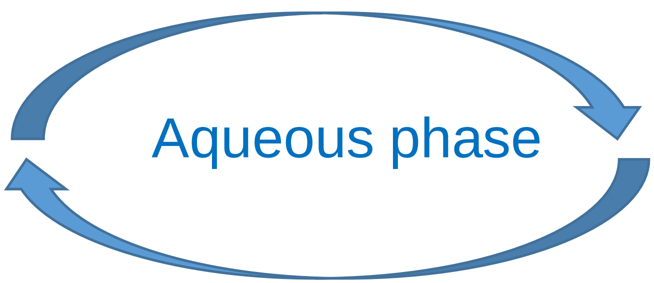
Quartz
Feldspars
Illite Chlorite
Smectites
Kaolinite
Oxyhydroxydes (Fe, Al, Mn)
Phosphates
Sulfates, Carbonates
Nitrates, Chlorides

Transformation & Neoformation

Soil formation

Primary rock minerals	Soil minerals
Thermodynamic stability	Primary rock composition
Dissolution kinetics and mechanisms	Thermodynamic stability & Precipitation mechanisms and kinetics of new minerals
Bio-physicochemical conditions	Bio-physicochemical conditions

Dissolution



Transformation & Neoformation

Soil formation

Reactions - Soil solutions

Processes (left to right)	Reaction equation (solution / atmosphere or in solution)		Processes (right to left)
Dissociation H_2O	$2H_2O$	$OH^- + H^+$	Protonation OH-
Dissociation CO_2	CO_2 HCO_3^-	$HCO_3^- + H^+$ $CO_3^{2-} + H^+$	Protonation HCO_3^-
Dissociation of organic acids	ROOH	$ROO^- + H^+$	Protonation
Complexation of metal ions L= organic ligand or OH^-	$HL + M^+$	$ML + H^+$	Decomplexation of metal ions
Oxidation of H_2S / SO_2	$H_2S + 2O_2$ $SO_2 + ½\ O_2 + H_2O$	$SO_4^{2-} + 2H^+$	Sulphate reduction
Nitrification NH_4^+, NO_x, N_2	$NH_4^+ + 2O_2$ $No_x + ¼\ (5-2x)O_2 + 1/2\ H_2O$ $N_2 + ½\ O_2 + H_2O$	$NO_3^- + H_2O + 2H^+$ $NO_3^- + H^+$ $2NO_3- + 2H^+$	Denitrification

Soil formation

Reactions – Soil mineral - solutions

Processes (left to right)	Reaction equation (solution / mineral)		Processes (right to left)
Formation metal hydroxyde mineral	$M^{m+} + m\ H_2O$	$M(OH)_{m(s)} + mH^+$	Dissolution metal hydroxyde mineral
Oxidation of FeII	$Fe^{2+} + 1/4\ O_2 + 5/2\ H_2O$	$Fe(OH)_3 + 2H^+$	Reduction $Fe(OH)_3$
Oidation of FeS	$FeS + 9/2\ O_2 + 5/2\ H_2O$	$Fe(OH)_3\ SO_4^{2-} + 2H^+$	Reduction $Fe(OH)_3$

Solubility product : $M(OH)_{m(s)} + mH^+ \leftrightarrow M^{m+} + m\ H_2O$ $K = \{M^{m+}\}.\{H^+\}^{-m}$

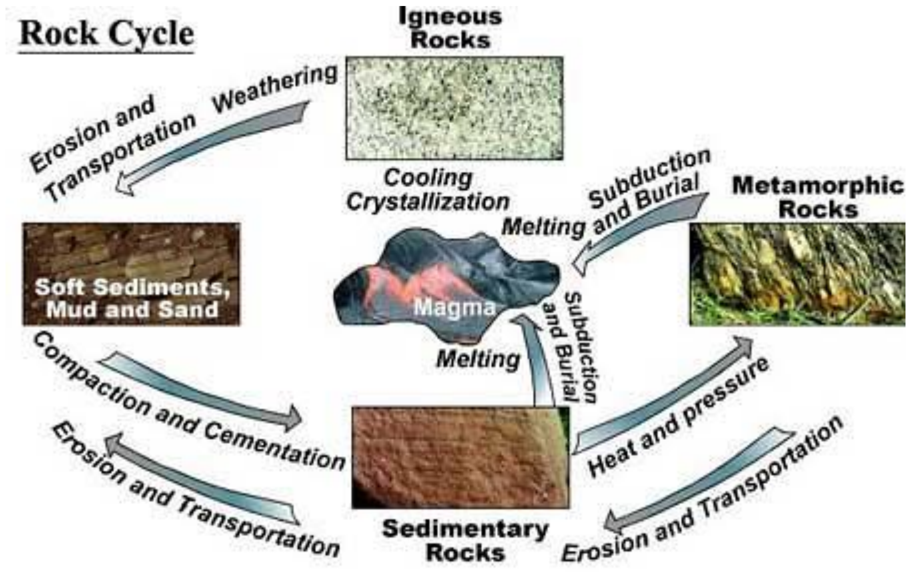
{ } denotes activities

But total solubility results from the sum of all M dissolved species

Soil formation

Rock minerals

Granite, diorite, gabbro
Basalt, andesite…



Sands, gravel, silt, clay…

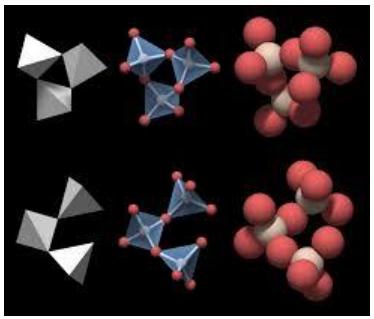
Argilites, quartzites, marble, gneiss…

Sandstones, mudrocks, limestones
(95% of sedimentary rocks with mudrocks representing 60%) siltstone, shale, gysum, salt, coal…

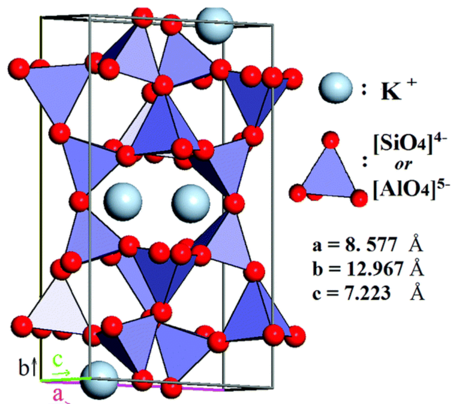
Soil formation

Rock minerals - Igneous

Framework silicates or « tectosilicates »



Quartz, SiO_2

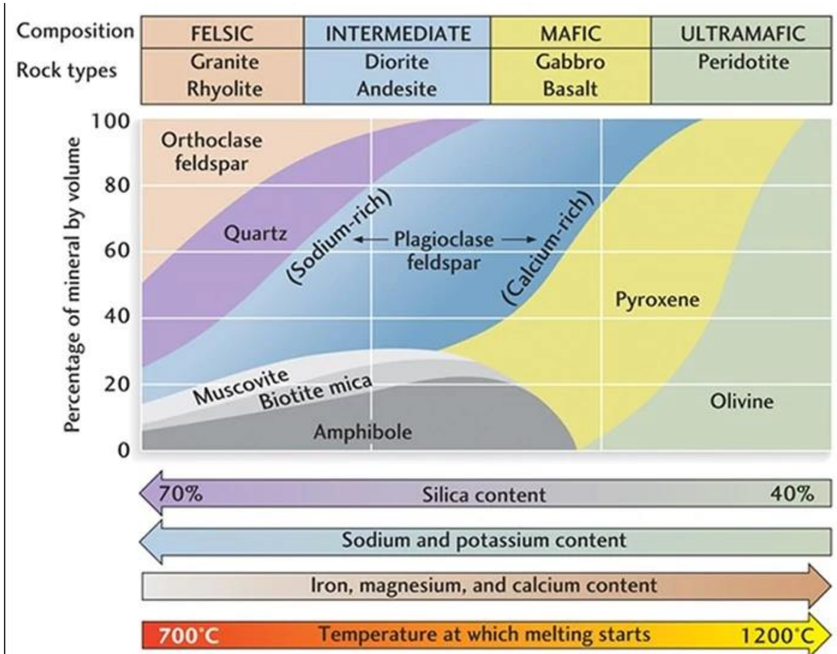


K-felspar, $KAlS_{i3}O_8$

Two other end-members of felspars : $NaAlS_{i3}O_8$ and $CaAl_2Si_2O_8$ forming solid-solutions (plagioclases)

Most important group in volume of the continental crust

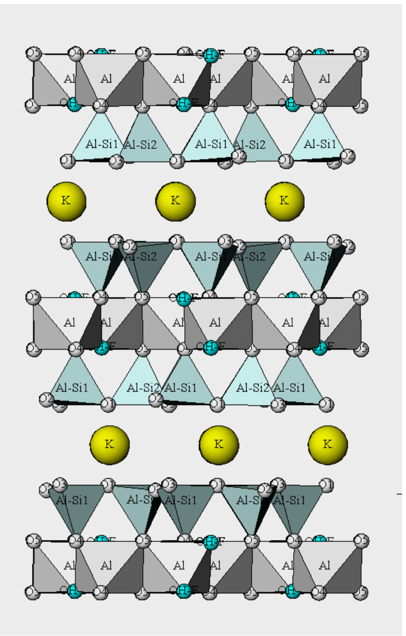
Classification and composition of igneous rocks



