Environmental Geochemistry

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ENVIRONMENTAL GEOCHEMISTRY

- **Environmental Geochemistry**: is the application of chemical principles to predicting the fate of organic & inorganic pollutants at surface & in atm

الفرق بين الجيوكيمياء والجيوكيمياء البيئية: الجيوكيمياء تعنى بدراسة المواد المكونة للارض وتفاعلاتها وسلوكها اثناء التفاعل، اما الجيوكيمياء البيئية فتعنى بدراسة الضرر التي تسببها هذه المواد للحياة

NATURAL Vs. ANTHROPOGENIC

- Human activity have introduced new substances into the environment that didn't exist prior to the Industrial Age (e.g. CFCs, & probably PCBs)
- **Contaminant**: substance present in _greater than natural concentration as a result of human activity_ عندمايزيد تركيز مادة عن حدها الطبيعي في البيئة بفعل الانسان
- **Pollutant (contaminants harms environment)**: is substance present in _greater than natural concentration by human activity that has a net detrimental effect on the environment_ مادة يزيد تركيزها عن حدها الطبيعي وتؤثر على الطبيعة
- **Toxic (Toxicant, Pollutant harms biota):** present in _greater than natural concentration as a result of human activity that has a net detrimental effect upon the life functions_ of one or more biota مادة يزيد تركيزها عن حدها ويصبح لها تأثير على المكونات الحيوية
- **Natural Compounds:** natural occurring, & can be classified as contaminants & pollutants
- **Anthropogenic Compounds:** materials affecting environment produced due to the human activities

BIOGEOCHEMICAL CYCLES

- **Biogeochemical cycle:** natural pathway by which elements of living matter are circulated
- **Elements:** mass of the same atoms can be divided to metal & non-metal based on physical properties
  - **Elements that form 99% of the crust are:** O_2, Si^{4+}, Al^{3+}, Fe^{2+}, Fe^{3+}, Ca^{2+}, Na^+, K^+, Mg^{2+}
- **Mineral:** _naturally_ occurring, _crystalline_, _solid_, _inorganic_, with characteristic _chemical & physical properties_ that allow it for some variation

السبب لوجود عناصر ال native elements كمعدن في الطبيعة وعدم وجود عناصر مثل Fe هو خصائص ال native elements التي تجعلها مستقرة (لا تتفاعل مع عناصر اخرى low reactivity)

- **Biosphere Elements (for life):** O_2, C, N_2, H_2, P, S
  - Make up the building units in living organisms (Carbohydrates, Proteins, Fats, DNAs, RNAs)
- **Reservoirs**: contains a quantifiable amount of material with definable borders, defined by distinct chemical, physical, or biological characteristics
  - Scales are depends on the scope of problem
  - e.g. reservoir of water are Oceans, atm…etc
- **Box models & steady-state assumption** used to trace the passage of bio-geo-hydro-atom-spheres constituent & assess impact of anthropogenic inputs on natural cycle
- **Box model:** consists of several boxes show reservoirs for a substance & the rate at which material is transferred

- **In steady-state system**: the total amount of a substance in each reservoir remains constant (rate of addition = rate of removal of a material)


Steady state scenario
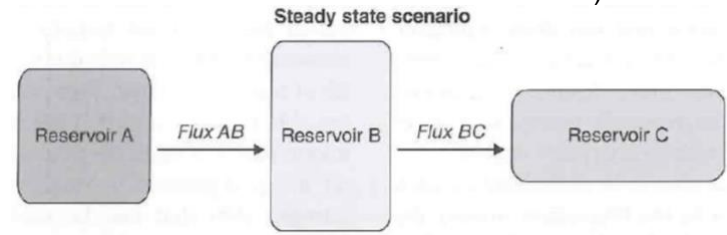
If **_Flux AB = Flux BC_** → B is in study state
If **_Flux AB > Flux BC_** → B will increase
If **_Flux AB < Flux BC_** → B will decrease

Dynamic equilibrium scenario
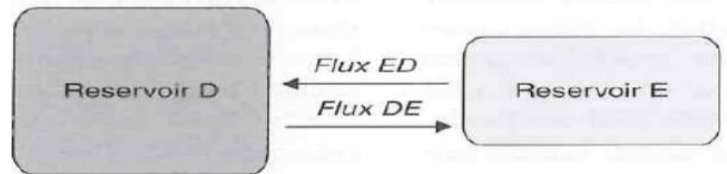
If **_Flux AB = Flux BC_** → the system is in dynamic equliperum (amount of materials will be constant)
If **_Flux AB ≠ Flux BC_** → system is not in dynamic equliperum (amount of materials will be changed)

- **Residence time**: is the average length of time a particular substance will reside in a reservoir

$$t_R = \frac{\Sigma amount\ of\ material\ in\ reservoir}{rate\ of\ addition\ or\ removal}$$

  - $t_{R_{atmospheric\ water}}$ is very short which suggest that change in the rate of addition of water lead to rapid increases in vapor &precipitation. This is referred to as _speeding up of hydrologic cycle due to warming_
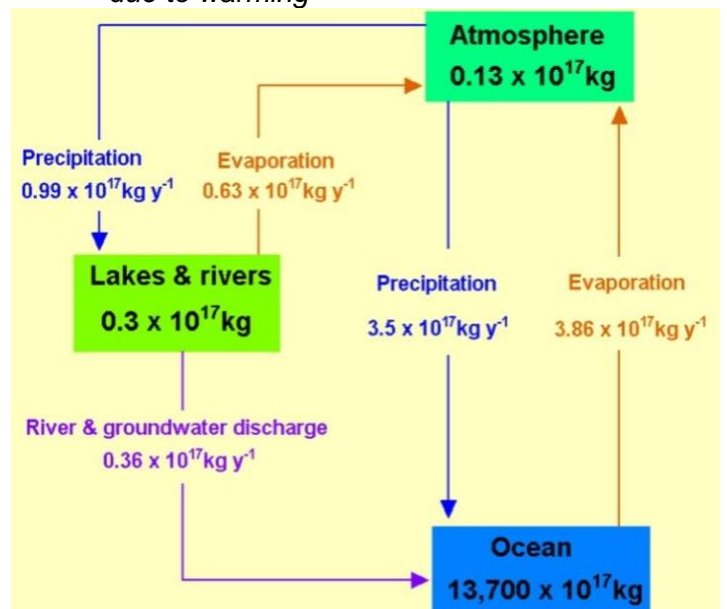


The hydrologic cycle box is the simplest box model

$$t_{ocean} = \frac{13.700 x 10^{17} Kg}{(3.5 + 0.36) x 10^{17} Kg/yr} = 3.549 yr$$

$$t_{Atm} = \frac{0.13 x 10^{17} Kg}{(0.63 + 3.86) x 10^{17} Kg/yr} = 0.0290 yr$$

NITROGEN CYCLE

- **The nitrogen cycle:** is the biogeochemical cycle by which nitrogen is converted into multiple chemical forms as it circulates among atmosphere, terrestrial, & marine ecosystems
- The conversion of nitrogen can be carried out through biological & physical processes
- **Processes in the nitrogen cycle:** fixation, ammonification, nitrification, & denitrification
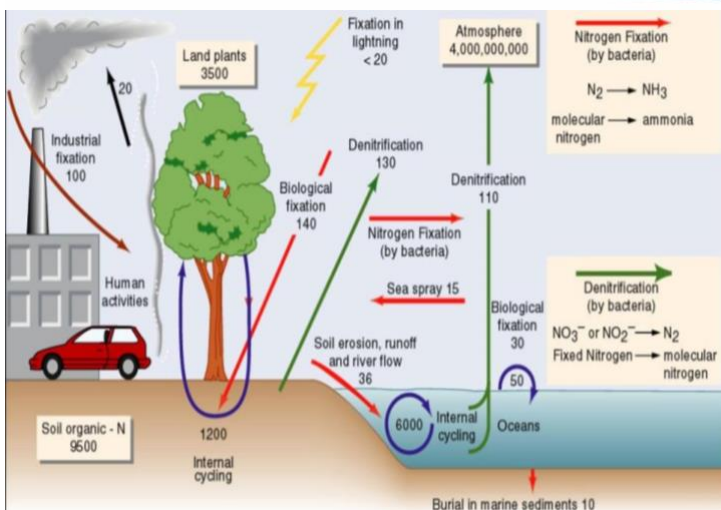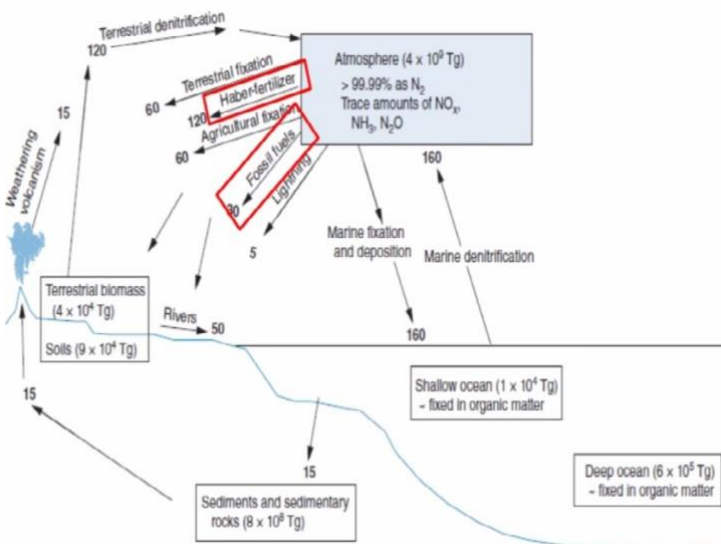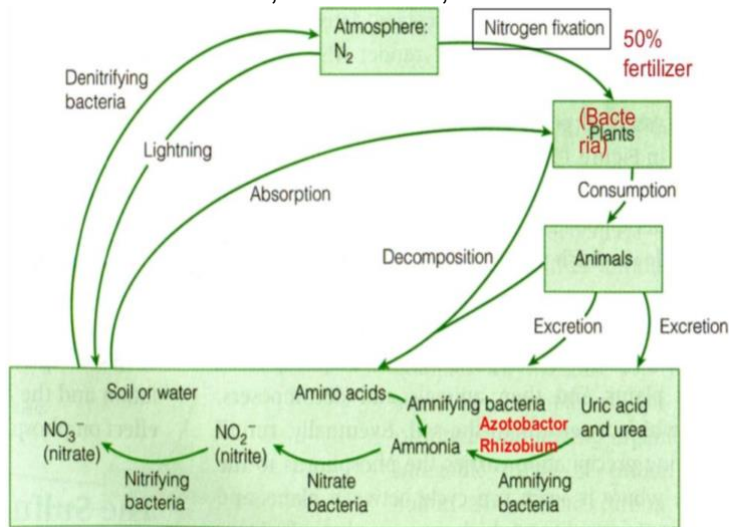

- **Nitrogen Fixation**: conversion of nitrogen gas (N_2) into nitrates (NO_3^-) & nitrites (NO_2^-) through atmospheric, industrial, & biological processes

Nitrogen Cycle	
Lightning fixation	تحدث اثناء البرق (تصل درجة حرارته الى 15 – 30 الف C) وهي حرارة قادرة على كسر الروابط) وتحول هذه الظروف N_2 الى NO_3 $N\equiv N$ ——lightning→ $N + N$, $N + O_2 \rightarrow NO_2$ $NO_2 + H_2O \rightarrow HNO_3 + H$ (in ground): $HNO_3 \rightarrow H + NO_3$ • Atmospheric nitrogen fixed into a usable form to be taken up by plants & fixed by lightning strikes
Biological Fixing	تقوم بعض انواع البكتيريا بتحول N_2 (Urea) Ammonia Acid وفي امعاء بعض الحيوانات يوجد بكتيريا قادرة على فعل ذلك ما يجعلنا نستخدم مخلفات هذه الحيوانات كاسمدة Fertilizers غنية بالنيتروجين • most fixation is done by free-living or symbiotic bacteria that have enzyme combines N with H to produce ammonia, which is converted by the bacteria into other organic compounds • Symbiotic N-fixing bacteria live in root nodules
Assimilation	Plants can absorb nitrate or ammonium from the soil by their root. If nitrate is absorbed, it is reduced to nitrite & then ammonium for incorporation into amino acids, nucleic acids, and chlorophyll
Ammoni-fication	**Ammonification or mineralization**: When a plant or animal dies, Bacteria or fungi convert the organic nitrogen back into ammonium • **Dissimilatory nitrate reduction to ammonium (nitrate/nitrite ammonification):** Microbes reducing nitrate into nitrite, & then ammonium ($NO_3^- \rightarrow NO_2^- \rightarrow NH_4^+$)
Nitrification	عملية حيوية: تمتص بعض البكتيريا حمض ال Ammonia وتحوله الى nitrate وبكتيريا اخرى تقوم بتحويل ال nitrate الى nitrite • Urine are broken down by nitrifying bacteria in the soil to be used by plants • **Nitrification**: The conversion of ammonium to nitrate by soil-living & nitrifying bacteria 1. The oxidation of ammonium (NH_4^+) is converts by bacteria into nitrites (NO_2^-) 2. Other bacterial converts nitrites (NO_2^-) into nitrates (NO_3^-), & It is important for ammonia (NH_3) to be converted to nitrate or nitrite because ammonia toxic to plants
Heber Fertilize	هي تحويل النيتروجين الى امونيا صناعيا industrial fixation $N_2 + 3H_2 \rightarrow 2NH_3$ • Today, about 30% of the total fixed nitrogen is produced industrially using the Haber-Bosch process, which uses high T-P to convert N_2 & H-source (gas or petroleum) into ammonia
Fossil Fuels	ممكن اعتباره من industrial fixation نتيجة لحرق الوقود الاحفوري ينتج اكاسيد النيتروجين وهي من غازات الدفيئة وتساعد بانتاج الاوزون
De-nitrification	هي العملية التي تغلق الدورة حيث تقوم انواع من البكتيريا باختزال مركبات النيتروجين لتحويله الى نيتروجين مجددا واعادته للغلاف الجوي • **Denitrification:** the reduction of nitrates back into nitrogen gas (N_2), completing the nitrogen cycle. & This process is performed by bacterial species under anaerobic conditions • Denitrifying bacteria use nitrates in the soil to carry out respiration & consequently produce N_2, which is inert & unavailable to plants • occurs in free-living microorganisms
Anaerobic ammonia oxidation	nitrite & ammonia are converted directly into nitrogen gas (N_2). This process makes up a major proportion of nitrogen conversion in the oceans

- common Nitrogen species

| Species	Name	ON	Species	Name	ON
NH_3	Ammonia	-3	N_2O	Nitrous Oxide	+1
NH_4^+	Ammonium	-3	NO	Nitric Oxide	+2
$(NH_2)_2CO$	Urea	-3	HNO_2	Nitrous Acid	+3
N_2H_4	Hydrazine	-2	NO_2^-	Nitrous	+3
NO_3^-	Nitrate Ion	-1	NO_2	Nitrous Oxide	+4
N_2	Nitrogen	0	HNO_3	Nitric Acid	+5
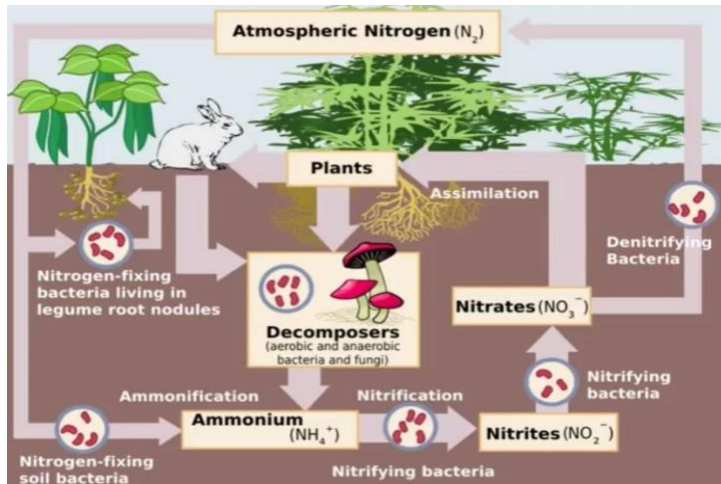
لماذا النبات لا يأخذ النيتروجين؟ لانه غاز خامل (مستقر) بسبب احتواؤه 3 روابطه الكيميائية تساهمية (covalent bond 3) تجعل منه غاز خامل ويصعب تفاعله مع المواد الاخرى (يحتاج طاقة كبيرة)

Common Nitrogen Species	
Nitrous oxide (N_2O)	• **A Greenhouse, 300 times > potent than CO_2** • **Formed by (Origin) :** 1. **denitrification of fertilizers** notably in tropical & subtropical soils 2. **non anthropogenically enhanced denitrification & nitrification:** soil,marine
N-oxide (NOx)	• Include N monoxide (NO) & dioxide (NO_2) • Form during combustion & grouped together
Nitric acid (HNO_3)	• **Formed by (Origin):** 1. forms in atm by oxidation of N-oxides 2. product of volcanic eruptions
Nitrate (NO_3)	• A highly soluble ion that is a product of natural oxidation of organic matter & molecule
Urea ($(NH_2)_2CO$)	• **Environments**: crustal with low dissolved O, wetland sediment, deep marine water • **May be formed by** decaying of organic matter