Soil formation

Rock minerals

Phyllosilicates



Dioctahedral micas : Muscovite $KAl_2(AlSi_3O_{10})(OH,F)_2$

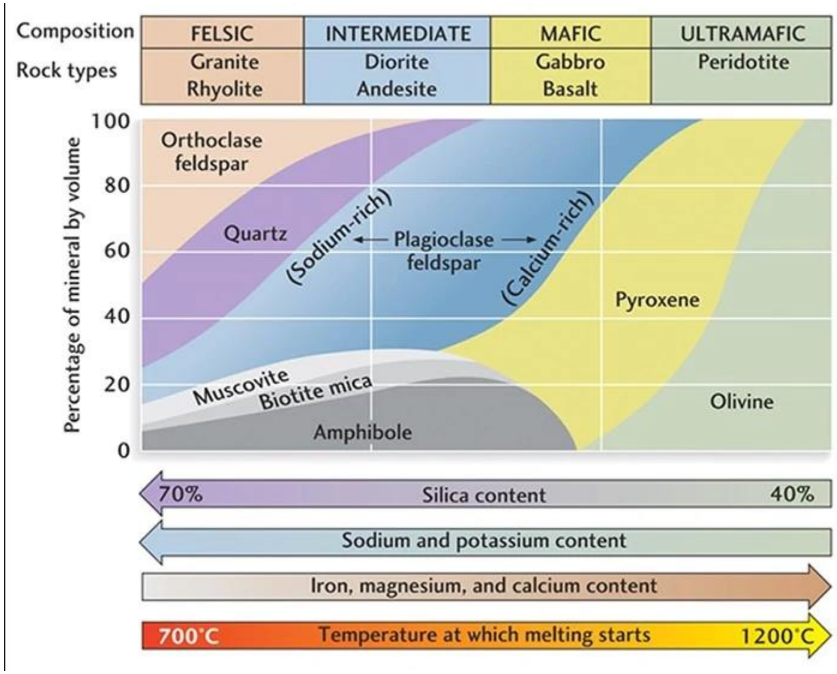
Forms a solid solution with $NaAl_2(AlSi_3O_{10})(OH,F)_2$ and $K(Mg,Fe)(Fe,Al)[Si_4O_{10}](OH)_2$

Traces of Cr, Li, Fe, V, Mn, Na, Cs, Rb, Ca, Mg

Trioctahedral micas: Biotite $K(Mg, Fe)_3(AlSi_3O_{10})(OH,F)_2$

Traces of Mn, Ti, Fe, Li, Ba, Na, Sr, Cs, Cl

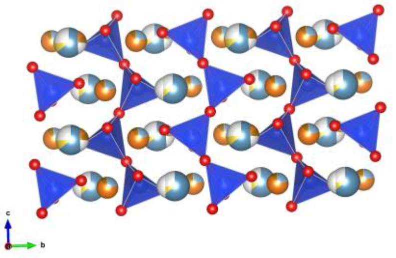
Classification and composition of igneous rocks



Soil formation

Rock minerals

Inosilicates : Chain silicates



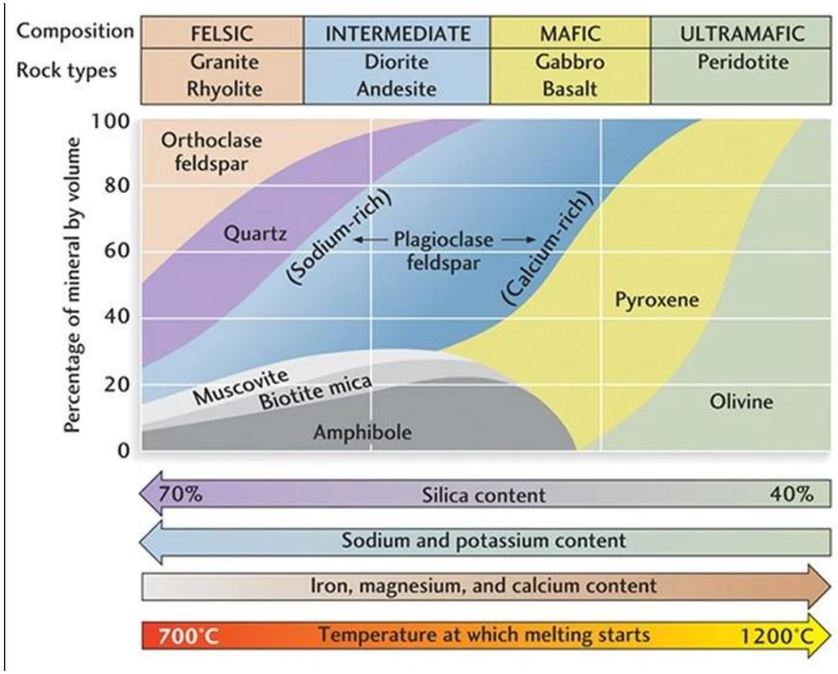
Pyroxenes : $XY(SiO_3)_2$
1 bridging O atom

X = Na^+, Ca^{2+}, Li^+, Mg^{2+}, Mn^{2+} ; Y = Mg^{2+}, Fe^{2+}, Mn^{2+}, Fe^{3+}, Al^{3+}, Cr^{3+}, Ti^{4+}

Amphiboles are two chain inosilicates (2 bridging O atoms)

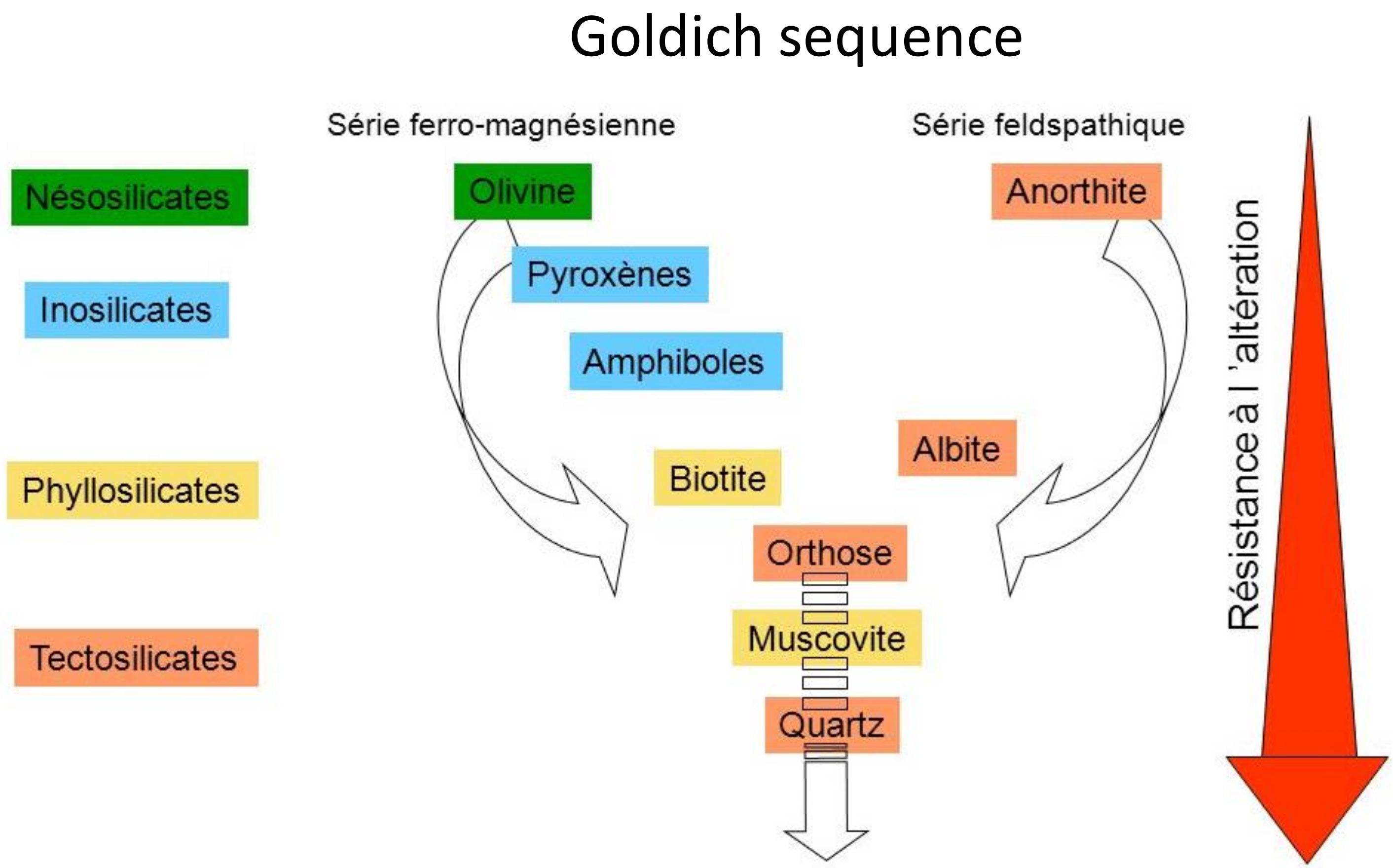
Nesosilicates have isolated tetrahedra (olivines, zircons...)

Classification and composition of igneous rocks



Resistance of primary rock minerals to weathering

Among common rock-forming silicate minerals, the sequence of cristallization (high to low temperature) from an igneous melt determines approximately the stability of the minerals during chemical weathering

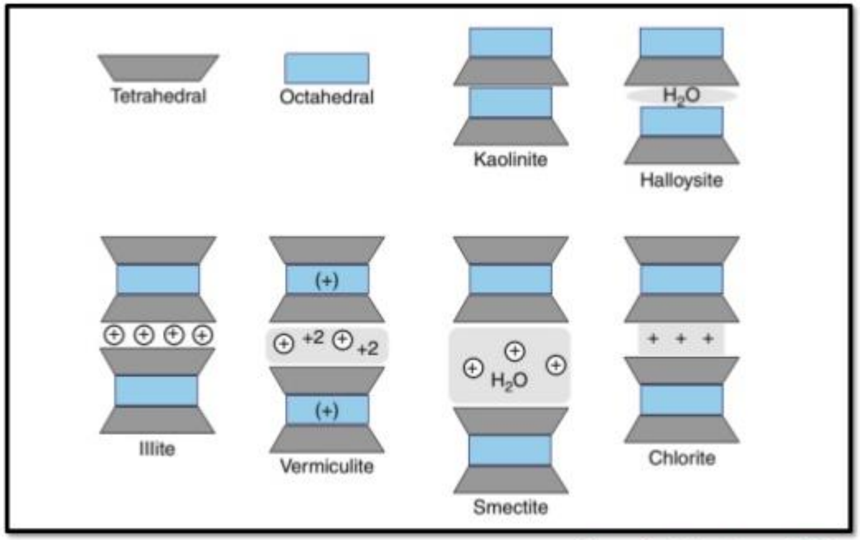


Soil formation

Rock minerals - Sedimentary

73% of cover of the Earth's crust surface but only 8% in volume
95% of sedimentary rocks are represented by sandstones, mudrocks (60%) and limestones

Classification of clays (phyllosilicates)

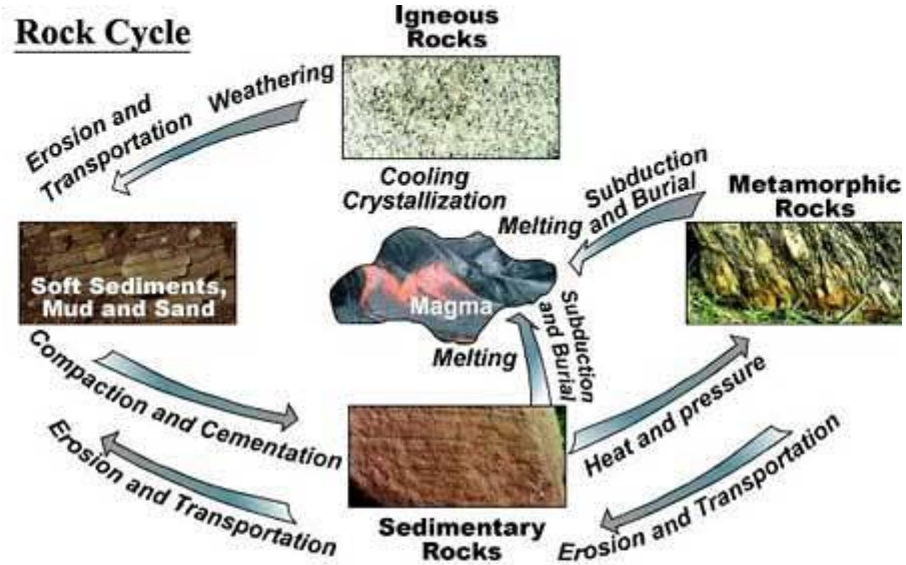


Negrón-Mendoza, 2011

Mineral Composition	Mudrocks %	Sandstones %
Clay minerals	60	5
Quartz	30	65
Feldspar	4	10 - 15
Carbonate minerals	3	<1
Organic matter, hematite, & others	<3	<1

An interesting feature of U cycling

- Basalts : 1 ppm U (Fayek et al. 2011); Granite : 3-5 ppm (Alloway, 2013) with exceptions (50ppm in W Australia, Kreuzer et al., 2010)



- Significant in zircons (Rose and Wright, 1980)

- Limestones : 4 ppm U (Alloway, 2013); 12-84 ppm in organic matter rich sediments (Cuney, 2010)
- Phosphorite black shales deposits : up to 700ppm (Bowell et al. 2011)
- Lignites Ebro Valley (Spain) : 500-2500ppm U (Douglas et al., 2011)
- 20% U in Oklo low-T sedimentary deposits (Gauthier Lafaye et al.1989)

An interesting feature of U cycling

Evolution of U species on Earth into 4 periods (Cuney, 2010) :

(1) Mantle melting (3.2 Ga)

(2) Mantle cooling and cristallisation of U in granites (3.3 – 2.2 Ga)

(3) Oxygenation of atmosphere at 2.2 Ga : a threshold in evolution:

O intensified weathering : oxidation of U(IV) to mobile U(VI), increasing diversity in U minerals, eucariot and expanded biomass and production OM-rich sediments capable of U enrichments (Dill, 2010) : **U redox cycling leading to mobilization / deposits**

(4) Angiosperm plants during Cretaceous

Increased availability of **phosphate** which is uranophilic (400 U deposits in sandstones and OM-rich layers)

Through tectonic, granites cycled to Earth surface → U in sediments → sediments with U metamorphosed at high T-P conditions (Hazen et al., 2009)

Humification involving microbes and algae; mobile U trapped within humus

Weathering has led to U enrichments over geological times

Soil formation

Mineral dissolution and precipitation

Dissolution of K-Feldspar

$$K = \mathrm{IAP}_{\acute{e}q} = \frac{[K^{+}][Al^{3+}][H_4SiO_4]^3}{[H^{+}]^4}$$

$$KAlSi_3O_8 + 4H^+ + 4\,H_2O \leftrightarrow K^+ + Al^{3+} + 3H_4SiO_4$$

K is equilibrium constant determined from Gibbs free energies of formation, [ ] are activities. Comparaison between IAP calculated from data measured in environmental systems and the K value (composition at equilibrium) indicate if the system is at equilibrium (Q=K, ΔG=0), if reaction is spontaneous (Q<K, ΔG<0) or impossible (Q>K, ΔG>0)

Solubility of Olivine (Forsterite)

$$Mg_2SiO_4 + 4H^+ \leftrightarrow 2Mg^{2+} + H_4SiO_4$$

Solubility of Calcite (depend on PCO_2)

$$CaCO_3 + H_2O + CO_2 \leftrightarrow Ca^{2+} + 2HCO_3^-$$

$$K = \frac{[Ca^{2+}][HCO_3^{-}]}{[H^{+}]}$$

Soil formation

Mineral dissolution and precipitation

Silicates often dissolve incongruently (partial hydrolysis)

$2KAlSi_3O_8 + 2H^+ + 12\ H_2O \leftrightarrow 2K^+ + KAl_3Si_3O_{10}(OH)_2 + 6H_4SiO_4$

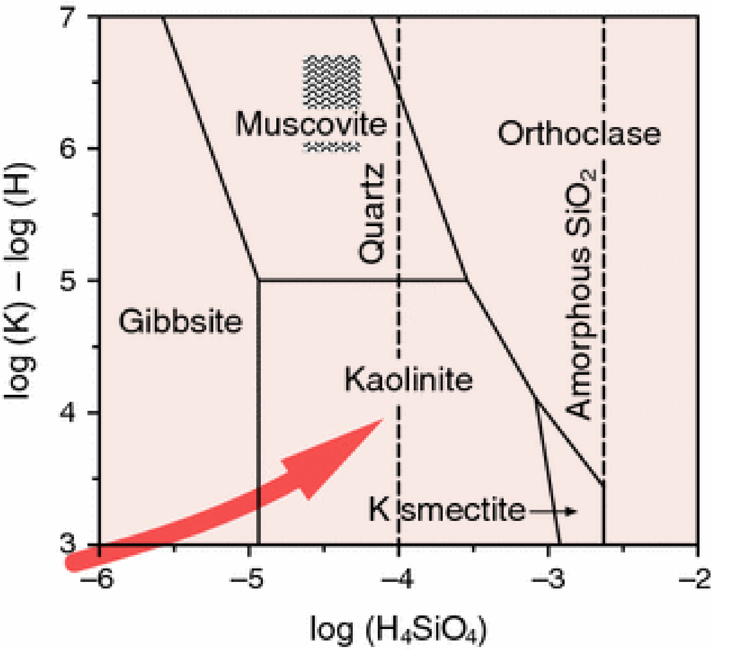
Muscovite

$2KAl_3Si_3O_{10}(OH)_2 + 2H^+ + 3\ H_2O \leftrightarrow 2K^+ + 3Al_2Si_2O_5(OH)_4$

Kaolinite

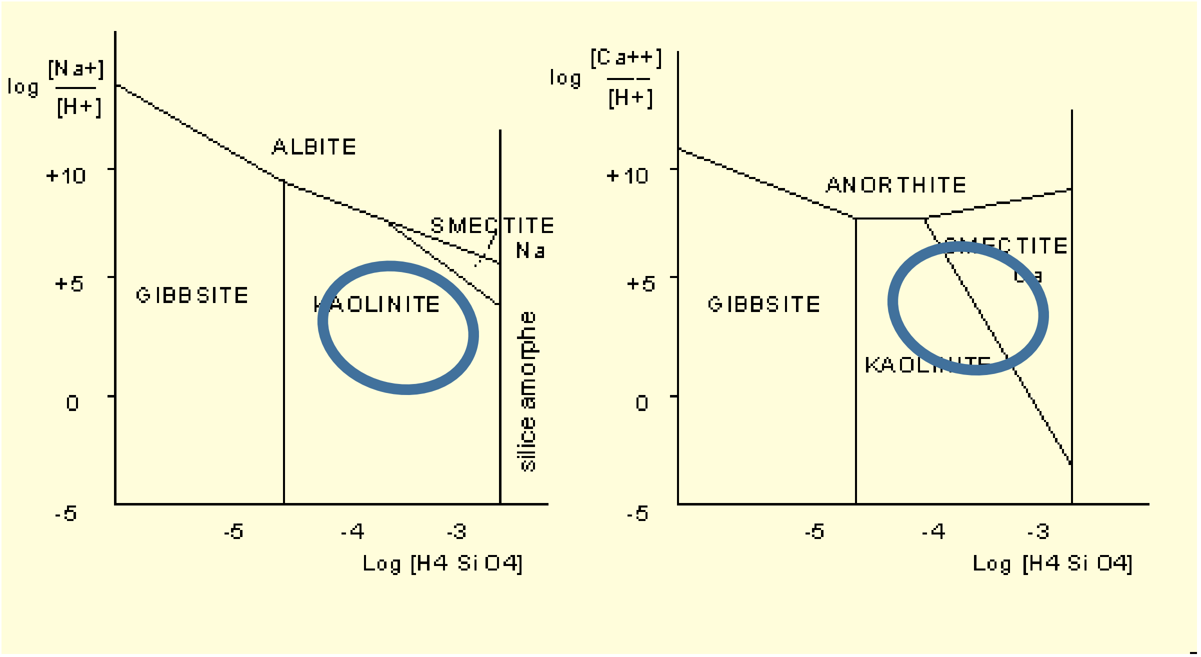
$Al_2Si_2O_5(OH)_4 + 5\ H_2O \leftrightarrow Al_2O_3.3H_2O + 2H_4SiO_4$

Gibbsite



Soil formation

Mineral dissolution and precipitation



Weathering : K, Ca, Mg and Al are partially leached

Clays are amongst major secondary minerals forming under temperate climates

Soil formation

Mineral dissolution and precipitation

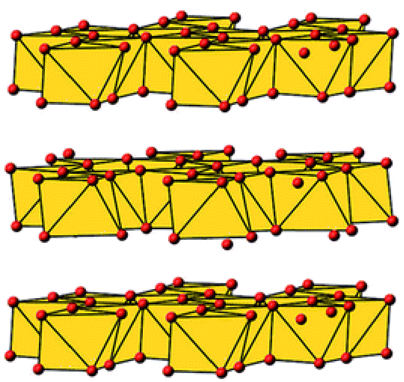
Solubility of oxihydroxides

$M(OH)_m + mH^+ + \leftrightarrow M^{m+} + mH_2O$

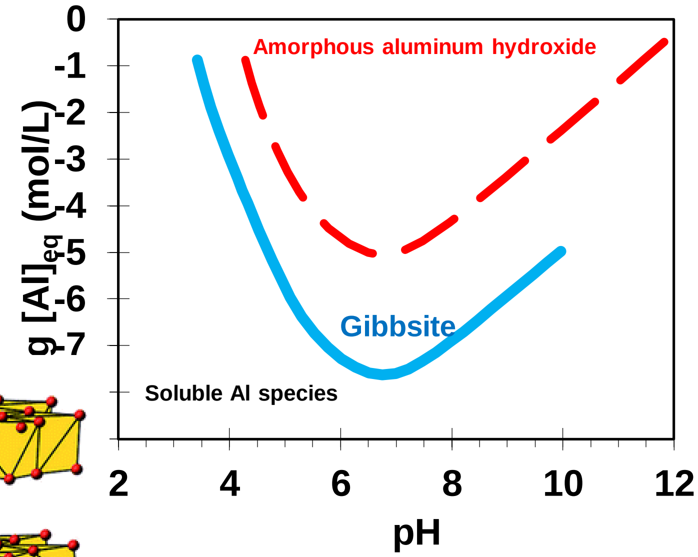
$Al(OH)_3 + 3H^+ + \leftrightarrow Al^{3+} + 3H_2O$

$$K = \frac{[M^{m+}]}{[H^+]^m}$$

$Al(III)_{tot,diss} = Al^{3+} + Al(OH)^{2+} + Al(OH)_2^+ + Al(OH)_3 + Al(OH)_4^-$ Hydrolysis products