• **How are Human Activities Affecting N-Cycle?** Industrial fixation N-oxides from fuel combustion
• **Effects of increased use of nitrogen fertilizer:**
1. Eutrophication of industrie & marine ecosystem associated loss of plant & animal diversity
2. acid rain (nitric); & acidification of soils & water
3. acid rain-related losses of essential soil nutrient (i.e. Ca & K important in forested ecosystems)
4. Increased concentration of potent greenhouse gas nitrous oxide (NO) in the atmosphere
5. increased concentrations of nitrogen oxides (contribute to formation of photochemical smog)
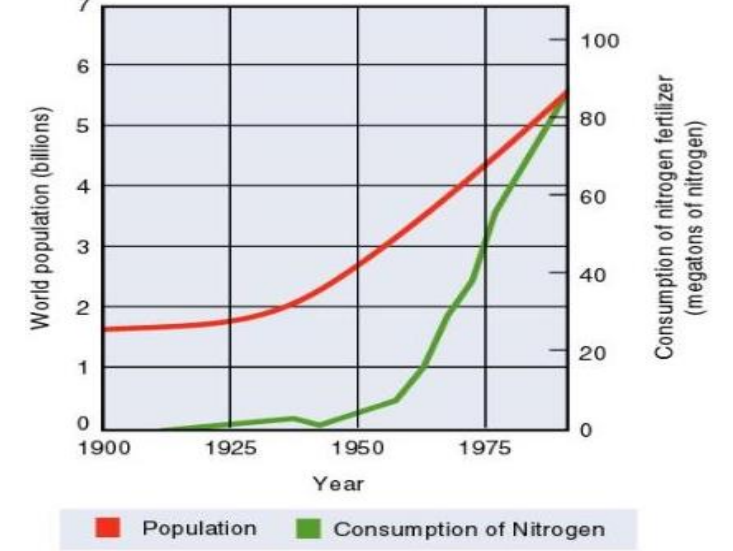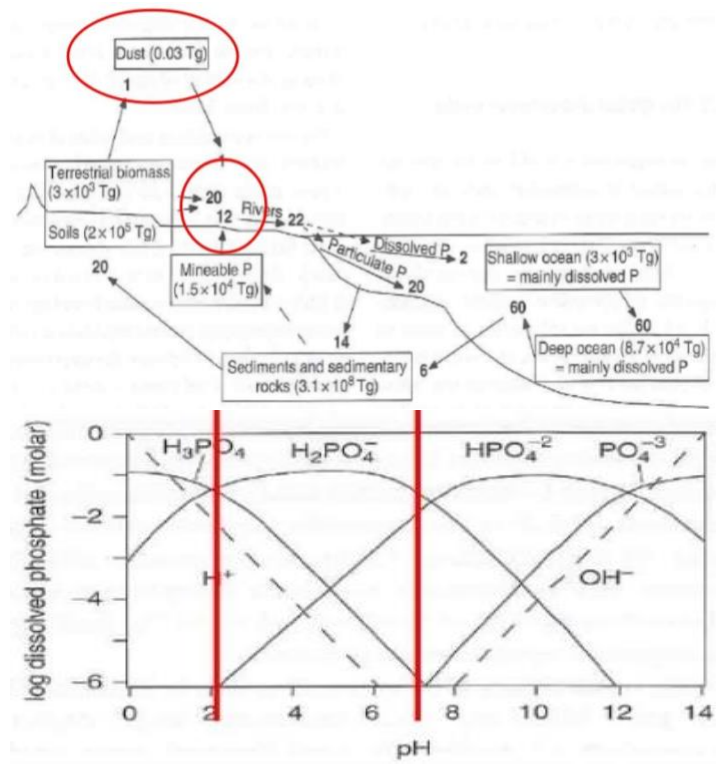
الفوسفيت يوجد بالصخور ويتحلل في ال weathering وينتقل عبر للانهار والامطار للمحيط حيث يترسب مجددا بالصخور، وعند تعدين البشر له جزء منه يذهب للغلاف الجوي كغبار ما يؤدي لل eutrophication

• **The phosphorus cycle:** is the biogeochemical cycle that describes the movement of phosphorus through the lithosphere, hydrosphere, & biosphere
• **Phosphorus cycle is simpler cycle** because has no any gas phases, & only one valance state P^{5+} (unlike many other cycles, the atmosphere does not play a significant role in the movement of phosphorus, because phosphorus are usually solids at the typical ranges of T-P)
• **Phosphorus is vital for living organism:**
1. Very important component of DNA & RNA
2. Energy transferred via ATP
• **Sources**: major receivers are soils & rocks
  ➢ major source is soils in apatite
  ➢ can be found in chemical sedimentary rocks
  ➢ can be found in igneous rocks (within some rare minerals e.g. turquoise, autunite, monazite)
• A good starting point for the P-cycle is chemical weathering of hydroxyapatite in soils

$$Ca_5(PO_4)_3OH + 4H_2CO_3 \rightarrow 5Ca^{2+} + 3HPO_4^{2-} + 4HCO_3^- + H_2O$$

Soil Conditions	Dominant
pH = 2-7	$H_2PO_4^-$
pH = 7-12	HPO_4^{2-}
Very acidic situation(acid mine drainage)	H_3PO_4
extremely alkaline	PO_4^{3-}

• **Factors make P limiting nutrient in soil &aquatic ecosystem (dominantly bound in solid phases)**
1. Insoluble or sparingly soluble in most conditions so in soils their anion (PO_4^{3-}) tends to form poorly crystalline hydrated solids (bonded Ca)
2. Apatite resist erosion (stable), slowly released to soil during weathering ($Ksp_{apatite} = 10^{-58}$ الذائبية قليلة جدا value that would produce equilibrium concentration of dissolved P of = 10^{-8} molar)

	Nitrogen	Phosphorous
Phase	gas in atmosphere	no gas phase
Source	Atmosphere	Rock
Fixing	Fixing microbes introduce reactive N to soil & ecosystems	Cannot be fixed from air & introduced by rivers, wind-blown dust, & weathering
State	Numerous states	Only +5
Redox control	Prone to strong redox controls	Prone to redox control if sorted to Fe-oxide
Solubility	On surface water occure as highly soluble nitrite	insoluble & partitioned into particulate fraction (silt, Clay..)
Limiting nutrients	limiting nutrients in aquatic ecosystem	truly limiting nutrient in ecosystems

لو كان هناك نبات لم يتم اضافة N له سينمو لانه ستنشأ بكتيريا قادرة على اخذه من الغلاف الجوي، لكن لو لم نضع P في التربة فلن ينمو لان الفوسفور لا يتواجد بالغلاف الجوي وهو incorporated in solid phases لذا لا تستطيع النباتات امتصاصه وبالتالي الفوسفور هو ال limiting reactant

- Humans have caused major changes to the global P-cycle through shipping of P-minerals, & use of phosphorus fertilizer
  - 80% of the mined phosphorus is used to make fertilizers that cause pollution in lakes & streams
  - Over-enrichment of phosphate in marine waters lead to massive algae blooms. the death & decay of these blooms leads to eutrophication
- **Eutrophication**: enrichment of water by nutrient, lead to structural changes to the aquatic ecosystem
  - primary source contributes to the eutrophication is considered as nitrogen and phosphorus
- Phosphorus does enter the atmosphere in very small amounts when the dust is dissolved in rainwater but remains mostly on land, rock, & soil
- **Phosphorus Cycle:**
  1. occur as orthophosphate $(PO_4)_3^-$ in rocks
  2. Phosphorus-rich deposits are formed in the ocean or from guano, & geologic processes bring ocean sediments to land
  3. Weathering & minerals release phosphorus in a soluble form where it is taken up by plants, & transformed into organic compounds
  4. Plants consumed by herbivores & phosphorus is incorporated into tissues & after death the organisms decays, & phosphorus is returned to the soil where a large part of the phosphorus is transformed into insoluble compounds
  5. Runoff carry part of P back into the ocean
  - Phosphates move quickly through plants & animals, the processes that move them through the soil or ocean are very slow, making the phosphorus cycle one of the slowest cycles
  - Generally with time soils become deficient in phosphorus leading to ecosystem retrogression
- **phosphorus transportation processes**
  1. Tectonic uplift & exposure of phosphorus-bearing rock (e.g. apatite) to surface weathering
  2. Erosion & weathering of P-bearing rocks to provide phosphorus to soils, lacks, & rivers
  3. Riverine & subsurface transportation of phosphorus to lakes & run-off to the ocean
  4. Sedimentation of particulate phosphorus & eventually burial in marine sediments

SULFUR CYCLE

- Sulfur occurrence:
  1. **Biosphere**: In amino acid, protein, & in plants
  2. **Lithosphere (Dominant)**: soil, & as pyrites in sediment, & in Marine (SO_4^{2-} oxic & S^{2-} anoxic)
  3. **Withosphere**: less in S-minerals (e.g. gypsum)
  4. **Atmosphere:** as SO_2 & H_2S gases
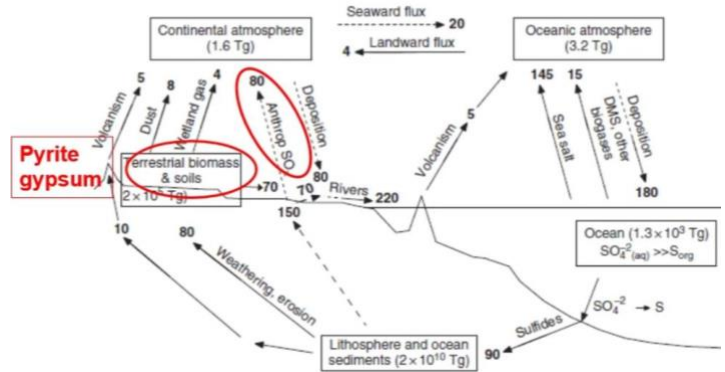
يحدث weatheringلل Gypsum او Sulfite في lithosphere جزء منه ينتقل عبر الانهار للمحيط وجزء اخر يبقى بال Soil وتأخذه النباتات:

1. عندما تموت النباتات ولا تدفن يحدث decay لاهوائي وتعود للتربة
2. عندنا تدفن النباتات يحدث لها تحلل لاهوائي بفعل البكتيريا وجزء منه يدخل بتركيب المادة العضوية وجزء يدخل في تركيب ال fossil fuel
3. ينتقل من البراكين للغلاف الجوي ويتحد مع الماء ليصنع مطر حمضي ويحدث له reducing فيتحول من Sulfate الى sulfur S^{-2} وممكن ان يتخد مع H او مع Fe لتكوين sulfite او pyrite
- **تأثير الانسان** حرق الوقود يحرر S^{-2} الموجود به بسرعة اكبر وتكمن خطورته بتكوين المطر الحمضي والذي يذيب كربونات الكالسيوم
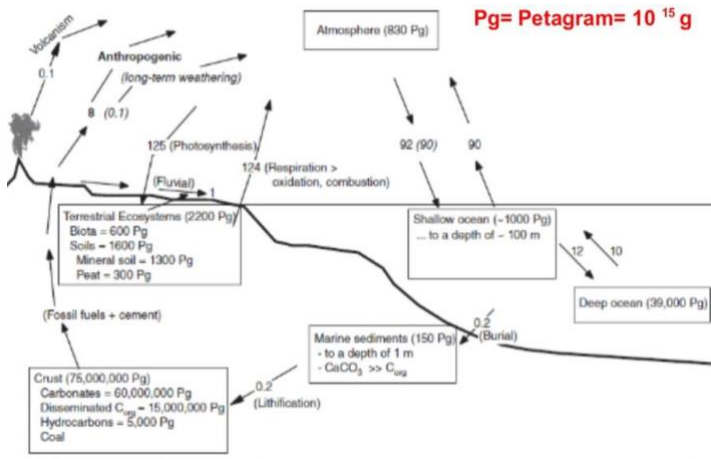
- **Sources of sulfur:**
  1. *Natural Source*: volcanic activity
  2. *Industrial Source*: Human Activity (fossil fule)
- **Environmental impact of sulfur on environment**:
  1. **Acid rain (SO_2)**: cause deforestation, acidify waterways to the detriment of aquatic life, & corrode building materials & paints
  2. **Acidic drainage (mines)**: formation & movement of acidic water rich in heavy metals, that forms through reaction of surface & shallow subsurface waters with rocks contain S-bearing minerals, case sulfuric acid

$$FeS_2 + H_2O \rightarrow Fe(OH)_3 + 2H_2SO_4$$

Species	Name		Environments
PbS	Galena (lead sulfides)	-2	**Reducing environment** (Wetland sediments, Low oxygen crustal environments, & Deep marine)
ZnS	Sphalerite	-2	
CuFeS₂	Chalcopyrite	-2	
HgS	Cinnabar	-2	
(CH₃)₂S	DMS	-2	
(CH₃)₂SO	DMSO	-2	
C₇H₁₄N₂O₂S	Aldicarb (synthetic)	-2	
H₂S	Hydrogen Sulfide	-2	
COS or OCS	Carbonyl sulfide	-2	
CS₂	Carbon disulfide	-2	
FeS₂	Pyrite (Iron sulfide)	-2	
FeAsS	Arsenopyrite	-2	
SO	Sulfur Monoxide	+2	**Oxidizing Environment**
H₂SO₃	Sulfurous Acid	+2	
SO₃⁻	Sulfite Anion	+4	
SO₂	Sulfur Dioxide	+4	
SF₆	Sulfur Hexafluoride	+4	
SO₃	Sulfur Trioxide	+4	
BaSO₄	Barite (barium Sulfate)	+4	
CaSO₄.2H₂O	Gypsum (calcium sulfite)	+6	
KFe₃³⁺(OH)₆(SO₄)₂	Jarosit	+5	
H₂SO₄	Sulfuric Acid	+5	
SO₄²⁻	Sulfate Anion	+6	

CARBON CYCLE

Pg= Petagram= 10^{15} g
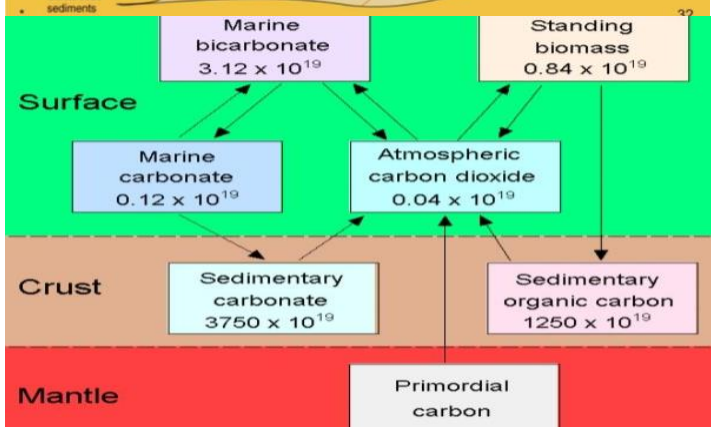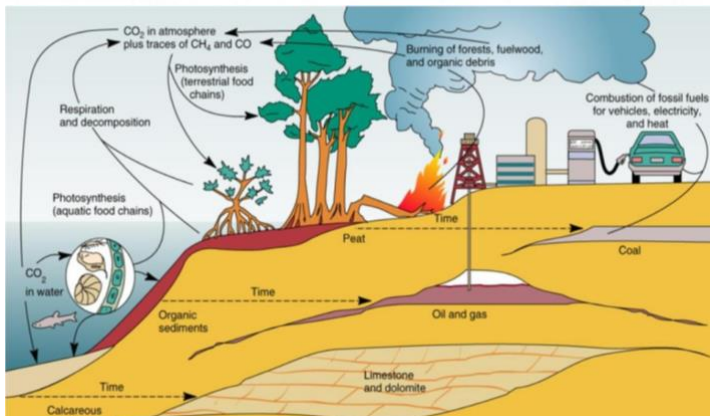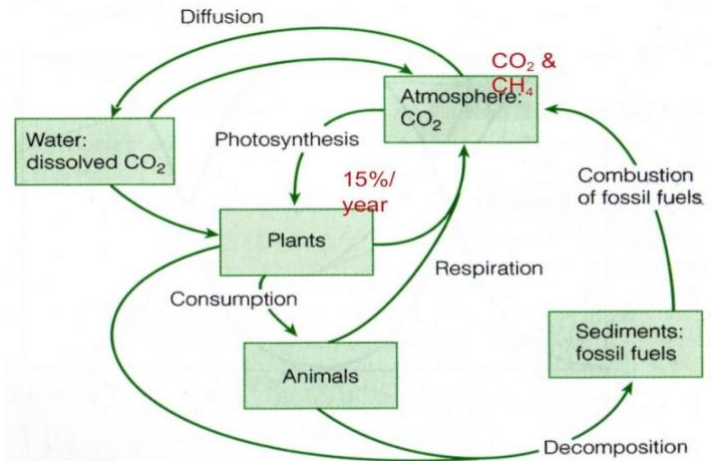
دورة الكربون: يوجد بالغلاف الجوي على هيئة CO_2 وتأخذه الاشجار بالبناء الضوئي وعند حرق الاشجار او اكلها من كائنات اخرى وموت وتحلل الكائنات يعود للغلاف الجوي مجددا او يتحلل لاهوائيا بعد دفنها لينتج غاز الميثان والفحم اما البترول يأتي من عمليات التحلل اللاهوائي بالمحيط حيث يتحول CO_2 الى HCO^- او CO^{2-} والذي تستهلكه الكائنات الحية ببناء اصدافها وعندما تموت تترسب بقاع المحيط وتكون الصخور الكلسية التي يحدث لها uplifting ويتكون من هذه العملية البترول

التدخل البشري: يفترض ان يحبس الكربون بالوقود لملايين السنين لكن الانسان يحرره بكميات كبيرة وبوقت اقل عند حرق هذا الوقود الاحفوري وتكمن خطورته بانه من ال Greathouse Gasses

- Carbon Occurrence:
  1. **Biosphere**: Forms the basis of life
  2. **Atmosphere**: major role in earth's climate
  3. **Lithosphere:** major agent of chemical Weathering & soil formation (as carbonic acid)
- **Forms**: occurs in organic & inorganic forms & important constituents of all reservoirs (lithosphere , atmosphere , oceans and living organisms)

Formula	Name	Formula	Name
CO_2	Carbon dioxide	HCO_3^- , CO_3^{2-}	bi carbonate ion
HCHO	Formalde Hyde	CO_2H-CO_2H	Oxalatic acid
C_2H_4	Enthylene	CHO-CHO	Glyoxal
C_2H_6	Ethane	CH_2OH-CH_2OH	Glycolic Acid
CH_4	Methane	CH_2OH-CH_2OH	Enthylene Glycol

Oxidation state = [4, -4]

Reservoir	Amount [$\times 10^{14}$g C]	*Carbonites rock 600,000,000 Dispersed organic C 150,000,000 Hydrocarbons (coal) 50,000
Crust*	750,000,000	
Ocean	400,000	
Soils	16,000	
Atmosphere	8,300	
Land Plants	6,000	
Mantle	In form of graphite or diamonds	

COMPARISON BETWEEN CYCLES

- **Common in all cycles**
  1. essential element in living organisms
  2. cycled between biota, organic & inorganic forms
  3. can react with Oxygen
  4. important of terrestrial & marine ecosystems
  5. play roles in global climate
  6. Improving environmental quality of terrestrial & aquatic ecosystems & the atmosphere will require better management of these critical elements
- **as a result of immobility behavior of P^{5+}** it should be easier to control movement from soil to aquatic system
- **N & P limiting nutrients:** control primary productivity in terrestrial & aquatic ecosystems & affect cycling of C (by controls of photosynthesis & S via plants uptake)
- Formation of carbonic acid in atmosphere exerts a strong control on weathering rates & release P & S to soil
- Formation of sulfuric acid (anthropogenic>>natural rate) can enhance cycling of all dements by speeding up chemical weathering & oxidation of organic matter
- Various species of C,N, & S released to air during combustion of fossil fuels so this anthropogenic activity greatly affects the cycles of these 3 elements

	N	P	S	C
Atmospheric fluxes	✔	✘	✔	✔
Mobile (Fixing)	✔	✘	✔	✔
Phase	All	No Gas	All	All
Source	Atm	Rock	Litho.	All
State	-3, +5	Only +5	-2, +6	-4, +4

PROBLEMS

1. Describe the difference between steady state & dynamic equilibrium & provide an example of each
2. What is the most oxidation state of N?
3. Why microbes exert a strong control on N transformations.
4. What is the most oxidation state of S?
5. Main ways by which humans have altered S cycle
6. Reservoirs from which humans are extracting S
7. Indicate chemical reactions responsible for transfer of sulfur into other reservoirs
8. Indicate 2 problems resulting from altered S cycling
9. microbe facilitate nitrification & denitrification. How
10. Both P & N cause eutrophication, indicate by what processes N & P commonly enter aquatic bodies. Show these pathways with a schematic sketch
11. Which process returns nitrogen gas into the atm?
12. The mean residence time of C in atmosphere
13. Describe 2 main means by which C is transferred from atm to ocean (i.e. organic vs. inorganic). & indicate which tends to result in long-term storage
14. Main factor limiting practical application of mineral carbonation as a strategy for managing carbon?