Gibbsite
$Al(OH)_3$



For kinetic reason, the more stable phase is often not preferred

Solubility is increased in presence of complexing agents

Soil formation

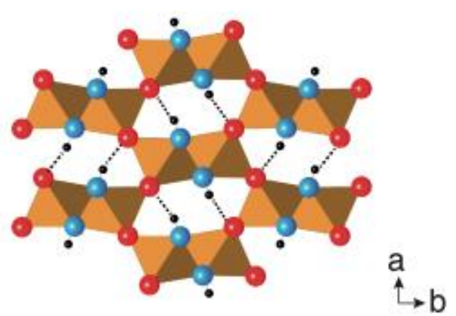
Mineral dissolution and precipitation

Fe-oxihydroxides formation & Redox

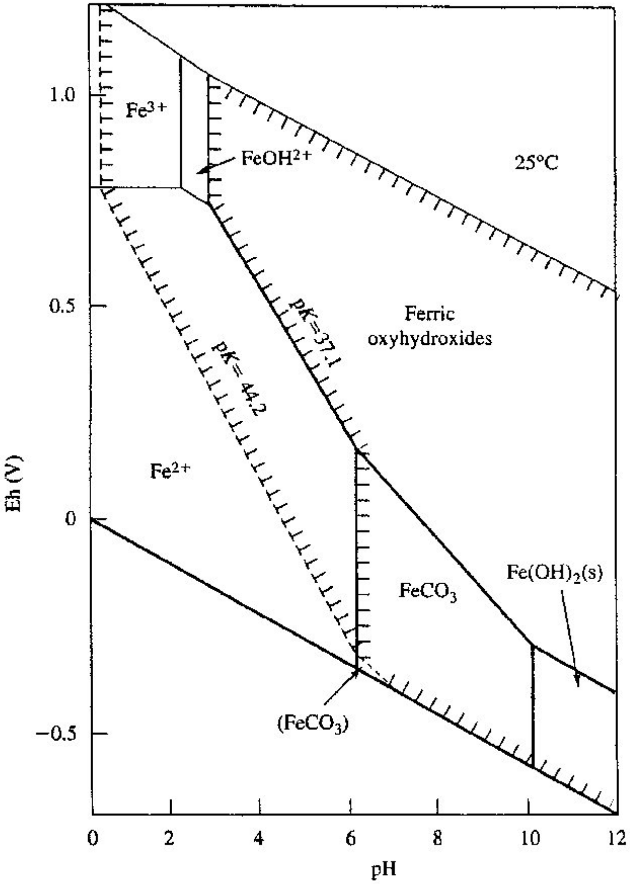
$M(OH)_m + mH^+ + \leftrightarrow M^{m+} + mH_2O \qquad K = \frac{[M^{m+}]}{[H^+]^m}$

$Fe(OH)_3$ ferrihydrite; FeOOH goethite; Fe_2O_3 hematite

Goethite

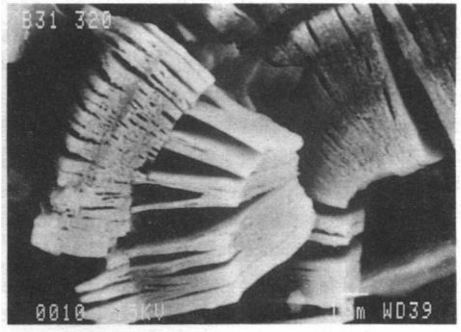


Eh-pH diagram (Pourbaix) for the $Fe-CO_2$ - H_2O system, TIC = 10^{-3} mol/kg and total dissolved Fe = 10^{-3} mol/kg at aqueous solid boundaries. Position of the aqueous/solid boundaries for amorphous $Fe(OH)_3$ with pK_{sp} = 37.1 and goethite with pK_{sp} = 44.2. After Whittemore and Langmuir, 1975.

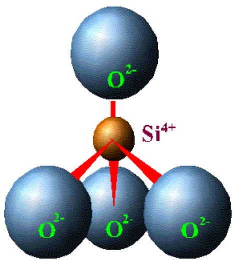


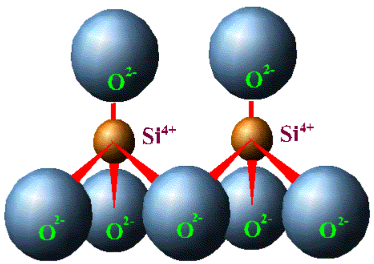
Soil formation

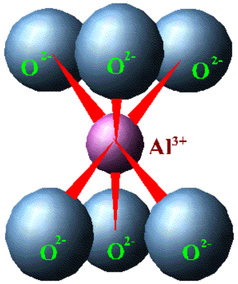
Clay minerals : an essential role in the soil

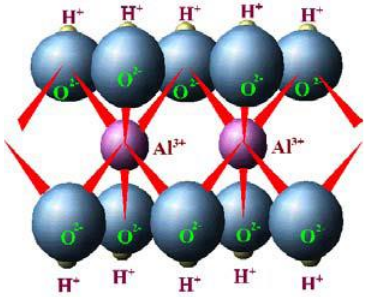


Small platelet crystals consisting of a stacking of sheets (phyllosilicates) themselves consisting of octahedral layers Al(OH)3 and SiO4 tetrahedrons.





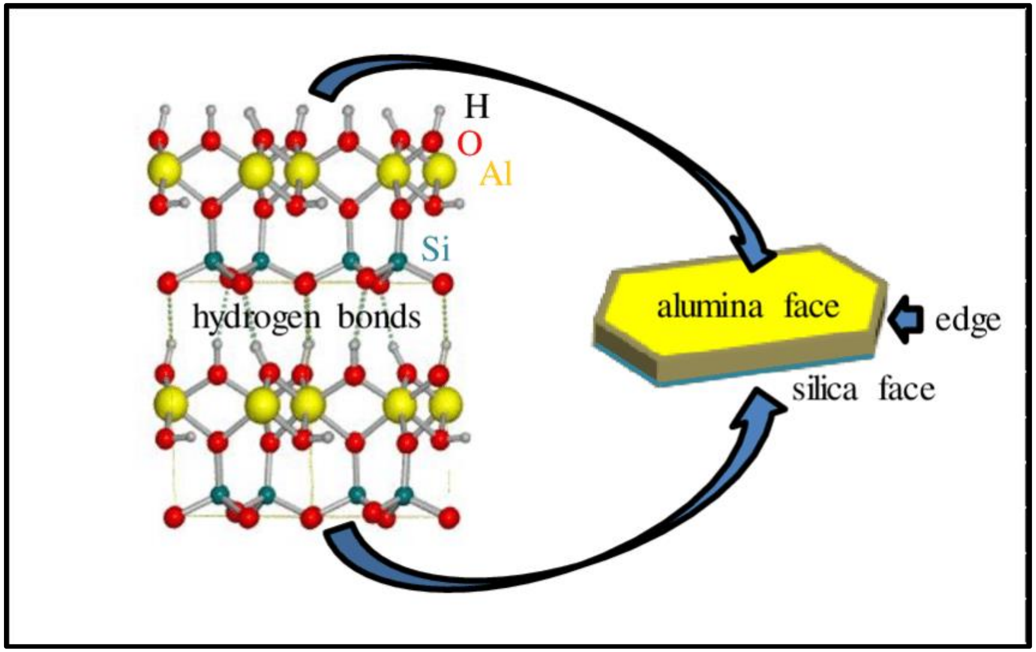


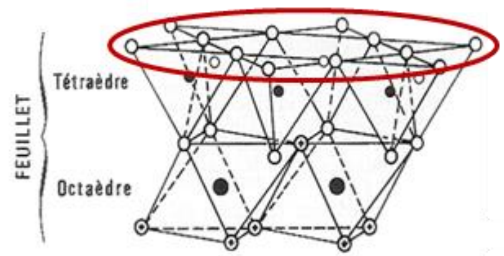


Soil formation

Clay minerals : an essential role in the soil

KAOLINITE (TO) **$Al_2\ Si_2\ O_4\ (OH)_4$**



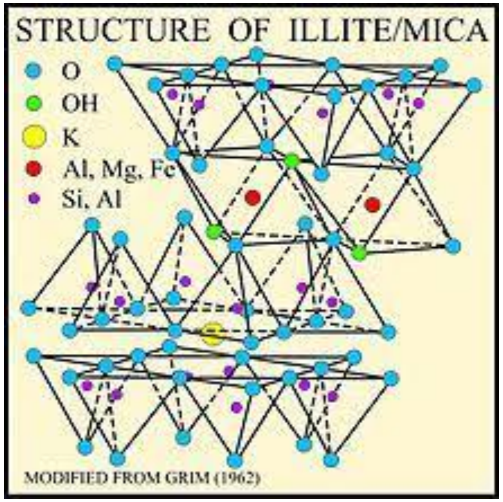


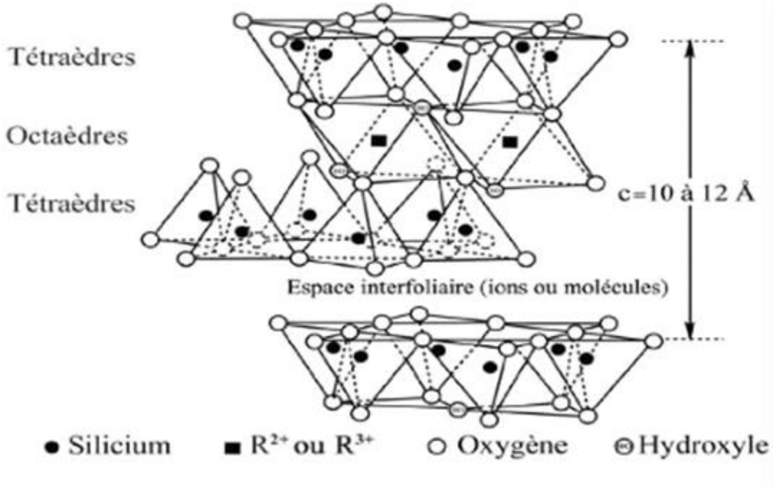
No substitutions
No permanent charges of layers
(halloysite if H2O in interlayer space)

Soil formation

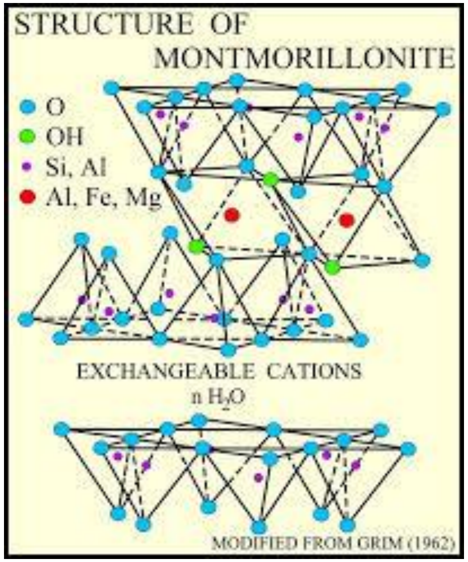
Clay minerals : an essential role in the soil

ILLITE (TOT)





SMECTITES (TOT)

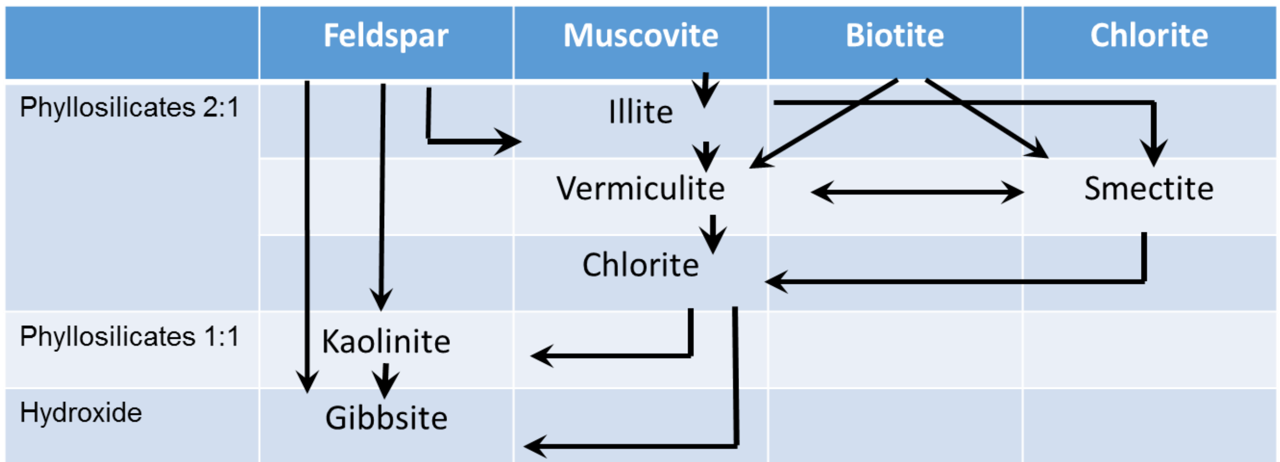


$(Si_{4-x}\ Al_x)(Al,M1,M2)_2\ O_{10}\ (OH)_2\ K$

Isomorphous tetrahedral substitutions Si^{4+}/Al^{3+} (>0.6)
Highly permanently charged layers (1.4 to 1.8),
compensated by K (by Ca = vermiculites)

Isomorphous tetrahedral substitutions Si^{4+}/Al^{3+} (<0.6),
octahedral substitutions Al^{3+}, Mg^{2+}, Fe^{2+}
Weakly permanently charged layers (0.6 to 1.2),
compensated by cations, waters in interlayers …
A huge vaviety. High surface area – Swell -

Soil formation



High surface area : up to 800 m ^{2} / g (poorly-cristallized Fe-oxyhydroxides, smectites)

Swelling properties

Cation exchange capacity : 2-15 kaol → 20-40 illite 60-100

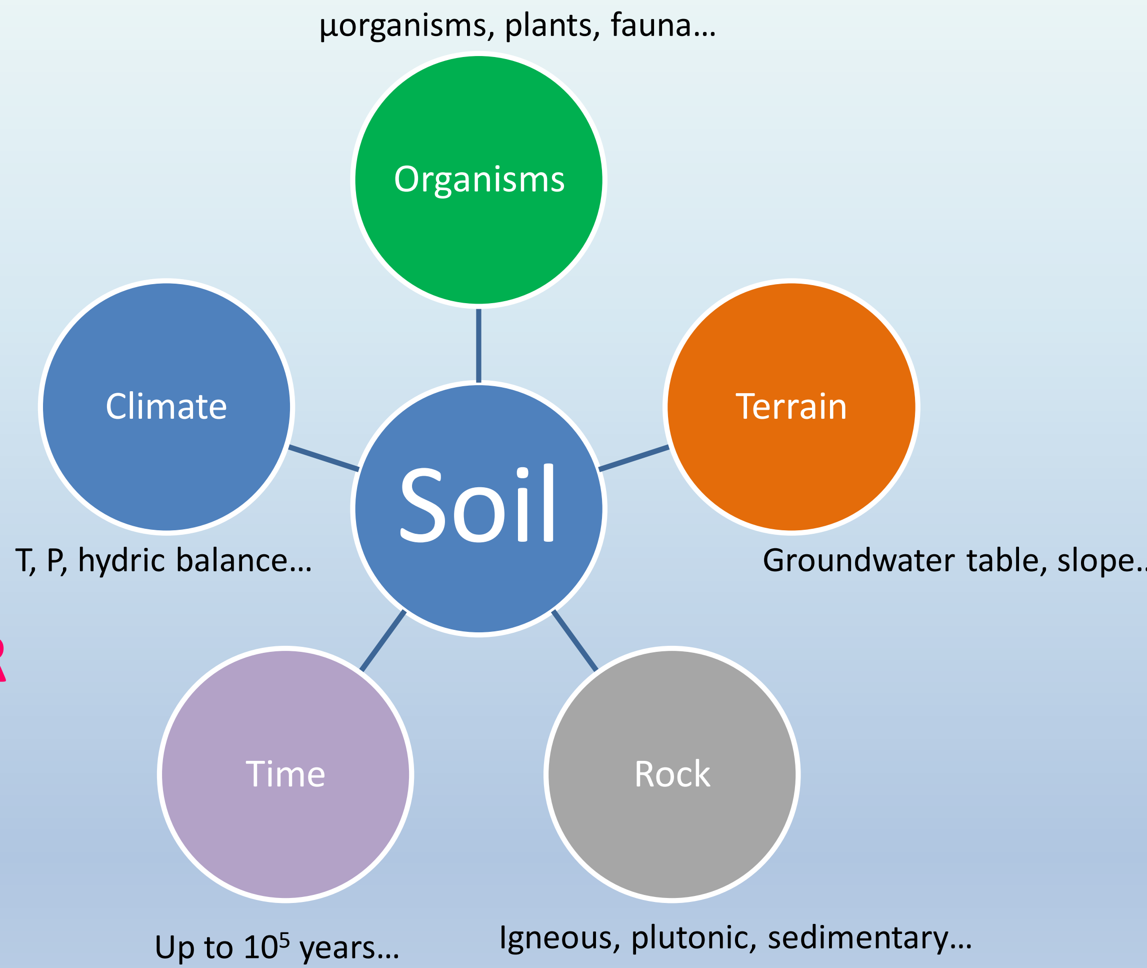
Cmol of positive charge /kg

SOIL FORMATION

BIO&ORGANIC MATTER

SORPTION PROCESSES

CHALLENGES



Biological and organic matter

Oxidation of natural organic matter

Organic compound + O_2 (or other electron acceptor → CO_2 + H_2O+ inorganic nutrients + E

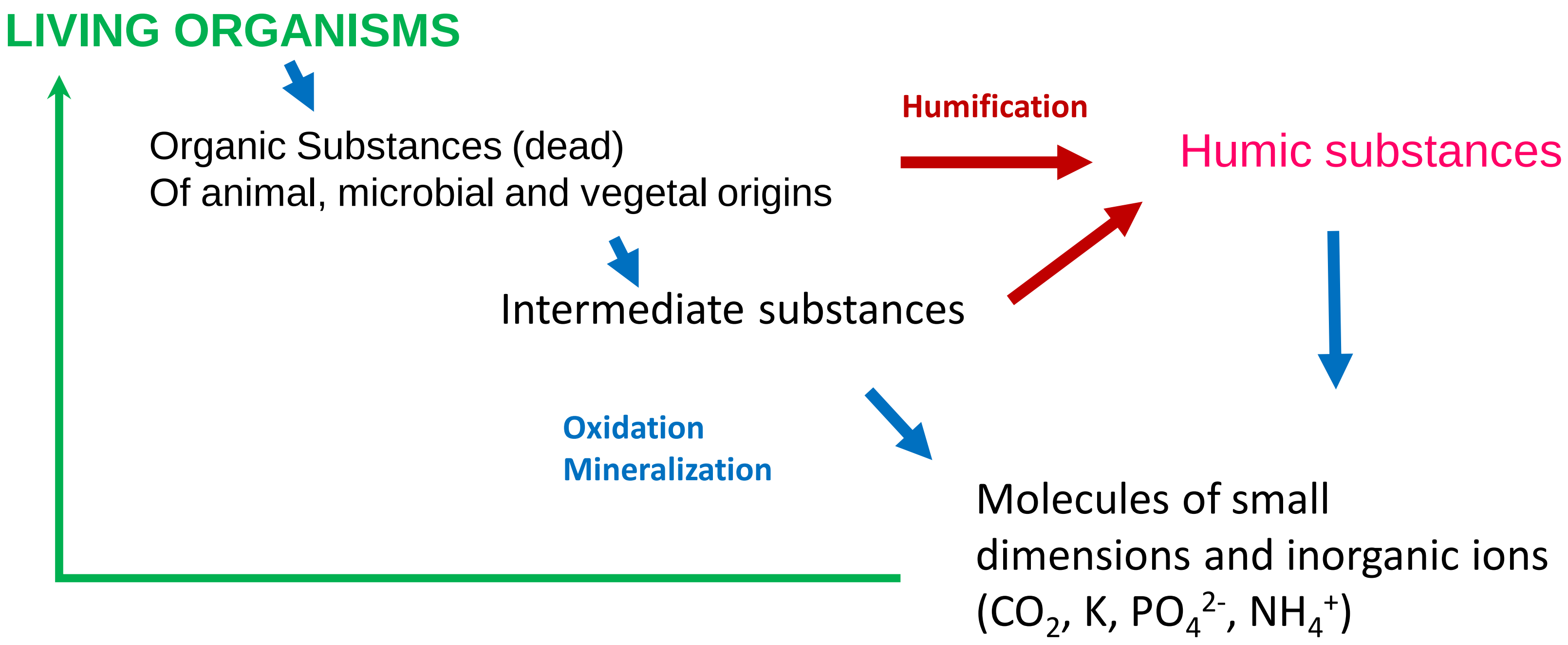
$C_6H_{12}O_6 + O_2 \rightarrow CO_2 + H_2O$ (+ E)