Q1	**Steady State**: flux of a given component into the reservoir is equal to the flux out. $dC/dt = 0$ $$\text{rate}_{\text{form (increase [C])}} = \text{rate}_{\text{remove (decrease [C])}}$$ • Ca-flux into sea by rivers transportation = rate at which it is removed by precipitation of $CaCO_3$. way by which Ca is added to oceans not reversible **Dynamic equilibrium**: if $\text{rate}_{\text{forward}} = \text{rate}_{\text{reverse}}$ so the concentrations don't change over time (only in a closed, or isolated system). $A \Leftrightarrow B$ $$\text{rate}_{\text{forward rex}} = \text{rate}_{\text{reverse rex}}$$ • Dissolution of $CaCO_3$ in closed system $$CaCO_3 + 2HCl \leftrightarrow CaCl_2 + H_2O + CO_2$$
Q2	From -3 to +5 (N^{2-} & N^{1-} : rare & not exist naturally)
Q3	Providing different forms of N-compounds able to be assimilated by higher organisms 1. **N-Fixing**: Some type of bacteria take N_2 from atm & turn it into ammonia $$N{\equiv}N + 8H^+ + 8e^- + 16ATP \rightarrow 2NH_3 + H_2 + 16ADP + 16Pi$$ 2. **Decomposition**: as plants die & buried, bacteria convert ammonia into ammonium in soil $$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$$ 3. **Nitrification**: convert NH_4^+ in soils into nitrites, & then another type converted nitrite into nitrate $$2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 4H^+ + 2H_2O$$ $$2NO_2^- + O_2 \rightarrow 2NO_3^-$$ 4. **Denitrification**: Other bacteria reduce nitrates to convert it into nitrogen $$NO_3^- + NO_3^- \rightarrow N_2 + 2O_2$$
Q4	From -2 to +6

Q5	Burning fossil fuels, where humans accelerated the process of releasing sulfur from fossil fuels
Q6	Lithosphere: majority in Marine environment exist as sulfate in soil & pyrites in sediments & rocks
Q7	Sulfide in marine fixed by reaction with iron in a process that can be represented as: $$8SO_4^{2-} + 2Fe_2(OH)_3 + 8H_2O + 15C \rightarrow 4FeS_2 + 16OH + 15CO_2$$ $$FeS_2 + H_2O \rightarrow Fe(OH)_3 + H_2SO_4$$ $$H_2SO_4 + H_2O \rightarrow HSO_4^- + H_3O^+$$ $$HSO_4^- + H_2O \rightarrow SO_4^{2-} + H_3O^+$$
Q8	1. **Acid precipitation:** sulfuric acid derived from fossil fuel combustion (coal) 2. **Acidic drainage (mines):** refining of metal contained in sulfide ore. formation & movement of acidic water rich in heavy metals, forms through reaction of surface & subsurface waters with rocks contain S-bearing minerals, case sulfuric acid
Q9	**Nitrification**: bacteria convert NH_4^+ in soils to nitrite & then another type converted nitrite into nitrate $$2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 4H^+ + 2H_2O$$ $$2NO_2^- + O_2 \rightarrow 2NO_3^-$$ In **Denitrification**: Other bacteria reduce nitrates to convert it into N: $NO_3^- + NO_3^- \rightarrow N_2 + 2O_2$
Q10	**Nitrogen:** enter the aquatic bodies through marine fixation & deposition process directly from atm, or trough rivers & rainwater from soils & rocks (the nitrogen enter the soil itself also by fixation process) **Phosphorus:** dissolved phosphorus also enter the oceans by rivers or rain water from dissolved phosphate in mines or phosphorus dust
Q11	Denitrification
Q12	$$t_r = \frac{830 Pg}{(125 + 92)} = 3.825$$
Q13	١. يوجد الكربون بالغلاف الجوي على هيئة CO_2 وتأخذه الاشجار في عملية البناء الضوئي لتصنع السليلوز وعند حرق الاشجار او اكلها من كائنات اخرى وموت وتحلل الكائنات يعود للغلاف الجوي مجددا او تتحلل لا هوائيا بعد دفنها لينتج غاز الميثان والفحم اما البترول يأتي من عمليات التحلل اللاهوائي بالمحيط حيث يذوب CO_2 في المحيط ويتحول الى HCO^- او CO^{2-} والذي تستهلكه الكائنات الحية ببناء اصدافها وعندما تموت تترسب في قاع المحيط وتكون الصخور الكلسية التي يحدث لها uplifting ويتكون من هذه العملية البترول ٢. ممكن ان يذوب ثاني اكسيد الكربون الموجود بالجو مباشرة في المحيط ويصنع من هذه العملية كاربونات الكالسيوم طبقا للمعادلات الاتية $$CO_{2\,\text{(from atmosphere)}} + H_2O_{\text{(from ocean)}} \rightarrow H_2CO_3$$ $$H_2CO_3 \rightarrow H^+ + HCO_3^-$$ $$HCO_3^- \rightarrow H^+ + CO_3^{2-}$$ $$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3$$
Q14	Global Warming (because C in Greathouse gas)

ONLINE QUIZZES
**NITROGEN CYCLE**
PHOSPHORUS CYCLE
CARBON CYCLE

ENVIRONMENTAL GEOCHEMISTRY

CHEMICAL BONDS

- **Ionization potential (IP):** energy required to remove electron from a neutral atom to infinite distance from the nucleus
- **Electron affinity(EA)** tendency of atom to attract e-
- **Electronegativity (χ):** ability of atom to attract e-

	IP	EA	χ	Electrons	Form
Metals	Low	Low	Low	Lose	Cation
Non-Metals	High	High	High	Gain	Anion

- **Ionic Bond**: formed via the electrostatic attraction between oppositely charged ion
  - Idolized ionic or electrovalent bonding
 - Electrostatic attraction represent by Coulomb's
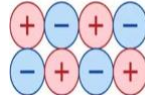
$$\overline{F} = \frac{1}{4\pi\varepsilon_0}\frac{Z_+Z_-}{r^2}$$

E: permittivity, for free space: 8.84×10^{-9} [farad/m, C/Volt m]
F: attraction force, Z: cation-anion charges, r: cat-ani distance

- **Covalent Bond:** by sharing of electrons
  - Found in gaseous (e.g. N_2) or organic compound, some mineral (Diamond)
  - **May have some ionic character** & vice versa because sharing of e- may not be equal
  - **Polar Covalent bond**: sharing of e- pair is unequal (one atom more +ve & other more -ve)
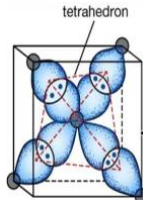
- **Metallic Bond:** once valence electrons released by a metal atom they aren't fixed with a specific atom but migrate through the crystal structure as cloud
  - Weaker than covalent & ionic & are part of the reasons why metal bearing sulfide minerals are relatively unstable at the Earth surface
  - Occurs in: **sulfide minerals** (e.g. pyrite), **native elements** (e.g. Cu, Ag), & **some elements in solid state** (e.g. Cu, Cr, Fe, Ni, & Zn)
- **Dipole bonds (VDW & H):** Exist between electrically neutral molecules or compounds with some unequal distribution of electrons
  - Occur in sheet silicate (e.g. Biotite), diamond & graphite, & in water molecules
  - Water has a permanent dipole but van der Waals bonds also exist between electrically neutral molecules or compounds where the electrostatic attractions are temporary
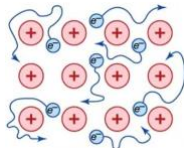
- **Ionic vs Covalent Character:** We use differences in electronegativity to determine ionic character %

Percentage of Ionic character of a single bonds with O												
Δχ	%	Δχ	%	Δχ	%	Δχ	%	Δχ	%	Δχ	%
0.1	0.5	0.7	12	1.3	34	1.9	59	2.5	79	3.1	91
0.2	1.0	0.8	15	1.4	39	2.0	63	2.6	82	3.2	92
0.3	2.0	0.9	19	1.5	43	2.1	67	2.7	84	From 3.2 to 3.9 >92	
0.4	4.0	1.0	22	1.6	47	2.2	70	2.8	86		
0.5	6.0	1.1	26	1.7	51	2.3	74	2.9	88		
0.6	9.0	1.2	30	1.8	55	2.4	76	3.0	89	4	100

Electronegativity (χ)

EXAMPLE calculate ionic character for CsF

$\Delta\chi_{CsF}$ = 4.0 - 0.7 = 3.3 → >92%ionic,<8%covalent

- **Ionic vs metallic character:** why Al good electrical conductor than Na or Fe? Or why Al behave as ductile material whereas Na are brittle (break)
  - The answer for 2 question that the Al have ionic character whereas Na have a metallic character

لماذا الالمنيوم electrical conductor اكثر من الحديد؟ لان عدد الكترونات Al في المدار الاخير اكثر ما يؤدي لنشوء رابطة ايونية لماذا ينكسر Al ولا يتكسر Na: لان الغيمة الالكترونية في Na تبقى تتحرك بين الذرات الموجبة ما يؤدي لتغير شكله بلا كسر (لاحتوائه metallic bond) اما Al فيحتوي ionic bond فعند ازاحة صف من الذرات ستكون الذرات الموجبة على نفس مستوى الموجبة بالصف الاخر والسالبة على نفس مستوى السالبة ما يؤدي لتنافرها وبالتالي انكسار العينة التى تعرضت للطرق
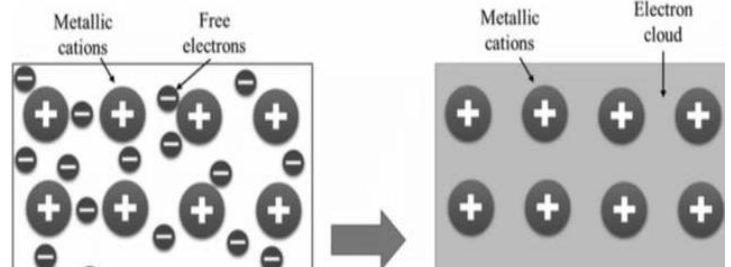

WATER MOLECULE

- The earth is only planet in the solar system where water occurs in all three phases (solid, liquid, gas)
- Water covers 70% of the surface, & The amount of water (1.4 Gkm³) in the earth system is constant
- The oceans accounts for over 97% of the earth's water, & 60-75% of the human body is water
- Water moving in circulation called hydrologic cycle

Occurrence of water on the earth   Occurrence of non-oceanic water
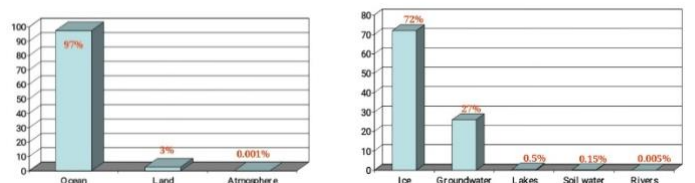
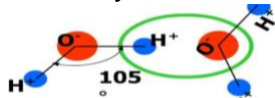| Classification of Waters	
Meteoric	Derived from atm as rain or snow
Formation	Pore water in deep sedimentary rock
Metamorphic	From dehydration reactions
Juvenile	From the mantle
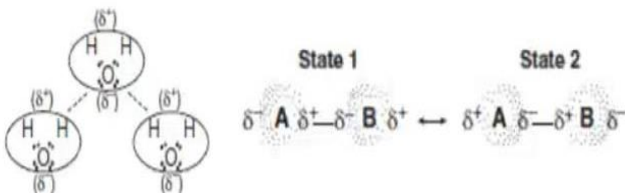
- **All physical & chemical properties of a compound depend on the character of the chemical bonds** (e.g. *like dissolves like*)
 - water is a polar covalent solvent so ionic compounds have high aqueous solubility

EXAMPLE NaCl are 67% ionic character so it soluble, but Diamond have 0% it nearly insoluble

- each water molecule has +ve & - ve end that can attract to form H-bond
- **The H-bonding of water is responsible for**
  1. high boiling point & melting point
  2. The maximum density is at 4°C
  3. Ice is less dense than the liquid water
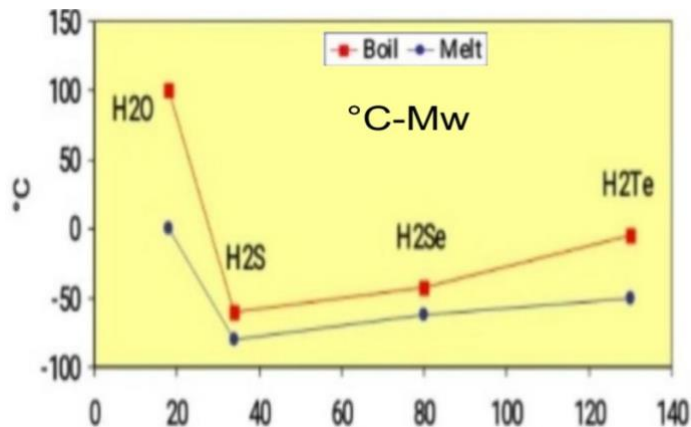
Properties of water	
Heat capacity	Highest of all solids & liquids (except NH_3)
Latent heat	**Of fusion**: Higher than most solids & all liquids (except of ammonia NH_3) **Of vaporization**: Highest of all substances
Dissolving ability	Dissolves more substances (ionic) & in greater quantity than other common liquid
Transparency	Relatively high for visible light
Physical state	only substance occurs naturally in all 3 states
Surface tension	Highest of all common liquids
Conductivity	Highest of all common liquids (except Hg)
Viscosity	Relatively low viscosity for a liquid

- **Water as Solvent**: Water dissolves every solid or gas, & due to polar nature of water ions will be surrounded by water dipoles (hydrated) in solution
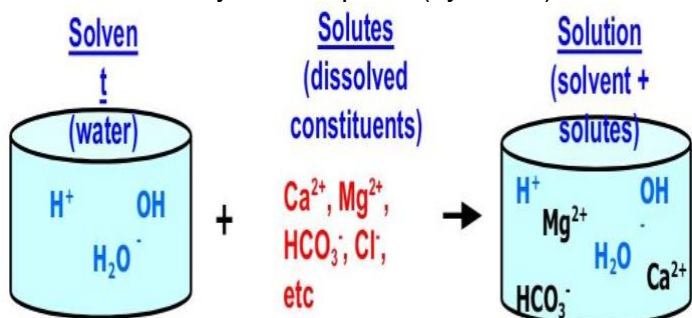
- **Hydration:** isolate ion from their neighbor & neutralize attractive forces that hold minerals together

UNITE OF EXPLORATION

- **Units of mass concentration:**
  1. **weigh/ weigh units (wt/wt)**: ppm , ppb
  2. **weigh/volume units (S)**: mg/L , g/L

$$ppm = \frac{m_{solute}\, in\, mg}{m_{solution}\, in\, Kg}$$

$$mg/l = \frac{m_{solute}\, in\, mg}{V_{solution}\, in\, L}$$

$$ppm = \frac{1g}{10^6\, g} = \frac{1mg}{1kg} = \frac{1mg}{L}\, x\, \frac{1}{\rho}$$