A form of respiration,
An oxidation reaction
Aided by microbial enzymes

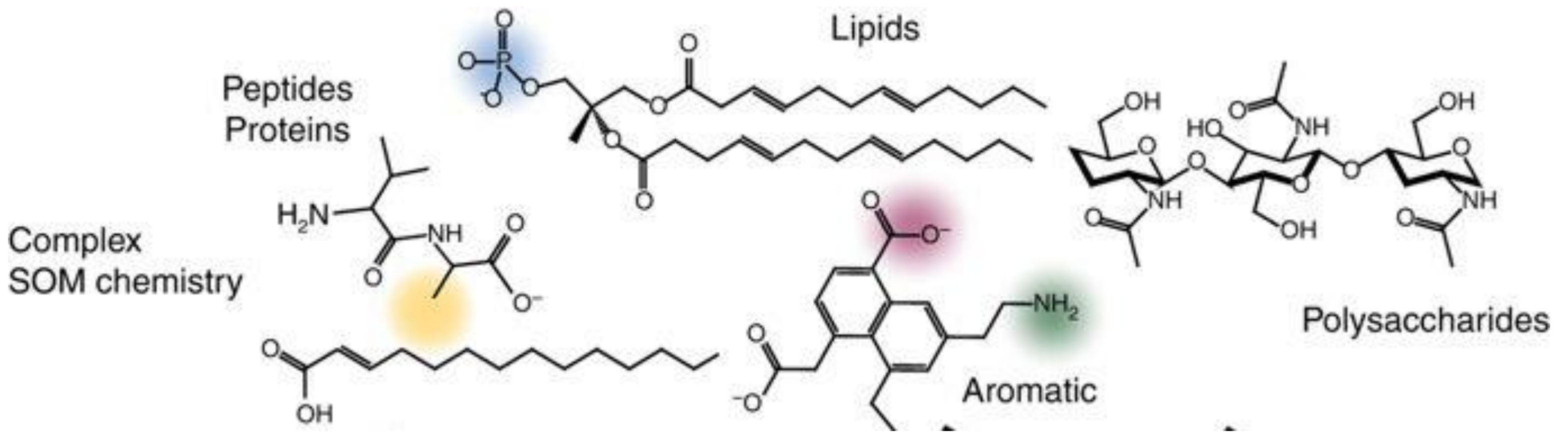
- Organic carbon may represent up to 30% of soil composition in forested areas
- Organics (from dead plants, organisms…) is oxidized by inorganic oxidant agents (O, N, S)
- Nutrient elements contained in organic substrate are mineralized : decomposition fees nutrients like N, P, S
- CO_2 escapes to soil atmosphere

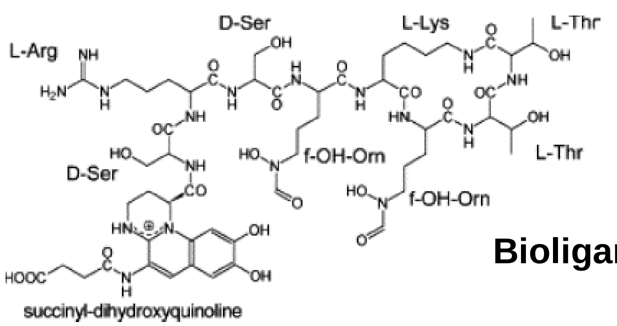
Biological and organic matter

1 g of soil contains 100,000 to 1 M bacteria

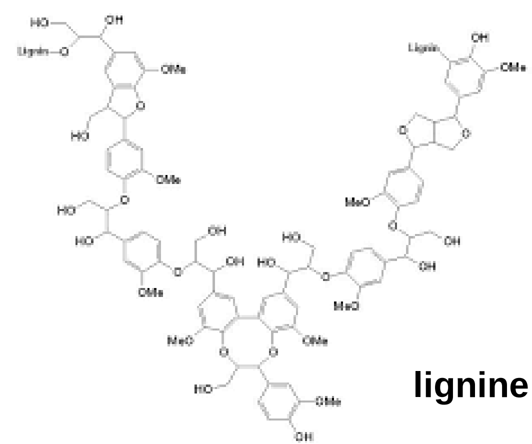


Biological and organic matter





Bioligands



lignine

Organic ligand - complexation

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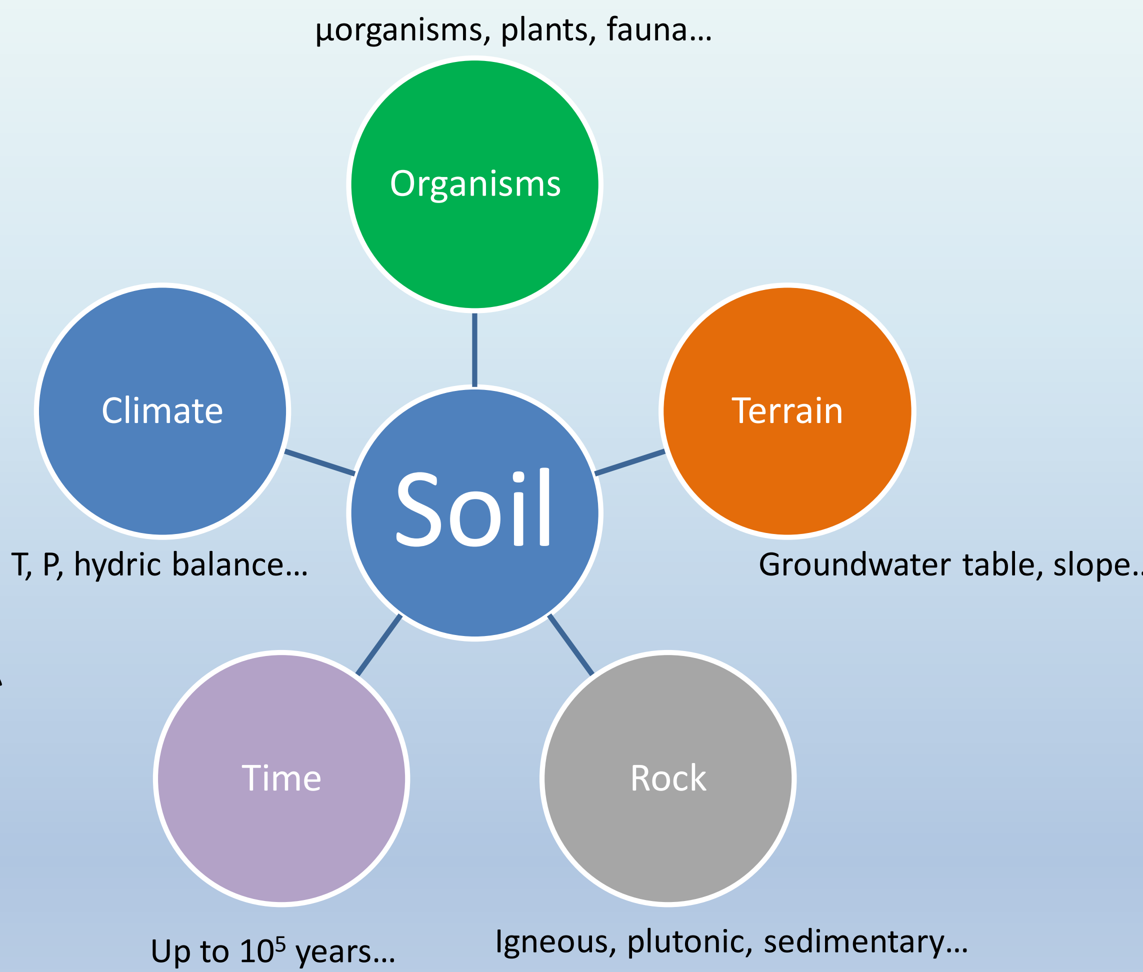
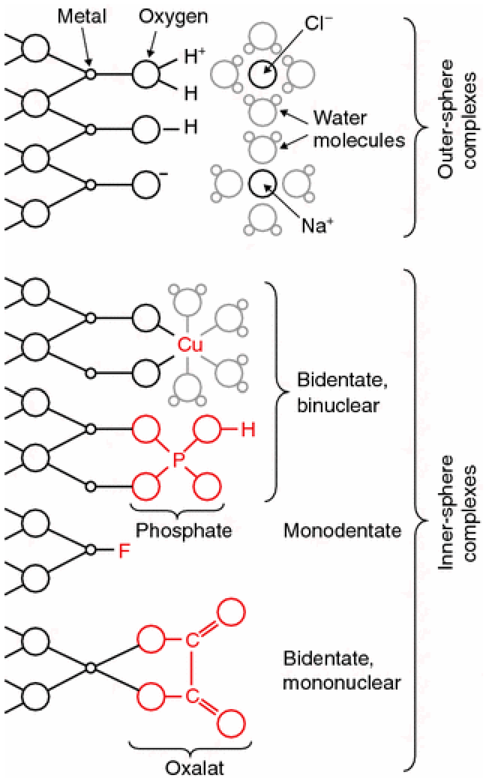
SORPTION PROCESSES
CHALLENGES



Sorption processes

Reactions at mineral-solution interfaces



Acid-base equilibria

$$S{-}OH + H^+ \rightleftharpoons S{-}OH_2^+$$

$$S{-}OH\ (+\ OH^-) \rightleftharpoons S{-}O^-\ (+\ H_2O)$$

Metal binding

$$S{-}OH + M^{z+} \rightleftharpoons S{-}OM^{(z-1)+} + H^+$$

$$2\ S{-}OH + M^{z+} \rightleftharpoons (S{-}O)_2M^{(z-2)+} + 2\ H^+$$

$$S{-}OH + M^{z+} + H_2O \rightleftharpoons S{-}OMOH^{(z-2)+} + 2\ H^+$$

Ligand exchange (L^- = ligand)

$$S{-}OH + L^- \rightleftharpoons S{-}L + OH^-$$

$$2\ S{-}OH + L^- \rightleftharpoons S_2{-}L^+ + 2\ OH^-$$

Ternary surface complex formation

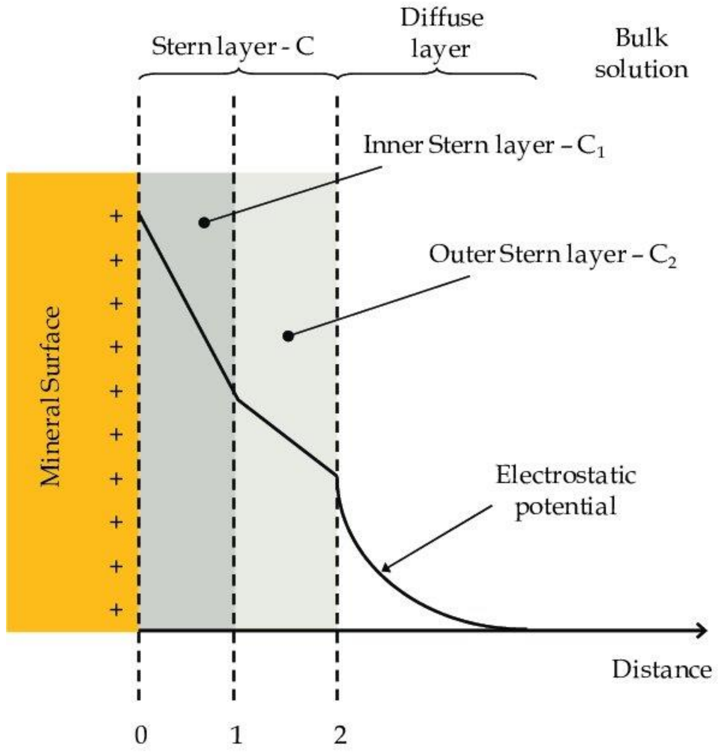
$$S{-}OH + L^- + M^{z+} \rightleftharpoons S{-}L{-}M^{z+} + OH^-$$

$$S{-}OH + L^- + M^{z+} \rightleftharpoons S{-}OM{-}L^{(z-2)+} + H^+$$

Secondary retention of Me, (in)organic ligands…

Sorption processes

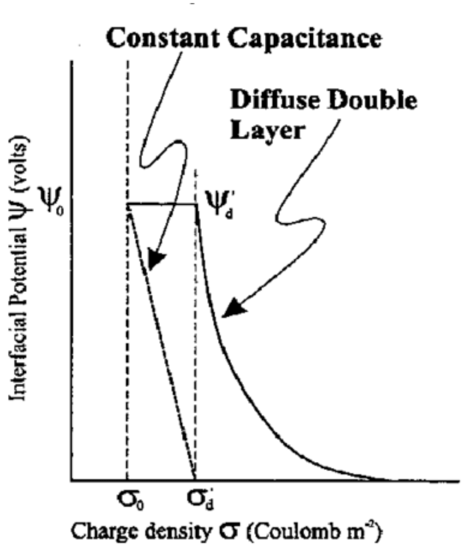
Reactions at mineral-solution interfaces



- Sorption takes place at specific coordination sites
- Sorption reactions can be described by mass law equations
- Surface charge results from the sorption (surface complex formation) itself
- The effect of surface charge on sorption can be taken into account by applying to the mass law constants for surface reactions a correction factor derived from the electric double-layer theory

Sorption processes

SCM



Reactions protonation / deprotonation of surface hydroxyls

$$\mathrm{S-OH + H^+ \overset{K_+^{int}}{\longleftrightarrow} S-OH_2^+}$$

$$\mathrm{S-OH \overset{K_-^{int}}{\longleftrightarrow} S-O^- + H^+}$$

Relation intrinsic constants and conditional constants

$$K_+^{\mathrm{int}} = K_+^{\mathrm{c}} \exp\left(+F\Psi_0/RT\right) = \left(\left[\mathrm{S-OH_2^+}\right]/\left(\left[\mathrm{S-OH}\right]\left\{\mathrm{H^+}\right\}\right)\right)\exp\left(+F\Psi_0/RT\right)$$

$$K_-^{\mathrm{int}} = K_-^{\mathrm{c}} \exp\left(-F\Psi_0/RT\right) = \left(\left(\left[\mathrm{S-O^-}\right]\left\{\mathrm{H^+}\right\}\right)/\left[\mathrm{S-OH}\right]\right)\exp\left(-F\Psi_0/RT\right)$$

Relation Charge – potential (DLM)

$$-\sigma_0 = \sigma_\mathrm{d} = -0.1174\sqrt{I}\sinh\left(zF\Psi_0/2RT\right)$$

$$\Psi_0 = \Psi_\mathrm{d}$$

Sorption processes

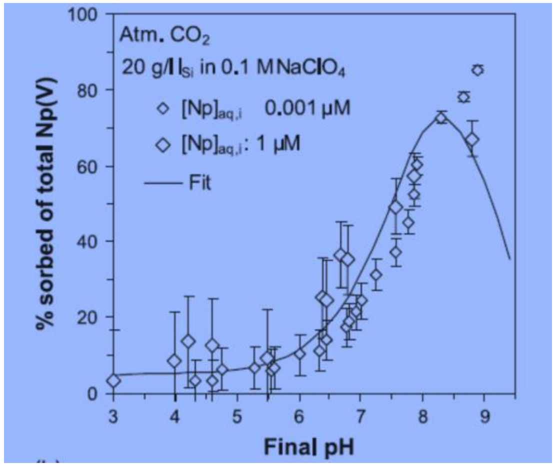
SCM

$$S-OH + xM^{m+} + yH_2O \overset{K^{int}_{species}}{\longleftrightarrow} (S-OM_xOH_y)^{(xm-y-1)+} + (y+1)H^+$$

$$K^{int}_{species} = \frac{[(S-OM_xOH_y)^{(xm-y-1)+}]\{H^+\}^{(y+1)}}{[S-OH].\{M^{m+}\}^x} \exp((xm-y-1)F\Psi_0/RT)$$

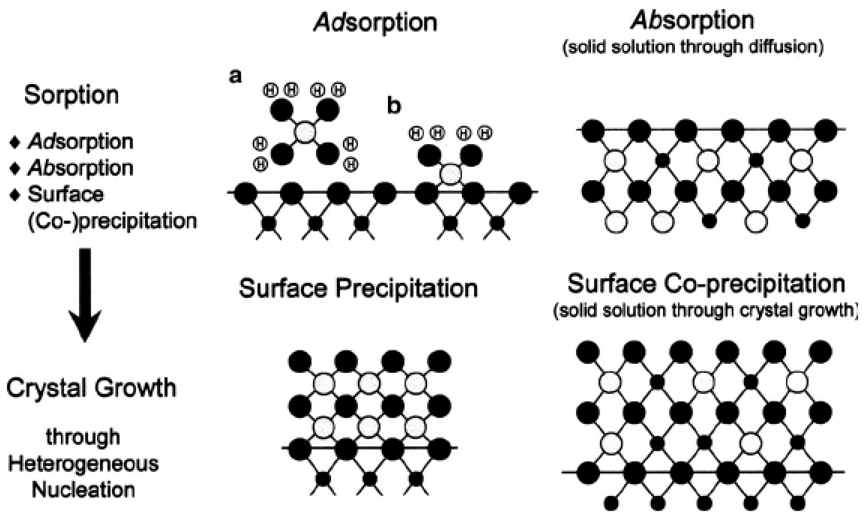
Experimental data and surface complexation modeling of Np(V) adsorbed on Silica

Del Nero et al., Chem Geol. 2004



Sorption processes

Reactions at mineral-solution interfaces



Exchange in interlayers of clays :

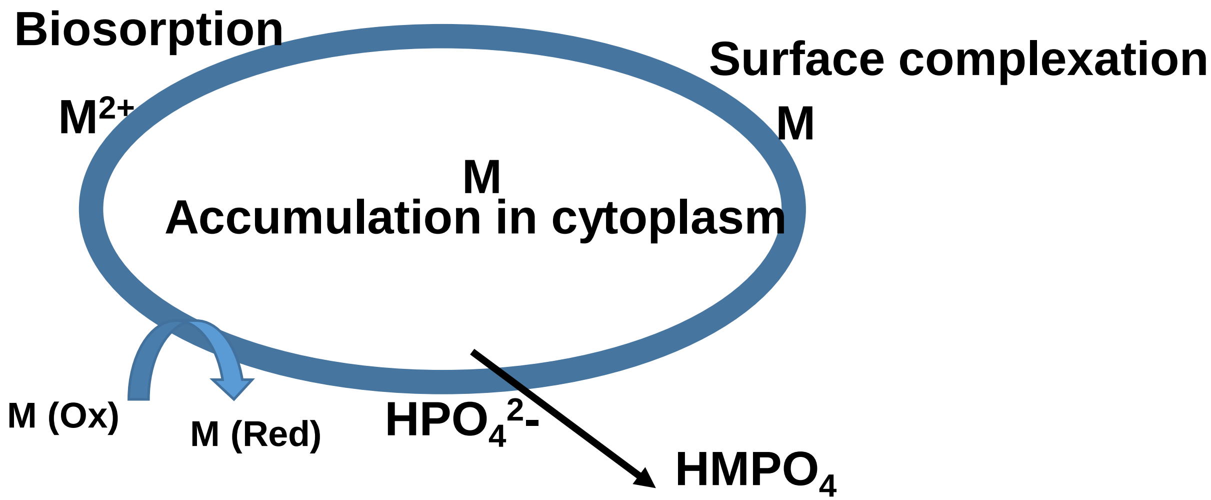
$Cs^{+}>K^{+}>Na^{+}>Li^{+}$
$Ba^{2+}>Sr^{2+}>Ca^{2+}>Mg^{2+}$

Coulombic interactions & inner-sphere formation !