- **Units of Molar Concentration:**
  1. **Mole (n)** = 6.023×10^{23} atoms or molecules
  2. **Mole faction (X):** is used for solid solutions
  3. **Molality (m), & Molarity (M):** involved in calculation deal with volumetric stoichiometry
  4. **Percentage (%):** ratio of solute to the solution, if [solution] is given as a percentage you can assume it is a mass% unless otherwise stated
  5. **Normality or mole equivalent (equ or N):** are similar to moles but take into account valence

$$X = \frac{n_{solute}}{\Sigma n}$$

$$M = \frac{n_{solute}\,[mole]}{V_{solution}\,[L]}$$

$$m = \frac{n_{solute}\,[mole]}{m_{solvent}\,[Kg]}$$

$$N\,(o\,equ) = n\,x\,|\zeta_{ion}|$$

$$\frac{mg}{L} = \frac{n\,x\,Mw\,x\,1000}{V[L]}$$

EXAMPLE a concentrated solution of HCl which is known to be 37.0% & has a solution density of 1.19 g/mL . What is the Molarity of HCl?

$$\%_{HCl} = \frac{37}{100}\,x100 \rightarrow m_{HCl} = 37g$$

$$n_{HCl} = \frac{37gmol}{36.5g} = 1.014mol$$

$$V_{solution} = \frac{m_{solution}}{\rho} = \frac{100g}{1.19g}\,mL = 0.0917L$$

$$[HCl] = \frac{1.014mol}{0.0917L} = 11.06M$$

EXAMPLE Calculate N for Ca^{2+}, Na^+, Al^{3+}, O^{2-}, & H_2O if each have a concentration of 0.002mol/L

N of $0.002M_{Ca^{2+}}$ = 0.002x2 = 0.004equ/L
N of $0.002mol/L_{Na^+}$ = 0.002x1 = 0.002equ/L
N of $0.002M_{Al^{3+}}$ = 0.002x3 = 0.006equ/L
N of $0.002M_{O^{2-}}$ = 0.002x2 = 0.004equ/L
N of $0.002M_{H_2O}$ = 0.002x0 = 0

- **Parameter Expressed in equ:** Alkalinity,Hardness

PROBLEMS

- **The laboratory reported the concentration of calcium ion (Ca^{2+}) in a water sample as 92mg/L. calculate the normality of calcium ion (Ca^{2+})**

$$[Ca^{2+}] = \frac{92 \text{ mg g mol}}{1000 \times 40.08 \text{ mg g L}} = 0.002295M$$

$$N = M \times \zeta = 0.002295 \times 2 = 0.004591 equ/L$$
$$N = 0.004591 equ/L = 4.591 mequ/L$$

- **What are the differences between bonds?**
  <u>Ionic (electrovalent)</u> bond of oppositely charged ions
  <u>metallic structure</u> showing electron paths around the nuclei of metal atoms (represented as a cloud of +ve ions immersed in a cloud of valence electrons)
  <u>Covalent bonds</u> involve electron sharing
  <u>van der Waals bond</u> weak dipole attraction, neutral molecules held together by this force

- **Why metal bearing sulfide minerals are relatively unstable at the Earth surface**
  Due to metallic bonding behavior, metallic bond are weaker than covalent & ionic bonds

- **Calculate the covalent character in Fe_2S (χ: Fe = 1.8, S = 2.5)**
  $$\Delta\chi = 2.5 - 1.8 = 0.7$$
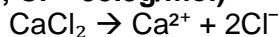 $$0.7 \rightarrow 12\% \text{ ionic character}$$
  Covalent character = 100% - 12% = 88%

- **Al is good electrical conductor than Fe. Why?**
  Because Al have an ionic character whereas Fe have metallic character (number of electrons in the last orbital os Al is higher than Fe, Which leads to formation of an ionic bond in Al)

- **Al behave as ductile material whereas Fe are brittle (break or fracture under stress). Why?**
  Because Al have an ionic character whereas Fe have metallic character (due to the electron cloud in the metallic substance that doesn't change)

- **What is the [Ca^{2+}] (in ppm, i.e. mg/L) in a $47\times10^{-4}M$ solution of $CaCl_2$? & What is the [$CaCl_2$] (in ppm) in the same solution? (Mw: Ca = 40.1g/mol, Cl = 35.5g/mol)**
  $$CaCl_2 \rightarrow Ca^{2+} + 2Cl^-$$
  $$n_{CaCl_2} = n_{Ca} \rightarrow [CaCl_2] = [Ca^{2+}] = 47\times10^{-4} mol/L$$

$$[Ca^{2+}] = 4.7x10^{-5}x40.1x10^3 \frac{mol}{L} \cdot \frac{g}{mol} \cdot \frac{mg}{g} = 1.9mg/L$$

$$[CaCl_2] = 4.7x10^{-5}x(40.1 + 2x35.5)x10^3 = 5.22mg/L$$

- **Which compound is more soluble in water MgO or CaO? Explain your reasoning**
  Water is a polar molecule, so the more the ionic character the more the solubility
  $\Delta\chi$ MgO = 3.5 - 1.2 = 2.3 → 74%ionic
  $\Delta\chi$ CaO = 3.5 - 1.0 = 2.5 → 79%ionic
  CaO are more soluble than MgO

- **In the previous question calculate the normality of both Ca & $CaCl_2$**
 $$N_{Ca} = 47x10^{-4} \times 2 = 0.0148 equ$$
  $$N_{CaCl_2} = 0$$

- **What is the importance of chemical bonds?**
  Determine the behavior (physical & chemical properties) of molecules & compounds

- **The hydrogen bond in water molecule held molecules together & responsible for many properties & behaviors of water. What is responsible for the formation of this bond?**
  The H-bond in water molecules formed due to polar covalent bonds between H-O in the same molecule which generate -ve partial charge on the O-atom & +ve partial charge on the H-atom (i.e unequal shearing of e- because O has much more χ than H)

- **Identify each of the following**
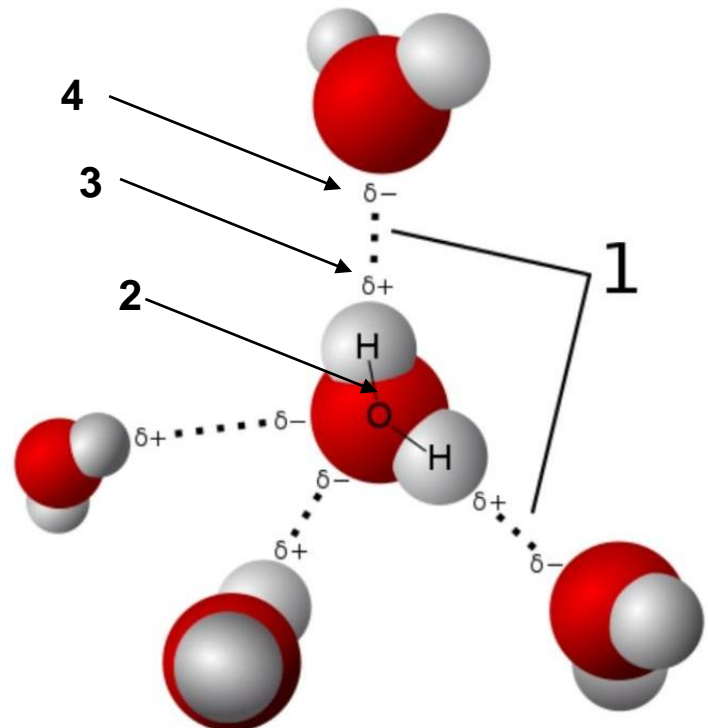
1: H-bond (intramolecular bond)
2: Polar Covalent Bond (intermolecular bond)
3: Partial +ve charge on H-atom
4: Partial -ve charge on O-atom

- **The maximum density of water is at 4°C. However, at temperature less than 4°C the density decrease, & at temperature more than 4°C the density also decreases (this called water abnormality). Explain this behavior**
  At T = 4°C water reach its maximum density due to H-bond. However, At T < 4°C the density decrease due to H-bond, & At T>4°C the H-bond become unstable (break & bond with another molecule) & The reason responsible for this behavior in this case is the polarity of water molecules

CARBON CHEMISTRY (ORGANIC COMPOUNDS)

- **Bonding in carbon compounds:**
  1. **Single (σ)**: inactive compounds. e.g. Alkanes
  2. **Double (σ, π)**: active such as Alkanes
  3. **Triple (σ, 2π)**: very active such as Alkynes
- **Saturation:**
  1. **Unsaturated**: not all C-atom involve in bonding (there is free e-) such as Alkenes & Alkynes
  2. **Saturated**: all C-atoms are involve in bonding
- **Chemical formula's types for C-compounds**:
  1. **Molecular**: Number of atoms (C_2H_6)
  2. **Structural**: arrangement (geometry) of atoms in the compounds in detail
  3. **Condensed**: same as structural but in simpler forms (CH_3-CH_3), the most commonly used
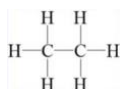
HYDROCARBONS

- **Contain:** C & H (major source is crude oils)
- **Major type**: alkanes, alkenes, alkynes, & aromatic
- **Major reaction:** Combustion, Substitution, Addition

	Alkane	Alkene	Alkyne
Bond	Single (σ)	Double (σ, π)	Triple (σ, 2π)
Saturation	Saturated	Unsaturated	Unsaturated
Formula	C_nH_{2n+2}	C_nH_{2n}	C_nH_{2n-2}
Reactivity	Unactive	Active	Active
Major Reactions	Combustion Substitution	Addition Substitution	Addition Substitution

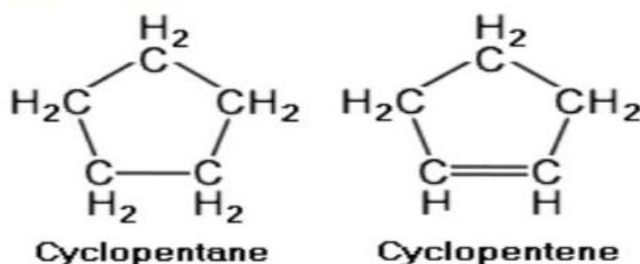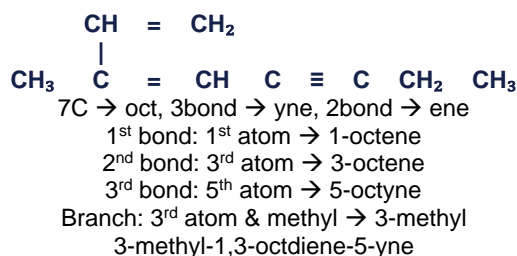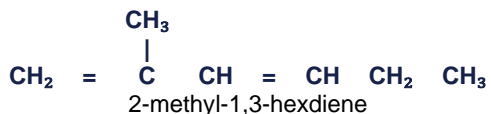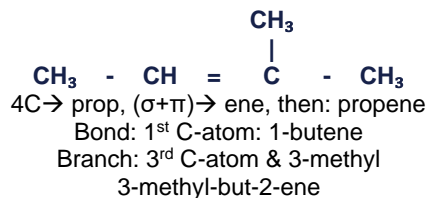**Physical properties of alkanes are depending on the size of molecules (number of C-atoms)**
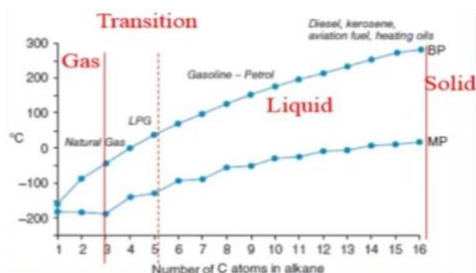
NAMING SYSTEM

1	2	3	4	5	6	7	8	9	10
Meth	Eth	Prop	But	Pent	Hex	Hept	Oct	Non	Dec

- لتسمية اي مركب اتبع الخطوات الاتية:
  1. عد ذرات الكربون في السلسلة باستثناء الافرع واكتب عددها
  2. حدد الروابط الموجودة فلو كانت كل ذرات الكربون بها رابطة واحدة ضتضيف المقطع *ane* واذا كان رابطتين تضيف المقطع *ene* واذا كان 3 تضيف المقطع *yne* لعدد ذرات الكربون (propane, propene...)
  3. اذا وجدت فروع فهي تسمى alkyls حيث تعد عدد ذرات الكربون بها وتضيف المقطع *yl* الى اخر الاسم (CH_3 methyl, C_2H_5 ethyl, C_3H_7 propyl..) ومعادلة الفروع هي C_nH_{2n-1}
  4. الاولوية في الترقيم: بحالة وجود فروع فقط تبدأ بالعد من الجهة الاقرب للفرع وفي حالة وجود روابط تبدأ بالعد من الجهة الاقرب للرابطة
  5. في حالة وجود اكثر من فرع نضيف عدد الافرع (*di, tri…*)
  6. في حال وجود مركبات عطرية (بنزين) نضيف كلمة *Cycle*
  7. بتفاعلات الاستبدال نضيف مقطع قبل الاسم مثل (cloromethan)
  8. في المركبات الكحولية تضيف (*Anol*)، وفي الحموض تضيف (*Nic*)

CH_3-CH_2-CH_2-CH_3
4C → *But*, (single σ) → *ane*
Name: **But**ane

CH_3-CH=CH-CH_3
4C → *But*, Double (σ+π) → 2-ene
Name: **2-But**ene

CH_3-$C≡C$-CH_3
4C → But, Triple (σ+2π) → 3-yen
Name: **3-Butyne**

CH_3 CH_2 CH_2 CH_2 CH_2 CH_3
6C → Hex, 14H → ane, then **Hexane**

CH_3
|
CH_3 - CH_2 - CH_2 - CH - CH_2 - CH_3
6C → Hex, single → ane, then *Hexane*
Branch: 3rd atom → 3, 1C → meth, then 3 meth*yl*
Name: **3-methylhexane**

CH_3 CH_3
| |
CH_3 CH_2 CH CH CH_2 CH_3
6C → Hexane
1st Branch: 3rd atom → 3, 1C → meth, then 3 methyl
2nd Branch: 4th atom → 4, 1C → meth, then 4 methyl
Name: **3, 4-dimethylhexane**

CH_3 CH_2 —— CH_3
| |
CH_3 CH_2 CH CH_2 CH CH_2 CH_2 CH_3
1st Branch: 3rd atom → 3, 1C → meth, then 3 methyl
2nd Branch: 5th atom → 5, 1C → ethyl, then 5 ethyl
5-ethyl-3-methyloctan

CH_3 CH_2 —— CH_3
| |
CH_3 C CH_2 CH CH_2 CH_2 CH_3
|
CH_3
8C with σ bonds: hept
1st Branch: 2nd atom → 2, 1C → meth, then 2 methyl
2nd Branch: 2nd atom → 2, 1C → meth, then 2 methyl
3rd Branch: 4th atom → 5, 1C → ethyl, then 4 ethyl
4-ethyl-2-2-dimethylheptan

CH_3
|
CH_3 - CH = C - CH_3
4C → prop, (σ+π) → ene, then: propene
Bond: 1st C-atom: 1-butene
Branch: 3rd C-atom & 3-methyl
3-methyl-but-2-ene

CH_3
|
CH_2 = C CH = CH CH_2 CH_3
2-methyl-1,3-hexdiene

CH = CH_2
|
CH_3 C = CH C ≡ C CH_2 CH_3
7C → oct, 3bond → yne, 2bond → ene
1st bond: 1st atom → 1-octene
2nd bond: 3rd atom → 3-octene
3rd bond: 5th atom → 5-octyne
Branch: 3rd atom & methyl → 3-methyl
3-methyl-1,3-octdiene-5-yne

Cyclopentane   Cyclopentene

ISOMERS

- **Isomers**: are molecules or polyatomic ions with identical molecular formulas (have same numbers of atoms of each element with distinct arrangement)
  - On other words: have the same molecular formula but different structural formula
- e.g. butane & 2-methylpropane have the same molecular formulas but differ in all chemical & physical properties & structural formulas

Butane (C_4H_{10}): CH_3-CH_2-CH_2-CH_3
2-methylpropane (C_4H_{10}): CH_3-CH-CH_3
**|**
CH_3
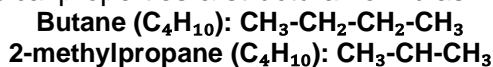
MAJOR REACTIONS

- **Alkanes**: are saturated hydrocarbons (unreactive) but are characterized by combustion & substitution (limited in high temperature)
  - **Combustion**: At high temperature alkanes react vigorously & exothermally with oxygen

$$C_nH_{2n+2\ (g)} + O_{2(g)} \rightarrow H_2O_{(g)} + CO_{2(g)} + E$$

  - **Substitution**: with halogens (F, B, Cl, & I) in the presence of light (UV wave)

Cl_2 (or Br_2) + UV $\rightarrow$ 2Cl (or 2Br)
$Cl + CH_4 \rightarrow CH_3 + HCl$
$CH_3 + Cl_2 \rightarrow CH_3Cl$ (chloromethane) + Cl
$CH_3Cl + Cl_2 \dashrightarrow CH_2Cl_2$ (dichloromethane) + Cl
…

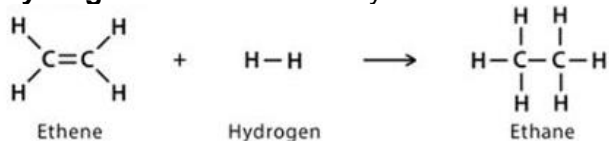- **Alkenes & Alkynes**: are unsaturated hydrocarbons (reactive) & characterized by additional reactions
  - **Halogenation**: convert Alkenes into halo-Alkanes by reaction with halogens (Cl, Br, I, F)
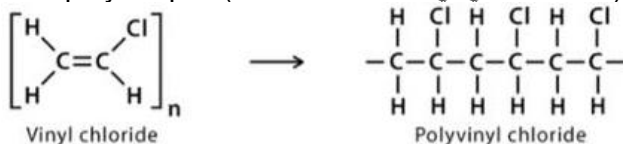
Ethene + Bromine → Dibromo ethane
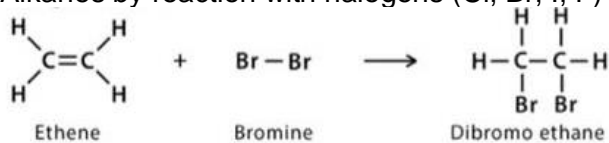
  - **Hydration**: convert Alkenes into Alkohol (-anol)

Ethene + Water → Ethanol
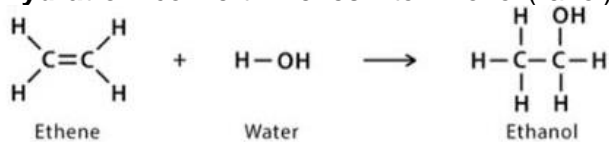
  - **Hydrogenation**: convert Alkynes into Alkanes

Ethene + Hydrogen → Ethane

  - **Polymerization**: convert Alkenes or Alkenes into polymorphs (التفاعل الاساسى فى الصناعات البلاستيكية)

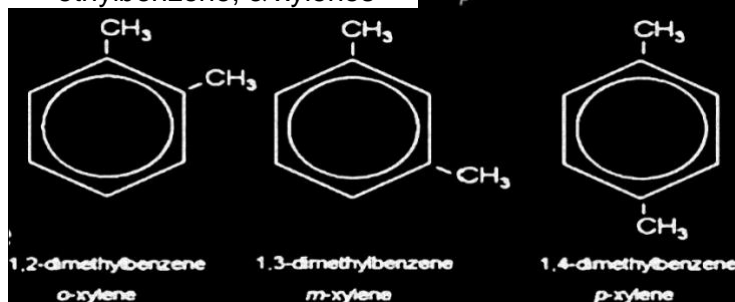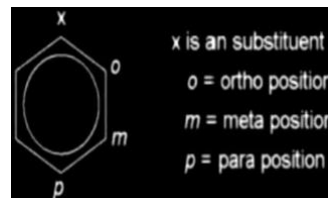Vinyl chloride → Polyvinyl chloride

AROMATIC (ARYL) HYDROCARBONS

- **Aromatic hydrocarbons:** have closed ring of 6C atoms, with H shape with 3C having double bond with connected C & single bond with another C

- Such a ring is referred to as a benzene ring & all hydrocarbons containing one or more rings are referred to as aromatics or aryl compounds
- Aromatic Hydrocarbons (contain benzene Ring)
- **BTEX**: acronyms, some of the volatile organic compounds (VOC) in petroleum, stands for benzene, toluene, ethylbenzene, & xylenes

x is an substituent
o = ortho position
m = meta position
p = para position

1.2-dimethylbenzene — o-xylene
1.3-dimethylbenzene — m-xylene
1.4-dimethylbenzene — p-xylene

Polycyclic Aromatic Hydrocarbons (PAH): is a compounds that formed by multiple benzene rings, some of PAH are precursors to cancer-causing metabolite & have significant environmental interest

Napthalene (PAHS)	2-ring PAH: component of coal tar & occurs as soil &aquifer contaminant near coal-tar facilities • considered as a common air pollutants • Formed by incomplete combustion of wood
Benzo(a)pyrene	5-ring PAH: product of incomplete combustion of other PAH, indoor air contaminant & widely distributed in the environments

Napthalene
Anthracene
Benzo(a)pyrene
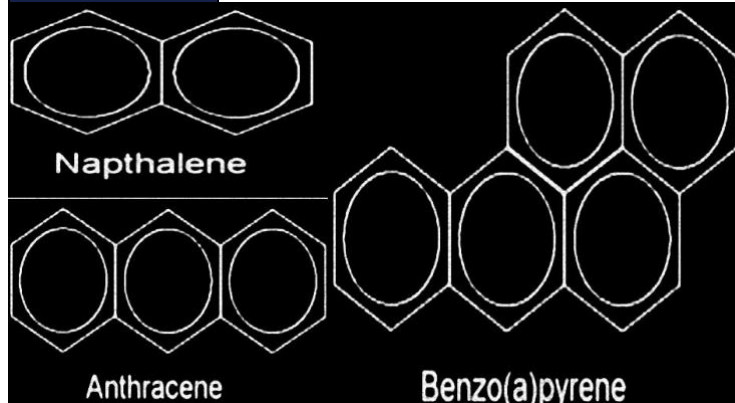
ORGANOCHLORIDES COMPOUNDS

- **Include**: Chlorofluorocarbons, Polychlorinated biphenyls (PCB's), & Chlorinated phenols
- **biomagnification**: concentration of organochlorine increases as one moves higher in food chain
- Organochlorine are soluble in organic solvent, so they concentrate in fatty tissues

Tertiary Consumer = 50 ppm
↑
Secondary Consumer = 5 ppm
↑
Primary Consumer = 0.5 ppm
↑
Primary Producer = 0.05 ppm

- **Non Aqueous-Phase Liquid (NAPL)**
  - **LNAPL**: slightly soluble halogenated hydrocarbon
  - **DNAPL**: Insoluble, Alkanes, & Petroleum

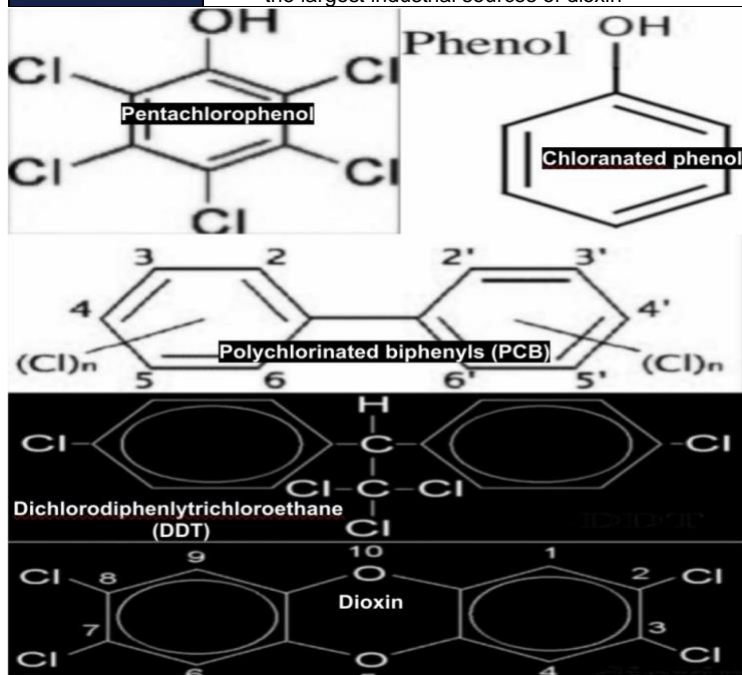| BTEX Hydrocarbon	Solubility in distilled water [ppm]	Solubility in sea water [ppm]
Benzene	1696	201
Toluene	580	50
Ethylbenzene	161	111
O-xylene	171	130
m-xylene	148	106
p-xylene	156	111

- **e.g of DNAPL:** Halogenated or Non-Halogenate volatile, Halogenated semivolatiles, & Miscellaneous (Coal Tar)
- **Polymers:** any long molecules formed by smaller units called monomers
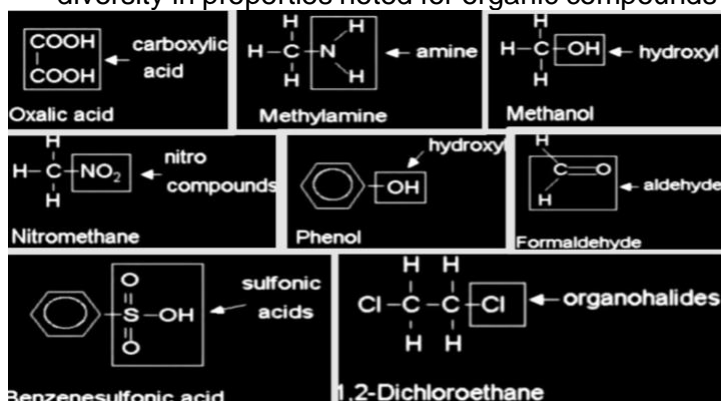 - ➤ **Addition Polymer**: formed by same monomers
  - ➤ **Condensation Polymer:** different monomers

Chloranated phenols	Derived from benzene rings by addition of at least once hydroxyl group in place of H atom
Pentachloro-phenol	Is a toxic liquid, result if all 5 H-atoms in benzene are replaced by Cl atoms
Polychlorinated biphenyls (PCB)	2 benzene ring joined by single bond with attached Cl-atoms. have significant environmental & health hazard • They are insoluble in water but very soluble in fatty or oily substances so accumulate in environment & subsequently in fatty tissues of birds & fish • used as coolant for power transformer & capacitor • **Dibenzofuran**: produced by combustion of PCB in presence of oxygen
Dichlorodiphenly-trichloroethane (DDT)	Polychlorinated molecule consist of 2 benzene rings joined by a chlorinated ethane group, Each ring has Cl atom substituting for H atom • Organochlorine insecticide, low mammalian toxicity & persistence in environment, it was considered as a good insecticides. But some animales metabolize it & form DDE which interfere with reproduction ➤ the most well-known consequences of this phenomenon were the recipitous drops in populations of eagles, peregrine falcons & other predatory birds due to biomagnification of synthesized rganochlorine (DDT & PCB) ➤ predatory bird populations begun to rebound in response to restrictions on DDT, & PCB
Dioxin	family of chemical compounds, unintentional byproducts of certain industrial, non-industrial, & natural processes, involving combustion • Different compound have different toxicity • **TCDD:** considered as most well studied & toxic form of dioxin. present in herbicides & fungicides • dioxin types vary greatly in toxicity, some of them 10,000 times less toxic than TCDD • **Origin**: No one makes dioxin on purpose. But through incinerators, the manufacture of certain herbicides, & pulp & paper bleaching were among the largest industrial sources of dioxin

Pentachlorophenol, Chloranated phenol (Phenol)

Polychlorinated biphenyls (PCB)

Dichlorodiphenlytrichloroethane (DDT)

Dioxin

FUNCTIONAL GROUP

- Organic molecules can contain other elements such as oxygen, Nitrogen, & halogens. These atoms occur in functional groups that are attached to the main carbon skeleton & lead to the great diversity in properties noted for organic compounds

Oxalic acid — carboxylic acid; Methylamine — amine; Methanol — hydroxyl; Nitromethane — nitro compounds; Phenol — hydroxy; Formaldehyde — aldehyde; Benzenesulfonic acid — sulfonic acids; 1,2-Dichloroethane — organohalides

Examples of organosulfates

Methanethiol; Benzenethiol; Dimethylsulfoxide (DMSO); Methylsulfuric acid; Dimethyl sulfide; Dimethyl disulfide; Thiourea; Thiourea; Dimethylsulfoxide (DMSO); Benzeneosulfonic acid
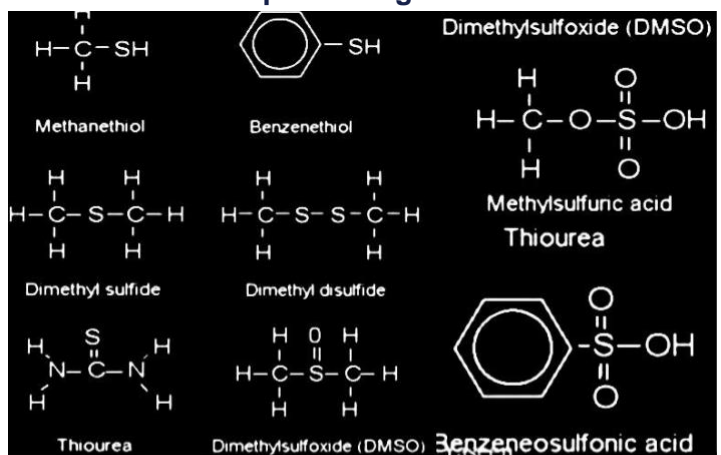
Examples of organophosphorus

Phosphinous acid; Phosphinic acid; Dimethylphosphinic; Trimethyl phosphate
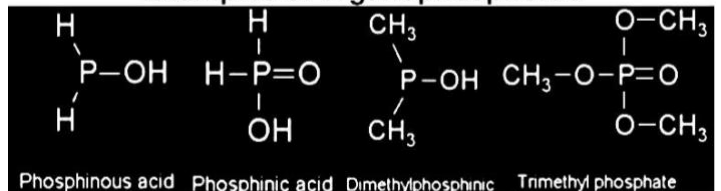
Condensation reaction to form ester from alkohol (methanol) & butanoic acid

Methanol + Butanoic acid ⟶ Methyl butanoate
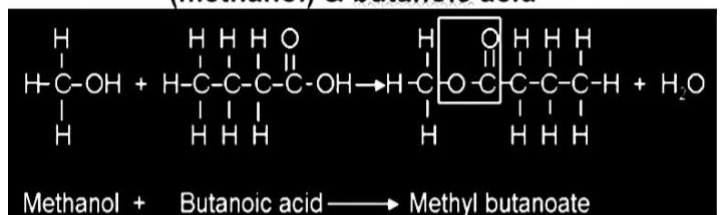
Examples of monomers used to build the polymer

Ethylene; Vinyl chloride; Tetrafluoroethylene; Propylene; Acrylonitrile; Styrene
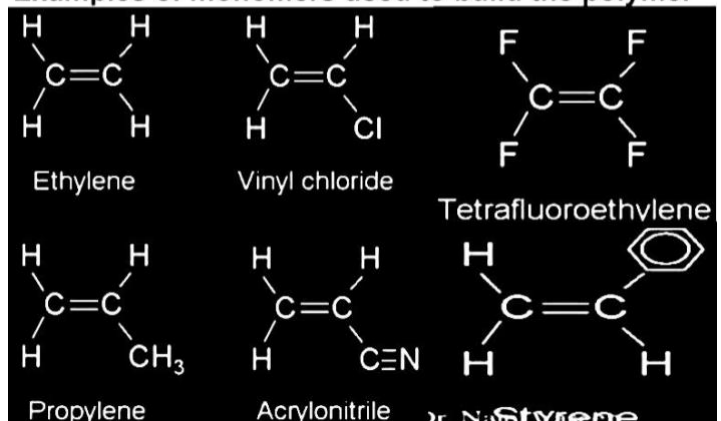
ORGANIC MATTER IN THE ENVIRONMENT

HUMIC SUBSTANCES

- **Humic Substances**: naturally occurring compound of biogenic, heterogeneous organic substances that can be characterized as being yellow to black in color, of high molecular weight & refractory
- Found at the surface in soils, brown coal, fresh to marine water, marine to lacustrine sediments
- Distinction between the types of substances is based on their solubility in acids & bases

Types of Humic Substance (Pigmented Polymers)			
	Humin	**Humic Acid**	**Fluvic Acid**
As acid	Insoluble	Soluble	Soluble
As base	Insoluble	Insoluble	Soluble
Mw	Higher	Intermediate	Lower
C%	Higher	Intermediate	Lower
O%	Lower	Intermediate	Higher
Acidity	Lower	Intermediate	Higher
IEC*	Lower	Intermediate	Higher
Solubility	Lower	Intermediate	Higher
Pz	Higher	Intermediate	Lower
Intensity of color	Higher	Intermediate	Lower
	Dark, Black	Gray-black, Dark-brown	Light-yellow, yellow-brown

*IEC: ion exchange capacity, Pz: Polymerization

- humic & fulvic acids don't have fixed compositions, but rather consist of a varied array of alkane chains & rings, aromatic, carboxyl & hydroxyl groups, & some Sand N-based functional groups
  - Humic acid is richer in C more than fulvic acid
  - fulvic acid is richer in O more than Humic acid

Composition	Humic Acids	Fulvic Acids
Carbon (%wt)	53.6 – 58.7	40.7 – 50.6
Hydrogen (%wt)	3.2 – 6.2	3.8 – 7.0
Nitrogen (%wt)	0.8 – 5.5	0.9 – 3.3
Oxygen (%wt)	32.8 – 38.3	39.7 – 49.8
Sulfur (%wt)	0.1 – 1.5	0.1- 3.6
Mol. Wt. (Daltons)	2000 – 5000	500 – 2000
H/C (atomic)	0.8	1.3
O/C (atomic)	0.5	0.8

Composition of humic substances in various environments

		Aromatic HC	H/C	Molecular wight
Water	**Ground**	-	0.7-1.2	500-10^4
	Surface	17-30%	0.7-1.1	<10^4
	Sea	<15%	1.0-1.6	10^3-10^6
Sediment	**Lack**	<15%	1.6	<10^3
	Marine	<15%	1.0-1.5	-
	Soil	20-35%	0.5-1.0	10^3-10^6

SOIL & MARINE ORGANIC MATTER

Organic Matter	Porosity	pH	Major sources & C/N ratios
Marine	60-90%	7-8	Surface layers are oxic, but with increasing depth pore water become anoxic (Low C/N ratio)
Soil	30-60%	4-8.5	• Input of organic matter fall (root) invasion with C/N>25 • Total microbial biomass = 2 - 3% with low C/N (<15)

- Soil = organic compound + Air (gasses) + water
- Organic compounds concentrated in O-horizon