CEC clays (cmol of positive charge / kg) : 2-15 kaolinite; 20-40 illite; 60-100 montmorillonite

Different processes of secondary retention of Me, (in)organic ligands…

Sorption processes



Possible reactions at microbe-water interfaces

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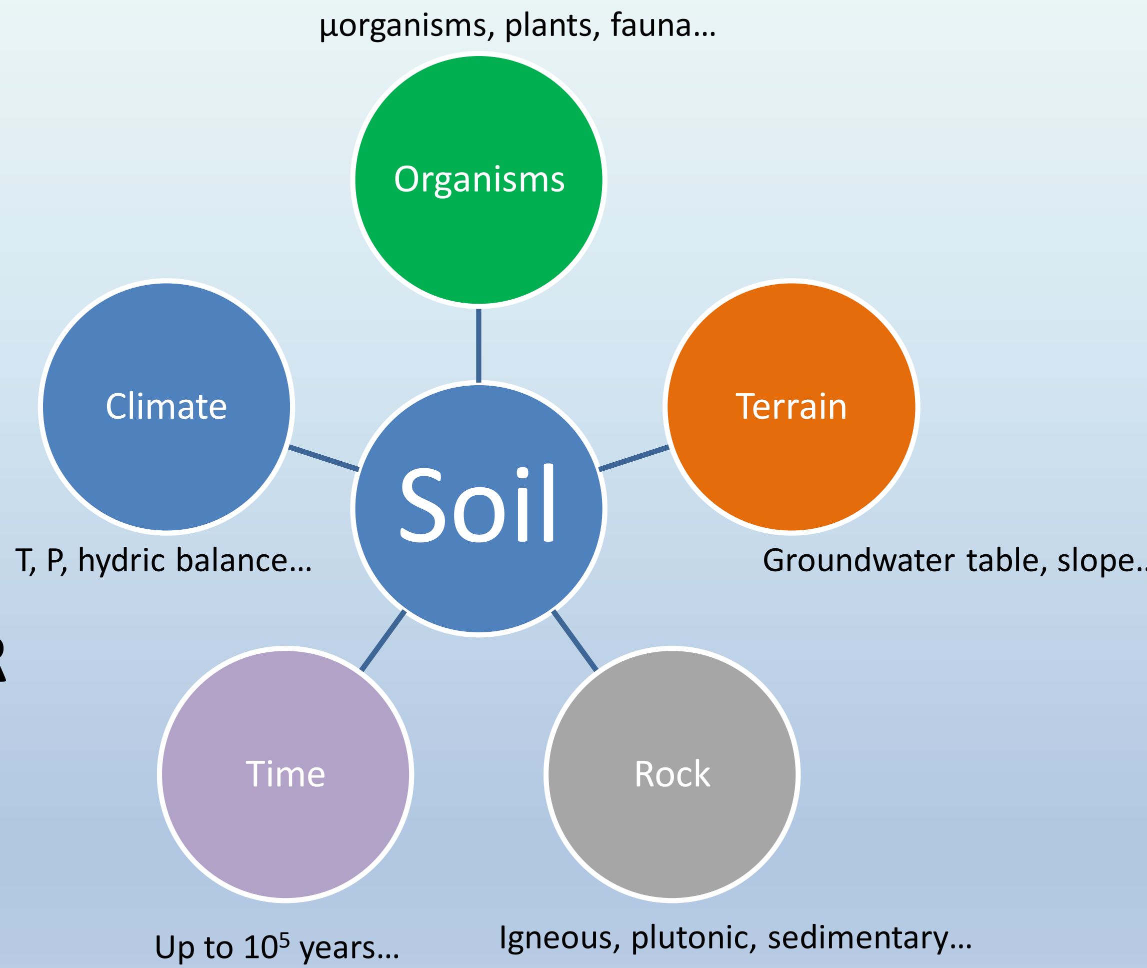
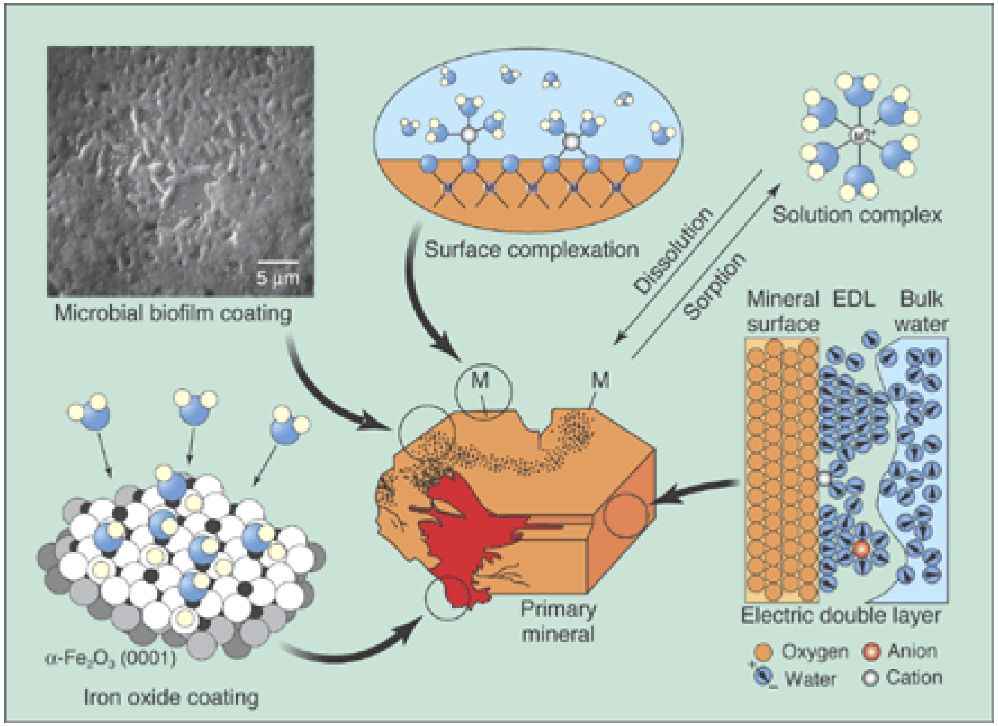
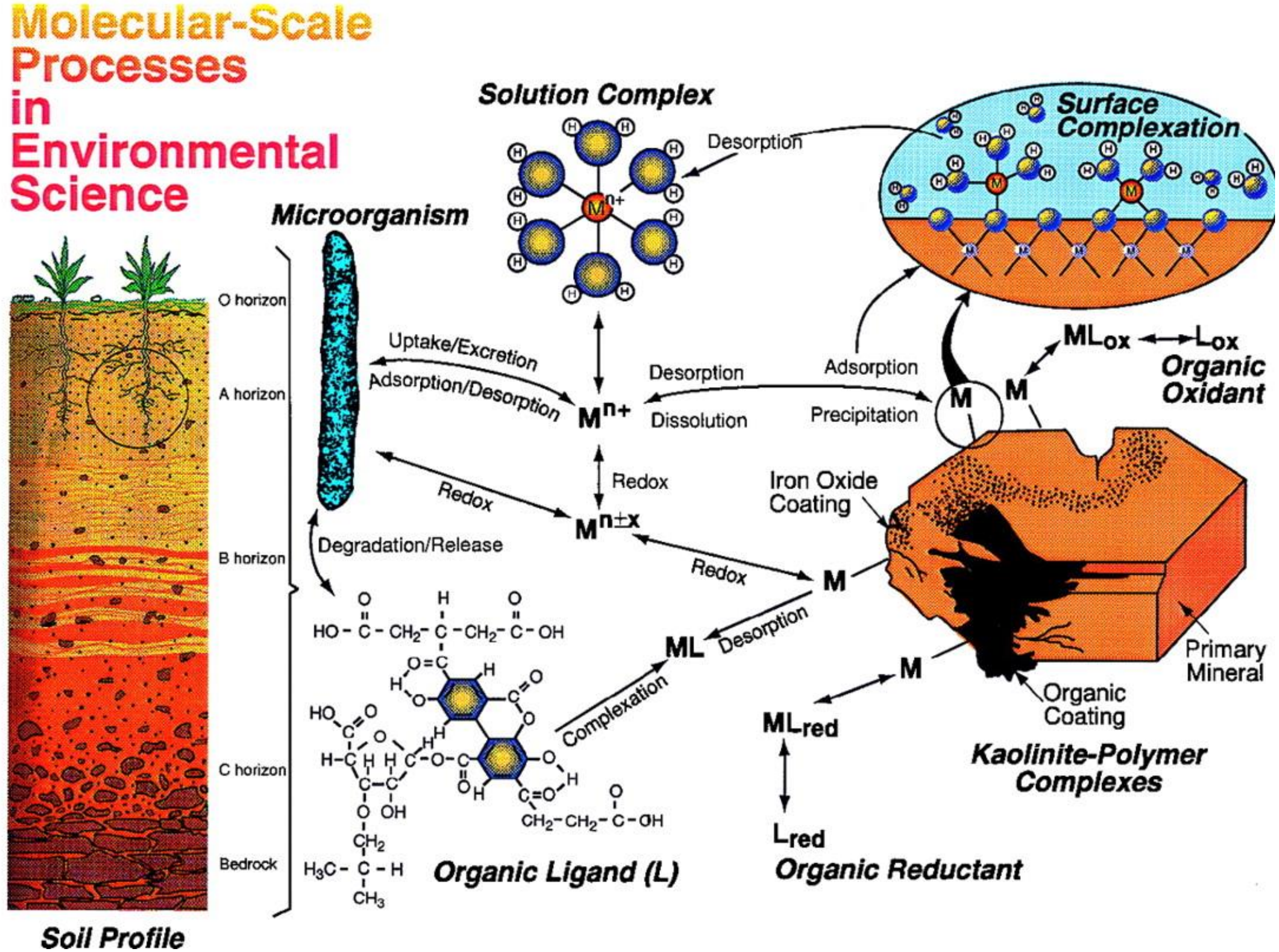
BIO&ORGANIC MATTER
SORPTION PROCESSES
CHALLENGES



Reactions at mineral-solution interfaces




Molecular-Scale Processes in Environmental Science
Solution Complex
Surface Complexation
Desorption
Microorganism
O horizon
A horizon
B horizon
C horizon
Bedrock
Soil Profile
Uptake/Excretion
Adsorption/Desorption
Desorption
Dissolution
Adsorption
Precipitation
Redox
Redox
Redox
Degradation/Release
Iron Oxide Coating
Organic Oxidant
Organic Reductant
Organic Ligand (L)
Complexation
Desorption
Primary Mineral
Organic Coating
Kaolinite-Polymer Complexes