Atomic C/N versus δ13C for various reservoirs of organic carbon

13δ = amount of C compared to the standard
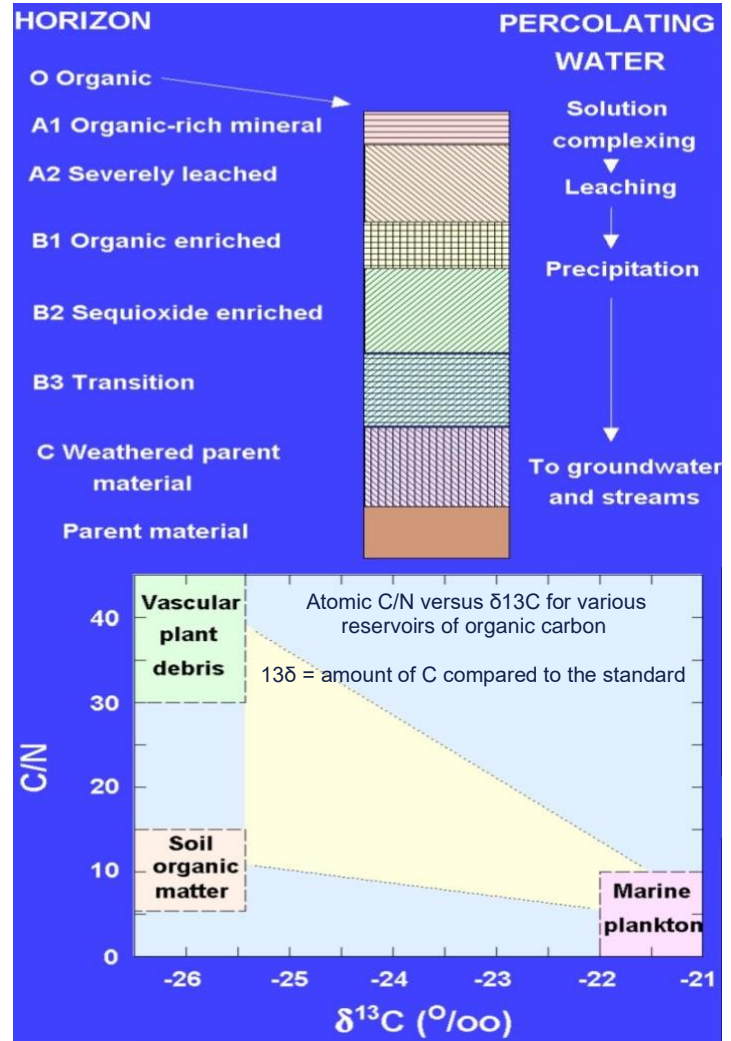
COALS

- **Humic Coals:** derived from humic substances via peat stage
- **Sapropelic coals:** formed from fairly fine-grained organic mud in quiet, O-deficient shallow water


Van Krevelen diagram: changes in H, O, & C during the coalification process
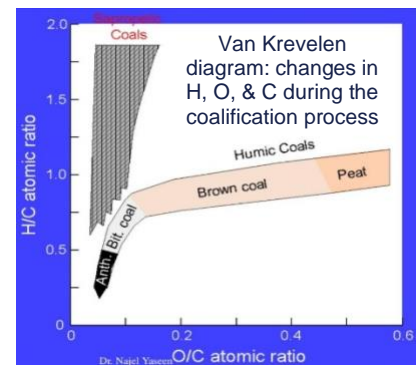
Concentration ranges in coal for some elements [ppm]					
Cr	2.6 – 25.4	**U**	0.2-3.8	**Ni**	2-50
Sb	0.1-7.3	**Pb**	3- 20	**Cu**	6-54
V	6- 109	**Se**	0.4-3.3	**Th**	0.5- 3.7
W	0.2- 1.3	**Co**	1.1 – 24.1	**Sc**	0.6 – 10.3
Zn	3- 65	**As**	0.7-31		

inorganic Association, **no association**

- **Inorganic Association**: from minerals in coal that aren't decomposed
- **No association:** the origin isn't known
- Sulfur in coal are combined with organic molecules or as *physically separate* sulfide minerals
- Sulfur occurs in reduced forms because organic rich depositional environment is reducing
  - In presence of Fe pyrite & marcasite forms
  - In absence of Fe, free H_2S & polysulfides form

PETROLEUM

- Is any hydrocarbon-rich fluid derived from kerogen by increases in pressure & temperature
- **Kerogen**: polymeric organic material, occur in sed. rocks as finely disseminated organic macerals
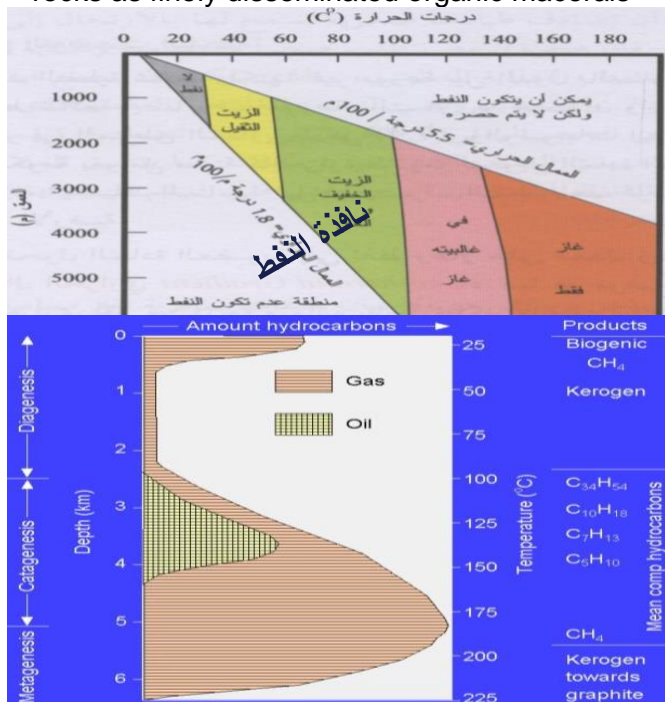

Production of petroleum from a typical reservoir rock assuming an average geothermal gradient. the narrow P-T range over which oil is produced (petroleum window). With increasing T, the size of the mean hydrocarbon molecule decreases. During catagenesis, hydrocarbon chains break off & are expelled from the kerogen. During metagenesis, only methane is released

Elemental composition of crude oil			
C (%wt)	82.2-87.1	N (%wt)	0.1-4.5
H (%wt)	11.8-14.7	Other (wt%)	<0.1
S (%wt)	0.1-5.5	Ni (ppm)	0.3-200
O (%wt)	0.1-4.5	V (ppm)	0.3-1000

Associates with resins & asphaltenes

- **Classification of petrol based on S-content:**
  1. **Bitter**: contains high amount of Sulfur
  2. **Sweet**: smaller amount of S (more valuable)
- **dissolved organic carbons (DOC):** remains after passing through 0.45μm filter
- **Particulate organic carbons (POC)**: particulate matter retained by 0.45μm filter
- **Total organic carbons (TOC)**: POC + DOC
- **Sources of Carbon**: depending on the water bodies that carries the carbon & Aquafer
  1. **Allochthonous:** from Soil & plants (outside the aquatic system), in small lakes (streams, lacks)
  2. **Autochthonous**: algea (from aquatic system), dominant in large lacks & oceans
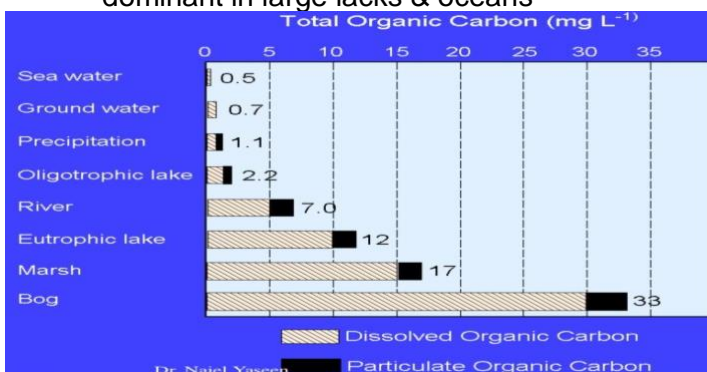
Average organic carbon concentrations for various systems. the actual range in TOC substantial & depends on a variety of factors.

Median concentrations of organic carbon (DOC) in aquifers			
Sands	0.70	Oil Shale	3.00
Gravels	0.70	Humic Colored	10.0
Sandstones	0.70	Petroleum Association	100
Igneous	0.50		

ANTHROPOGENIC CARBON INPUTS

- **Pesticides المبيدات الحشرية (BOD):** Insecticides, Herbicides, & Fungicides
- **Soft Pesticides**: organophosphors, have a short residence time in the environment & highly toxic
- **Hard pesticides:** organochlorine, persistent in the env. but have low toxicity in mammalian systems
- Toxicity usually expressed as Lethal Dosage (LD_{50})
- **Lethal Dosage (LD_{50}):** The amount of chemicals per unit of body mass required to produce death in 50% of an exposed animal population
  - pesticide with LD_{50} = 10 mg/kg is 10 times more toxic than a pesticide with LD_{50} = 100 mg/kg
  - This unit of measurement is specific for a certain animal usually rats & pigs
  - The lower the LD value, the higher the risk

		Solubility	LD₅₀	logKow	logBCF
Hard	HCB	0.0062	3,500-10,000	5.3	3.5
	DDT	0.0034	115	3.9-6.2	2.2-4.3
	Toxaphene	n/a	85	2.9-3.3	1.2-1.6
	Dieldrin	0.20	46	5.1-6.2	3.3-4.3
	Mirex	0.20	700	5.8	3.9
Soft	Malathion	145	1,375-2,800	2.7	1.0
	Parathion	24	3.6-13	n/a	—
	Atrazine	30	1,870-3,080	2.3	0.7

- **Factors controlling fate & transport of organic compound in environment**
  1. Partitioning of the compound into gaseous (Vapor pressures VOC), liquid or solid phases
  2. The solubility of the compound: Kow is directly proportional to the adsorption & solubility in organic compound (& inversely in water)
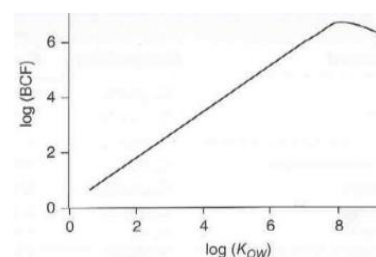
$$K_{ow} = \frac{[Octanol]}{[Water]}$$

Values of K reported as log

  3. The degree to which the organic contaminant in adsorb to mineral or organic matter in soil
  4. ρ of liquid organic compounds relative to water
  5. Extent in which compound undergo degradation (decomposition into CO_2, O_2, & other products)

BIOCONCENTRATION FACTOR (BCF)

- **Bioconcentration (Bioaccumulation) factor (BCF):** is the accumulation of a chemical in living organisms (biota) compared to the concentration in water, expressed the tendency of organic chemical in water to concentrate in the fatty tissue

$$log^{BCF} = 0.935 x log^{Kow} - 1.495$$

- Kw α strongly partitioned into the fatty tissue
- If logK = 7-8 or greater → strongly absorbed to sediments & unlikely to enter living tissue

ENVIRONMENTAL MINERALOGY

REMEDIATION PROCESS

Precipitation	Precipitation of organic matter occurs when there is a change in the ionic strength (I) • I are inversely proportional to the solubility • Occurs where fresh water meets sea water
Volatilization	non polar molecules with low Mw have greatest vapor pressure & mostly evaporated • **Henry's law**: represent the partition of organic compound between liquid & vapor • **Henry's constant (H)** is inversely related to the concentration of volatile liquid in water $$H_i = \frac{[in\ vapor]}{[in\ water]} \qquad Cycles = \frac{-ln[X_f]/[X_i]}{H_i}$$
Sorption & Partition	The dissolved organic carbon is partitioned between the aqueous phase & the particles $C_{ads} = K_d x C_{soln}$ • Organic Acid & Base *Adsorption* inversely related to pH & degree of dissociation • Partition of organic chemicals between soil & water: partition coefficient is normalized to organic C-content of the soil $K_{oc} = (k_a x\ 100)/(\%OC)$

Biological Processes	• **POC**: is removed by consumers & decomposers
	• **DOC:** is removed by microbial action
	• Microbial decomposition related to molecule's size
	• **Microbial Decomposition**
	  ▪ **in aerobic condition:** in streams & lakes (surface water reach in O) produces CO_2
	  ▪ **In anaerobic conditions:** produces CH_4
	• **Degradation halflife**: the time taken for 50% of organic compound to be degraded

Redox	Oxidation & Reduction

EXAMPLE if [benzene] in water is 1000ppm & water is in contact with air, calculate concentration of benzene in the air in mol/L. (H = 0.22849, Mw = 78g/mol)

$$1 mol = \frac{ppm}{1000 x Mw} \rightarrow 1000 ppm = \frac{1}{78} mol$$

$$H_i = \frac{78 L x X}{1 mol} = 0.22849 \rightarrow X = 2.929 x 10^{-3}$$

EXAMPLE how many liters of air must we pass through system for each liter of contaminated water to reduce benzene contamination to 10% of its original concentration in groundwater (H 0.22849, Mw 78g/mol)

$$Cycles = \frac{-ln(0.1/1)}{0.22848} = 10 \rightarrow 10 L_{H_2O}$$

EXAMPLE If napthalene concentration in groundwater was 3.2mg/L. Calculate concentration of napthalene adsorbed on the sedimentary particles. (K = 137 L/Kg)

$$C_{ads} = \frac{137 L}{Kg} x \frac{3.2 mg}{L} = 438 ppm$$

EXAMPLE If percolation rainwater via soil contains 3ppb DDT. Organic makes up 3% of the soil. Calculate the amount of DDT absorbed/g of soil. (Log Koc = 5.18)

$$C_{soln} = 3 ppb = 3 ng/g$$
$$C_{ads} = K_{oc} x C_{soln} = 1.513 x 10^5 x 3 = 454 \mu g/g$$
$$454, 0.03 = 13.6 \mu g\ DDT\ g^{-1} of\ soil = 13.6 ppm$$

Compound	Half-life in days			
	Aerobic decomposition		Anaerobic decomposition	
	Minimum	Maximum	Minimum	Maximum
Cresol	<1	29	10	49
Phenol	<1	4	8	28
Napthalene	20	20	25	258
Benzene	5	16	112	720
Xylene	7	28	180	360
Methyl parathion	15	70	1	7
Aldecarb	20	361	62	635
Lindane	31	413	6	31
Dieldrin	175	1080	1	7
DDT	730	5708	16	100

MINERALOGY

• Under certain conditions (redox, pH, dissolved solids, microbial community) a given mineral may dissolve, releasing into solution components that can range from major ions to trace elements
• under a different set of conditions, a given mineral will crystallize from solution, & in doing so will remove from solution major or trace components

Class	Chemical characteristics	Examples
Borates	Various element combination with boron	Borax
Carbonate	Metals in combination with carbonate	Cal,Cerrusite
Halides	Alkali metasl or alkaline earths in combination with halogens (F, Cl, Br, I)	Halite, & Fluorite
Hydroxide	Metal in combination with OH	Brucite
Elements	Metallic or nonmetallic pure elements	Au, C, Ag
Oxides	Metals in combination with oxygen	Hematite
Silicates	Metals in combination with silica SiO_4^{4-} that forming 3D networks, sheets, chains & isolated tetrahedra	Quartz Forsterite Orthoclase
Phosphate	Elements in combination with PO_4	Apatite
Arsenate	Elements in combination with AsO_4	
Vanadate	Elements in combination with VO_4	Carnotite
Chromate	Elements in combination with CrO_4	
Tungstate	Elements in combination with WO_4	Scheelite
Molybdate	Elements in combination with MoO_4	
Sulfates	Metals in combination with sulfate SO_2^{2-}	Barite
Sulfides	Metals in combination with reduced S or chemically similar elements (As,Se,Te..)	Pyrite Galena

• **Coordination Number (CN)**: is the packing of anions around a cation, calculated by radius ratio

$$RR = \frac{Ra}{Rc}$$

| RR	CN	Arrangement Of Anions (Geometry or Shape)
<0.155	2	Linear
0.155-0.225	3	Trigonal Planer
0.225-0.414	4	Tetrahedral
0.414-0.732	4	Square Planer
0.414-0.732	6	Octahedral
0.732-1.000	8	Body-Centered Cube
>1.000	12	Edge-Centered Cube

• **Bragg's law:** for crystal structure, is an angle of incidence & diffraction if Bragg's conditions are met
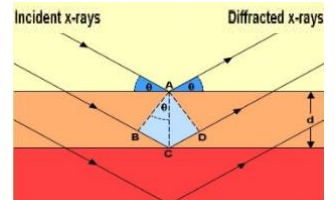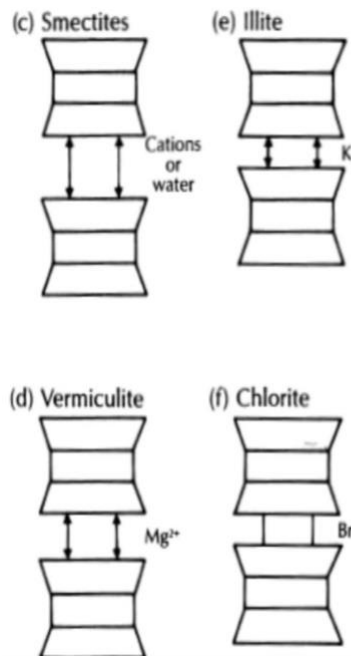
D = interplanar spacing

• Properties of the silicate crystal classes

Class	Other Terms	Si:O Ratio	Example	#shared Corners	Unit
Neso-		1:4	Olivine	0	SiO_4^{4-}
Soro-		1:3.5	Melilite	1	$Si_2O_7^{6-}$
Cyclo-	Ring	1:3	Beryl	2	SiO_3^{3-}
Ino-	Single Chain	1:3	Augite	2	SiO_3^{3-}
Ino-	Double Chain	1:2.75	Hornblende	2.5	$Si_4O_{11}^{6-}$
Phyllo-	Sheet	1:2.5	Kaolinite	3	$Si_2O_5^{2-}$
Tecto-	Framework	1:2	K-feldspar	4	SiO_2
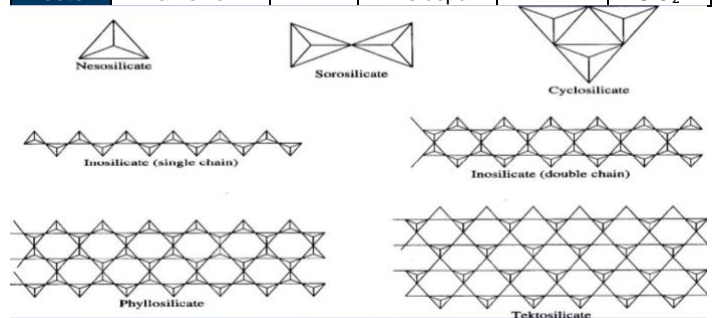
CLAY MINERALS

- **Clay mineral**: phyllo-or sheet-silicates, fine grained hydrous silicate composed of layers of tetrahedrally & octahedrally coordinated cations
- **Importance of Clay minerals:**
  1. **High reactive (due to fine grain size)**: play a role in adsorption or release of trace metals, organic compounds, & potential contaminants
  2. **Paleoclimate**: formed by Chemical weathering (major component of soils) so their composition reflects environment in which the soil is formed
  3. **Physically mobile (due to fine grain size):** play a role in transportation of adsorbed contaminants or plant nutrients
  4. Common **cement** in sed. rocks (illite, smectite)
  5. **Control rheology & fluid flow** (sedimentary aquifers & hydrocarbons sedimentary basins)
- **Structure of clay minerals**: sheet of clay minerals are made of T & O layers that joined to form 2 layers clays (T-O) or 3-layer clays (T-O-T) or mixture
  - T-center occupied by Si & to certain degree Al
  - O-layer may be *dioctahedral* or *trioctahedral*: O layers have trivalent (Al) or divalent (Mg) ions
    1. **Brucite**: In order of divalent cations all positions have to be filled in the forming of trioctahedral
    2. **Gibbsite**: In the former of dioctahedral only 2 sites have to be filled, with trivalent cation

Octahedral layer | Tetrahedral layer

Hydroxyl • Mg²⁺ or Al³⁺ | Oxygen • Silicon

Mg^{2+} in the O layer is *brucite*. Al^{3+} in the O layer is *gibbsite*

Hydroxyl • Aluminium Oxygen • Silicon | Hydroxyl • Al³⁺, Mg²⁺, Fe²⁺ Oxygen • Silicon

Kaolinite
Each structural unit consists of a gibbsite layer & T-layer. only 2 out of 3 O-sites in the O-layer are occupied

Montmorillonite
2:1,O-layer is a gibbsite layer. Substitution of Mg for Al in the O-layer is charge balanced by the addition of Na or Ca cations

- 2 layers clays permit limited substitution for their Si, & Al in the T-sites; while the 3 layers types are characterized by extensive substitution, & This substitution has to be counterbalanced by the substitution of the interlayer cations

(c) Smectites (e) Illite

Cations or water | K⁺

(d) Vermiculite (f) Chlorite

Mg²⁺ | Brucite

C. Mixed-Layer Clays
Complex interstratified two-layer and three-layer clay minerals following either a regular or a random pattern.

D. Fibrous Clay Minerals

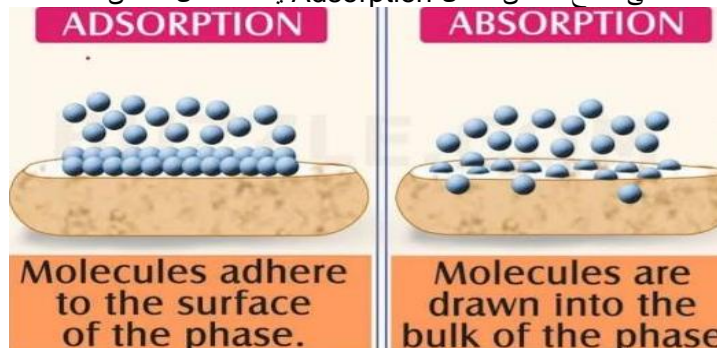|	
	palygorskite (attapulgite) sepiolite
Vermiculite	dioctahedral vermiculite
	trioctahedral vermiculite
Mica	dioctahedral illite muscovite paragonite glauconite
Mica	trioctahedral biotite phlogopite lepidomelane
Brittle mica	dioctahedral margarite
	trioctahedral seybertite xanthophyllite brandisite
Chlorite	dioctahedral cookeite (?)
	trioctahedral Fe-rich varieties thuringite chamosite Mg-rich varieties clinochlore penninite

	Kaolinites	Illites	Smectites	Vermiculites
T:O	1:1	2:1	2:1	2:1
O	Di-O	Mostly Di-O	Di-O, Tri-O	Mostly Tri-O
Inter-cation	Ni	K	Ca, Na	Mg
Inter layer-water	Only in halloysite	In hydro-muscovite	Ca 2 layer & Na	Ca 2 layer K layer to nil
Basal Spacing	7.1Å	10Å	Variable ≈ 15Å	14.4 (as fully hydrated)
Ethylene glycol	Taken by halloysite	No effect	2 glycol layers 17Å	1 glycol layers 14Å
CEC*	Nil (3-15)	Low (10-40)	High (80-150)	High (100-150)
Dilute acids	Scarcely soluble	Readily attacked	Attacked	Readily attacked
Heating 200°C	Unchange (except halloysite)	No marked change	Collapse to 10Å	Exfoliation, shrinkage of layer spacing
Examples	Kaolinite Dickite Nacrite Halloysite	Illite Hydro-mica Phengite Brammalite Glauconite Celadonite	Montmo-, Beidellite Nontronite Hectorite Saponite Sauconite	Vermiculite

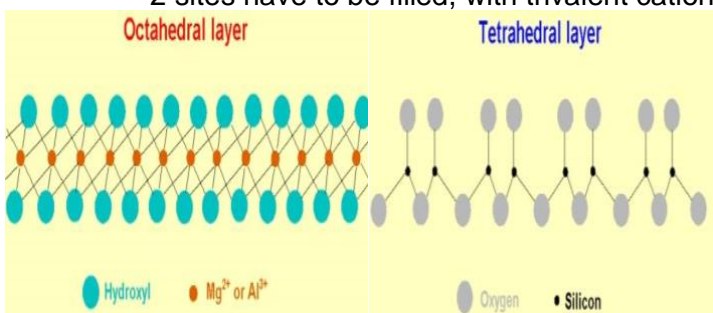*CEC: Cation exchange capacity in meq/100g clay

خاصبة ال expansion عند تعرض clay للماء السبب بها ال charge تتصل بمركب الماء القطبي فتزداد ال interlayer space وسيحدث landslides, liquefaction, Adsorption, & cation exchange
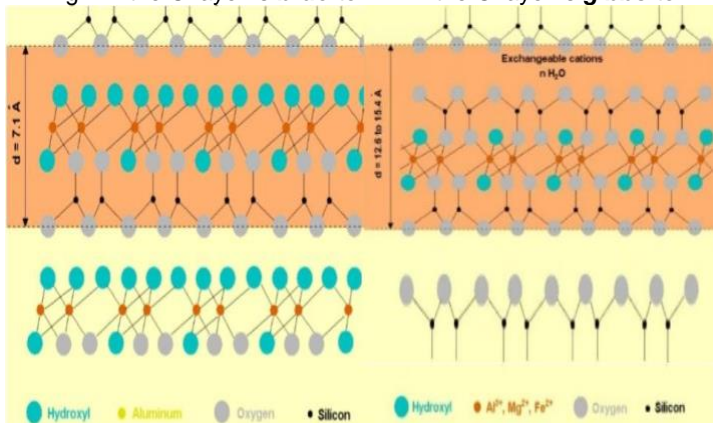
CATION EXCHANGE

الفرق بين ال Absorption وAdsorption هو ان ال Absorption يحدث على سطح المعدن اما ال Adsorption يحدث داخل المعدن

ADSORPTION | **ABSORPTION**

Molecules adhere to the surface of the phase. | Molecules are drawn into the bulk of the phase

- **Cation exchange**: type of adsorption characterized by attraction of cations to particle surface
- **Adsorption is controlled:**
  1. **Chemical attraction:** forms crystal edge bonds
  2. **Electrostatic attraction**: dissolved phase attracted to charged particle
  3. **Physical attraction:** Weakest, VDWs force

- **Surface Charge Causes:**
  1. Substitution in the T- & O-layers
  2. Defects or imperfections in the crystal structure
  3. Unsatisfied or broken bonds at corners & edges
  - ➤ The -ve charge in 3 layers clays (2:1) is developed mainly from the first 2 causes
- **Role of broken bonds can be demonstrated in:**
  1. Decreasing adsorption by decreasing pH
  2. Increasing CEC by decreasing grain size
- **Clay mineral can exchange cation with aqueous phase:** This have a significant impact on the distribution of metals in the environment
- **Cation exchange capacity (CEC):** varies as a function of pH, particle size, & types of ions
  - ➤ CEC is normally measured in meq/100g

| Surface Area of Illite with 2600kg/m³ density				Surface Area is inversely related to the size of particles & directly related to the cation exchange & absorptions
Length	cubes	Area of cube [m²]	Surface area [m²/g]	
1m	1	L*6 = 6	2.3×10^{-6}	
1cm	10^6	6×10^{-4}	2.3×10^{-4}	
1µm	10^{18}	6×10^{-12}	2.31	
0.1µm	10^{21}	6×10^{-14}	23.1	
0.01µm	10^{24}	6×10^{-16}	231	

- **IEP & PZC (effect of pH & absorption)**
  - ➤ **isoelectric point (IEP):** n pH at which the surface charge of a particles 0, a solution in which H & OH sorb to the mineral surface
 - ➤ **point of zero charge(PZC):** In natural solutions with range of ions

pH-Value	Surface charge
< IEP or PZC	+ve (dominated by H) & the particle attract anions
> IEP or PZC	-ve (dominated by OH) & the particle attract cation
pH< isoelectric	The mineral is an anion exchanger
pH> isoelectric	The mineral sorbs cations

|		IEP	PZC
Smectite	$Ca_{0.17}(Al,Fe^{3+})_2(Si_{3.66}Al_{0.34})O_{10}(OH)_2$	1-3	2-3
Kaolin	$Al_2(Si_2)O_5(OH)_4$	4	2-4
Humus	$C_{20}H_{20}O_{15}N$	2-3	2-3
Allophane	$Si_3Al_4O_8(OH)_8 \cdot 8H_2O$	5-6	5
Hematite	Fe_2O_3	6-8	4-7
Goethite	$FeOOH$	6-7	6-7
Gibbsite	$Al(OH)_3$	9	10

For example if the pH-value for goethite is 5 they attract +ve charge, & if pH is >7 (e.g. 9) attract -ve charge
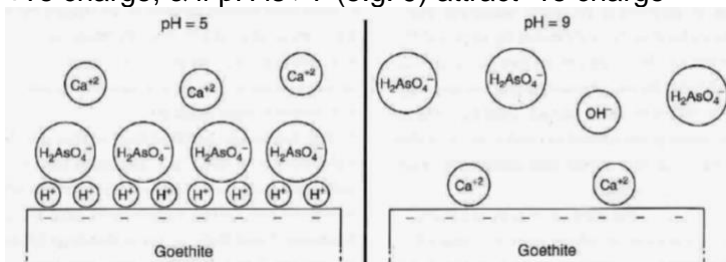
لذا لا تصلح الزراعة في تربة حامضية لان ال clay يكون ve+ ال cations تختلف عن بعضها في قابليتها لحدوث Adsorption والشكل الاتى يوضح العلاقة لبعض ال cations لل Adsorption-pH
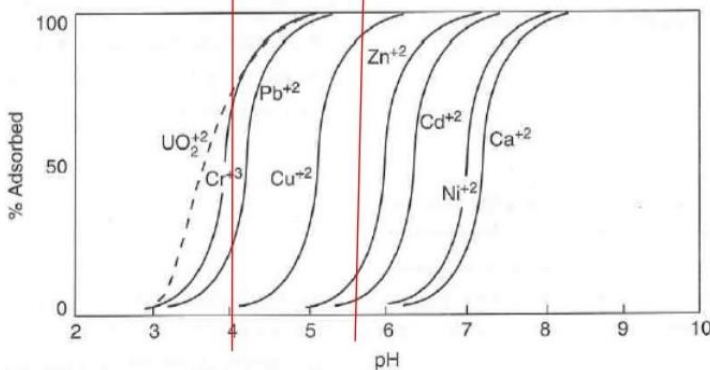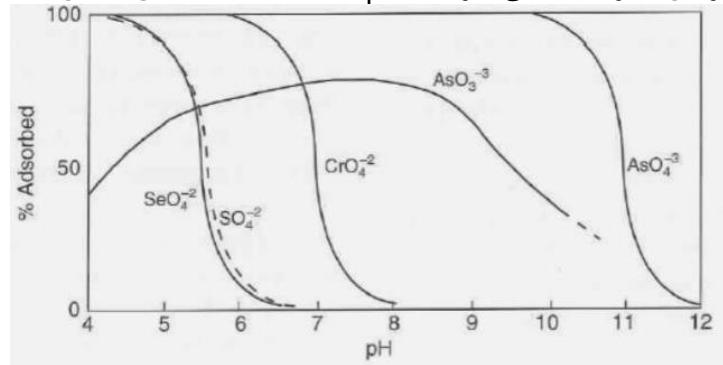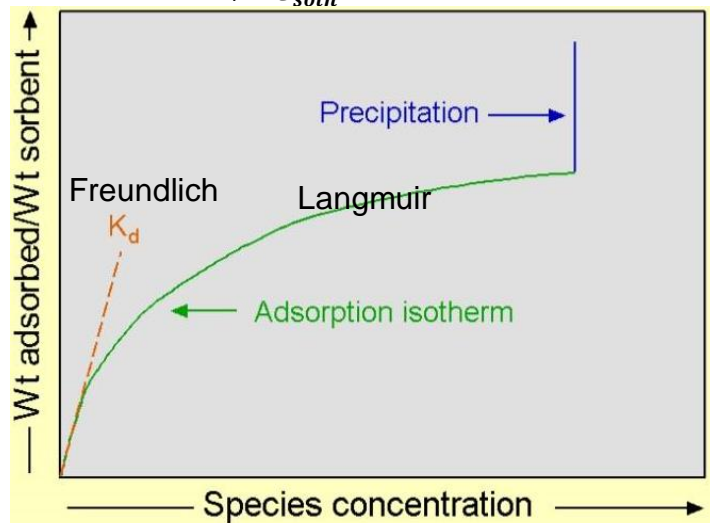
- **Batch method:** used to determine ion exchange properties, Adsorption isotherm represent partition of particular species in aqueous-solid phase
- There are 2 models of bathc method, Freundlich (linear relation), & langmuir (exponential relation)
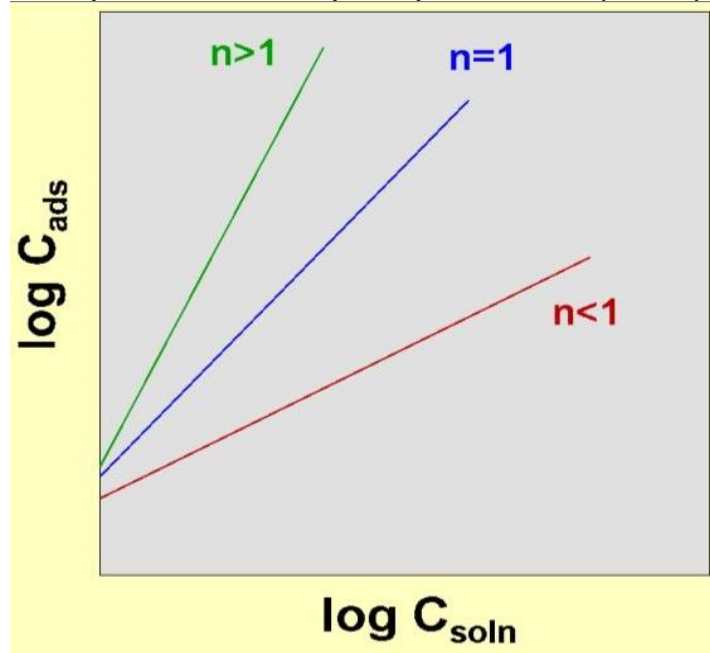
$$Freundlich\ Equation: C_{ads} = KC_{slon}^n$$
$$LogC_{ads} = LogK + nLogC_{soln}$$
$$Lanmuir = \frac{Q°KC_{soln}}{1 + KC_{soln}}, Q: Max\ soptive\ capacity$$


Representation of a adsorption isotherm showing distribution of a species between an aqueous phase & a solid (sorbent)

Plot of log[C]adsorbed on a particle (Cads) versus log[C]in water (Csoln). Linear plots indicate that the partitioning can be represented by a Freundlich isotherm. The slope of the line gives the exponent (n), & the intercept gives the value for log K.
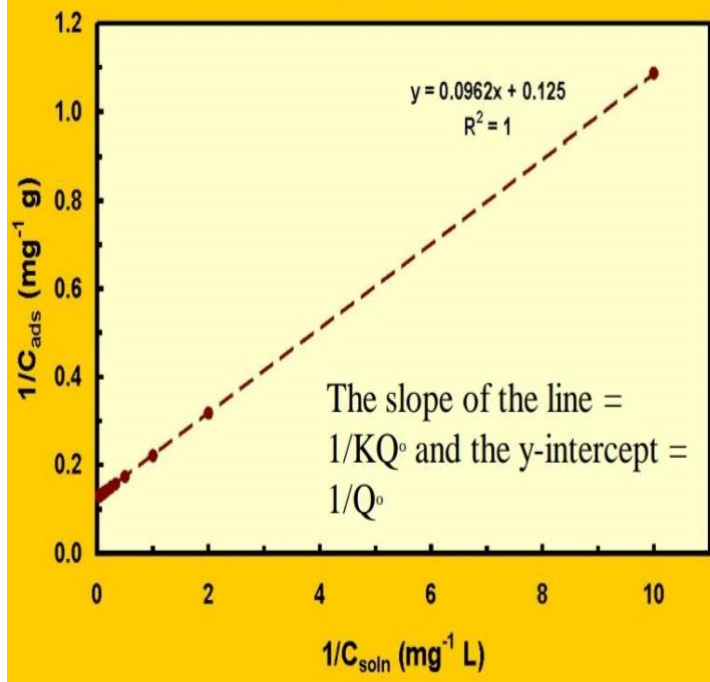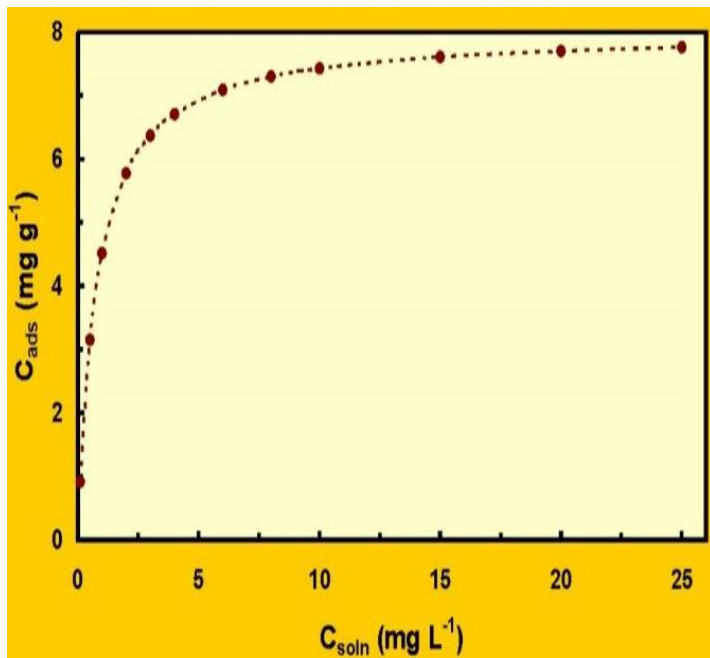
في ال langmuir اذا كانت العلاقة exponential فاننا نأخذ مقلوب التركيز فيتحول الى علاقة خطية ومن ثم نحسب المطلوب
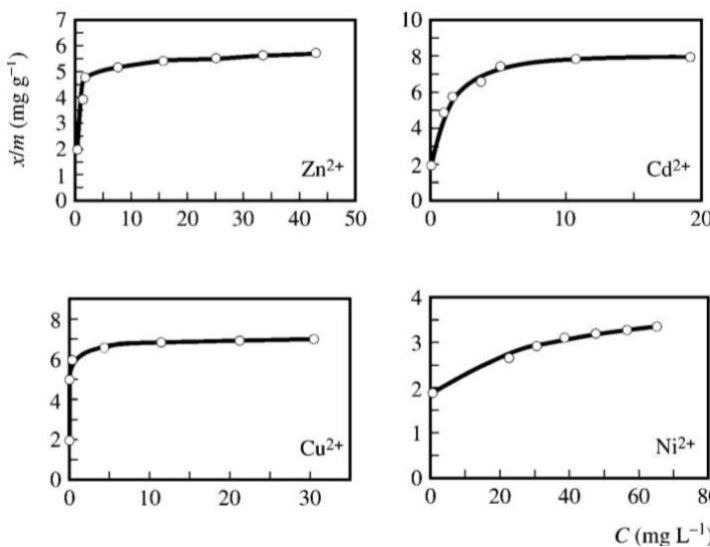
Adsorption isotherms for sepiolite
Adsorbent dose 10g/L, agitation time 3h, pH 4, & T 22°C. The Langmuir equation provided the best fit to adsorption isotherms

EXAMPLE a betch experiment was done to investigate the adsorption of Ni²⁺ onto kaolin. The experiment was done at 20°C & 5 pH, & agitation time was 3hr, the following data were obtained, calculate K & n

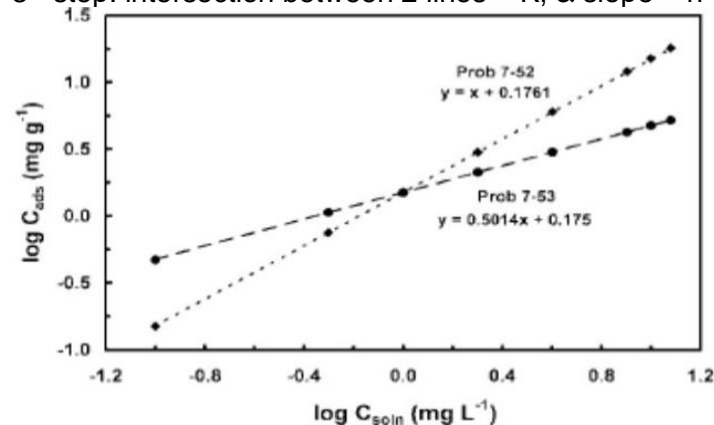| C_{soln}[mg/L]	C_{ads}[mg/g]	C_{soln}[mg/L]	C_{ads}[mg/g]
0.10	0.05	4.00	6.00
0.50	0.75	8.00	12.0
1.00	1.50	10.0	15.0
2.00	3.00	12.0	18.0

1st stepe: plot Cads – C soln & determine the model
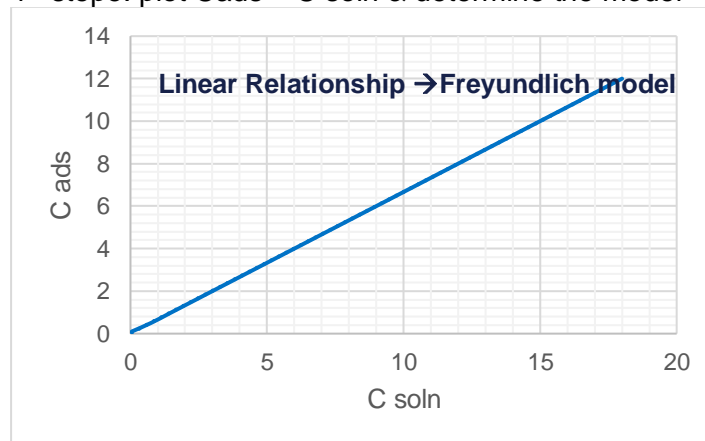
2nd step: to find n & K, we need to plot $\log_{Cads}$-$\log C_{soln}$
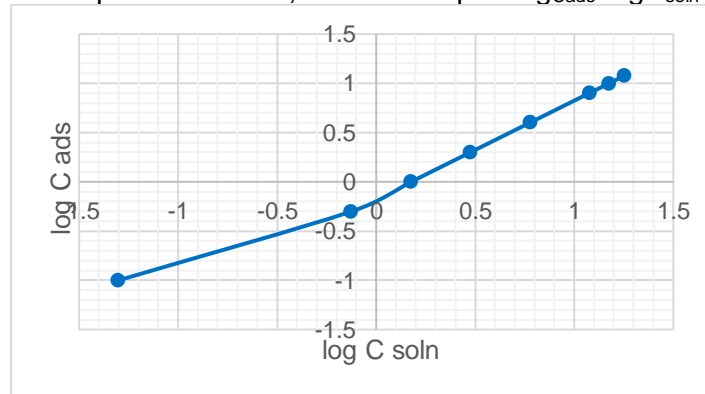
3rd step: intersection between 2 lines = K, & slope = n

K = 0.176, & n=1

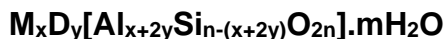- **Column test method:** to determine ion exchange

$$K_d = \frac{(C_i - C_f)}{C_f} x \frac{V}{M}$$

EXAMPLE 10g montmorillonite are placed in a column & 100ml of solution, The initial solution had [Zn] 20mg/L & After passing through the column, the solution had a [Zn] 14.1mg/L, Calculate the K_{dZn}

$$K_d = \frac{(C_i - C_f)}{C_f} \frac{V}{M} = \frac{20 - 14.1}{14.1} x \frac{100mL}{10g} = 4.18 mL/g$$

ZEOLITES

$$M_xD_y[Al_{x+2y}Si_{n-(x+2y)}O_{2n}]\cdot mH_2O$$

M= Na, K, or other monvalent
D= Mg, Ca, Sr, Ba, or divalent
M & D are the extra-framework exchangable cations
The ratio (Al+Si)/O always = 1:2
Al^{3+} substitution for Si^{4+} provides the excess charge

- **Zeolite**: crystalline substance with framework of linked tetrahedra consisting of 4O atoms, contains cavities (channels & cages) that occupied by H_2O & extra-framework cations that are exchangable

Mineral	Si:(Si+Al)	Voidspace	Free perture size
Erionite	0.75-0.78	0.36	3.6Å x 5.2Å, 8-ring ⊥ (001)
Mordenite	0.80-0.85	0.26	6.7Åx7.0 Å, 12-ring ‖(001) 2.9Åx5.7Å, 8-ring ‖ (010)
Clinoptilolite	0.74-0.84	0.34	3.5Åx7.9Å, 10-rings‖(001) 3.0Åx4.4Å, 8-rings
Phillipsite	0.54-0.75	0.30	4.2Åx4.4Å, 8-rings ‖ (100) 2.8Åx4.8Å, 8-rings ‖ (010) 3.3Å,8-rings ‖ (001)
Chabazite	0.59-0.80	0.48	3.7Å x 4.1Å, 8-rings

Si/Al ratio	High	Low
Selective for	Monovalent cations	Divalent cations
Charge	Fewer negative charges	More negative charges
Favorite	Large monovalent cations Li<Na<NH$_4$<K<Rb<Cs	Smaller divalent ions Mg < Ca < Sr < Ba
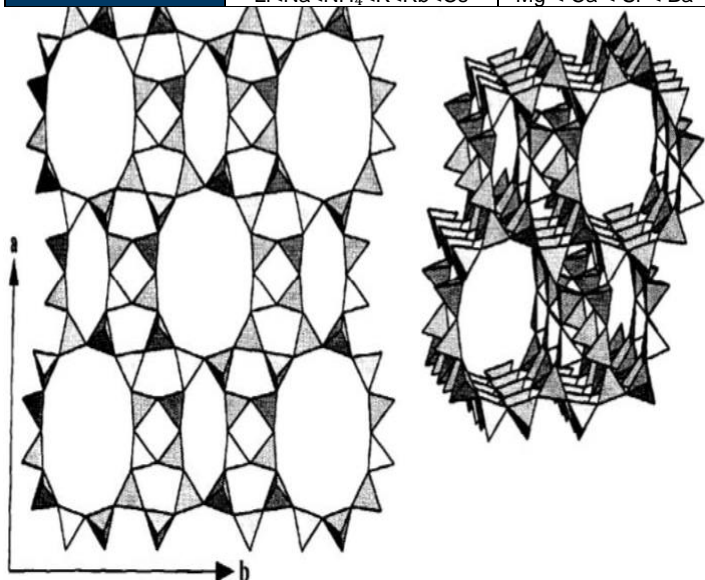
mordenite structure down c-axis & obliquely down the c-axis
There are 2 sets of channels, one consisting of 12-membered rings & the other 8-rings (count T around large & small channels)

- **Uses:**
 1. Treatment nuclear wastewater
  2. Treatment of muncipal & industrial wastwaters
  3. Remediation of acid mine drainage
  4. Soil remediation contaminated with heavy metal

Mineral	Formula	CEC
Erionite	Na$_2$K$_4$Mg$_2$Ca$_3$(Al$_8$Si$_{28}$)$_2$O$_{144}$·56H$_2$O	280
Mordenite	Na$_3$KCa$_2$(Al$_8$Si$_{40}$)O$_{96}$·8H$_2$O	220
Clinoptilolite	(Na,K)$_6$(Al$_6$Si$_{30}$)O$_{72}$·20H$_2$O	220
Phillipsite	K$_2$(Ca,Na$_2$)$_2$(Al$_6$Si$_{10}$)O$_{32}$·12H$_2$O	450
Chabazite	Ca$_2$(Al$_4$Si$_8$)O$_{24}$·12H$_2$O	390
Analcime	Na$_{16}$(Al$_{16}$Si$_{32}$O$_{96}$).16H$_2$O	450
Faujasite	Na$_{20}$Ca$_{12}$Mg$_8$(Al$_{60}$Si$_{132}$O$_{384}$).235H$_2$O	360
Ferrierite	(Na,K)$_2$Mg$_4$Ca(Al$_6$Si$_{30}$O$_{72}$)$_2$.40H$_2$O	230
Heulandite	(Na,K)Ca$_4$(Al$_9$Si$_{27}$O$_{72}$).24H$_2$O	320
Laumontite	Ca$_4$(Al$_8$Si$_{16}$O$_{48}$).16H$_2$O	430
Natrolite	Na$_{16}$(Al$_{16}$Si$_{24}$O$_{80}$).16H$_2$O	530
Wairakite	Ca$_8$(Al$_{16}$Si$_{32}$O$_{96}$).16H$_2$O	460

CEC: Theoretical cation-exchange capacity for selected zeolite minerals (in meq/100 g)

ASBESTOS MINERALS

- **Asbestos**: any mineral separate into long flexible
- Resistance to heat, friction, & acid condition
- **Serpentines** (chrysotile), & **Amphiboles** (amosite, crocidolite, , anthophylite, actinolite, & tremolite)
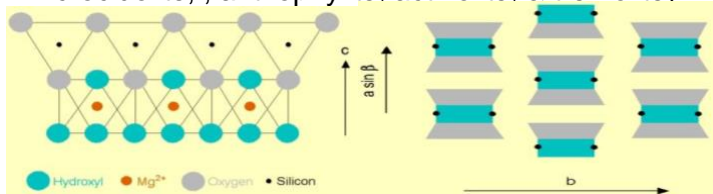
Crystal structure of chrysotile
1:1 layer consisting of T-layer & O-layer in which Mg^{2+} are surrounded by $4OH^-$ & 2O

Clinoamphibole Structure
The gray areas are the T-chains, the cyanide area is the O-layer, & the filled circles is M4 position

Mineral	Sys	Formula	H	G
Chrysotile	Mono	Mg$_3$[Si$_2$O$_5$](OH)$_4$	2.5	<2.55
Actinolite	Mono	Ca$_2$(Mg,Fe^{2+})$_5$ [Si$_8$O$_{22}$](OH)$_2$	5-6	3.0-3.2
Amosite	Mono	(Fe^{2+},Mg)$_7$[Si$_8$O$_{22}$](OH)$_2$	5.8	3.1-3.3
Anthophyllit	Ortho	(Mg,Fe^{2+})$_7$[Si$_8$O$_{22}$](OH)$_2$	5.8	2.9-3.1
Crocidolite	Mono	Na$_2$Fe^{3+}$_2$(Fe,Mg)$_3$Si$_8$O$_{22}$(OH)$_2$	5	3.2-3.5
Tremolite	Mono	Ca$_2$Mg$_5$ [Si$_8$O$_{22}$](OH)$_2$	5-6	2.9-3.2

- **Uses (95% used is chrysotile & 5% amphibole)**

|	
Chrysotile	is a good spinning fiber & used in the production of heat-resistant clothing • has a short residence time in the lung • contains little (or no) ferrous iron
Amphibole	fireproof clothing, glove, face masks, stage curtains, & pipe insulation • has relatively longer residence time in lung • contain significant amounts of ferrous iron • exposure to amphibole more significant than to chrysotile fibers in terms of cell damage

- **Health effects of Asbestos exposure:** Asbestosis, Mesothelioma, & Lung cancer
- **Mechanisms that responsible for cell damage by asbestos minerals:** the body responds to the introduction of a foreign material by attacking the material with phagocytic cells that attempt to engulf & ultimately remove the foreign material. These cells produce highly reactive compounds (e.g. H_2O_2 & OH-radicals) that kill foreign microorganisms.
  - The production of these short-lived O-species promoted by the presence of ferrous iron
  - The increased production of active O-species increases inflamation in area of foreign material & cause DNA damage in surrounding cells

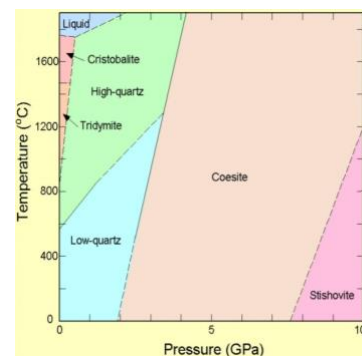$$H_2O_2 + Fe^{2+} \rightarrow 2OH^- + Fe^{3+}$$
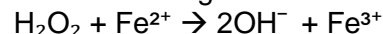
- **Factors of impact of asbestos fiber on the lung:**
  1. Persistence in the lung
  2. The presence of ferrous iron in the mineral
- **Respiratory diseases associated with exposure to silica dust**
  1. Silicosis leads to scarring of the lung tissue & a diminution in respiratory capacit
  2. Silicotuberculosis is due to a synergistic effect of silica, & M
  3. Lung cancer
  4. Tuberculosis promotes growth of the pathogen

MINERAL-ORGANISMS INTERACTION

Classification of microorganisms based on the cell type	
Procaryotes	no nucleus, all types of bacteria
Eucaryotes	well defined nucleus Include fungi, protozoa, & algae
Classification of microorganism based on energysource	
Photolithotrophs	Use light as source of energy, & inorganic compound as electron donors & carbon sources (e.h. plants)
Photoorganotroph	Use light as source of energy, & inorganic compound as electron donors & carbon sources
Chemolithotroph	Utilize oxidation of inorganic components (Fe^{2+}, Mn^{2+}, S^{2-}…) as their energy source & CO_2 as the source of carbon
Chemoorganotroph	Use organic compounds as both a source of energy & carbon

- **Microorganisms' role in dissolution & precipitation of minerals (Mechanisms)**
  1. Dissolution & release ions by acid & complexing molecule by auto- or hetero-trophic organisms
  2. REDOX reactions promoted by microorganisms
  3. Changes in Eh or pH due to the uptake & release of different compounds or ions
- Examples
  - oxidation of organic matter producing carbonic acid: $(CH_2O)n \rightarrow CO_2 + H_2O + H_2CO_3$
  - Production of organic acids which act as ligands & can form complex metal ions
  - Oxidation, in aerobic environments, of Fe^{2+} to Fe^{3+} leading to precipitation of oxyhydroxides
- **Factors that play a role in the rate at which a mineral dissolves**
  1. The zeta potential which affects the ability of a surface to attract charged species
  2. The size of the particle (surface/volume ratio)
  3. The atomic nature of the mineral surface with the presence of dislocations & defect structures increasing the reaction rate
  4. The presence of other ions in solution which may compete for the charged sites on the mineral surface
  5. The attachment of microorganisms which may act as organic ligands to the mineral's surface.