INDUSTRIAL EARTH RESOURCES

SHAAS N HAMDAN

CHAPTER ONE

INDUSTRIAL MINERALS

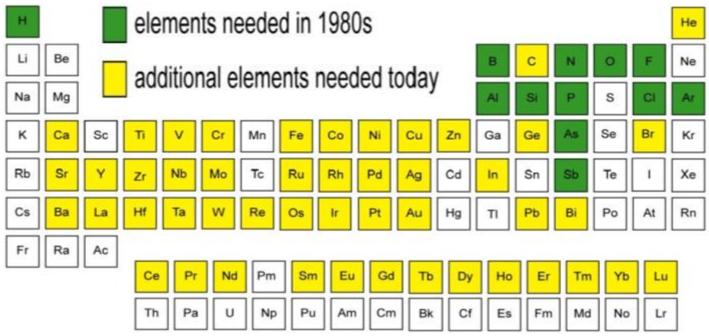
Shaas N Hamdan

- **Industrial Minerals**: any rocks, minerals, or other naturally occurring materials of economic value, including metallic minerals, non metallic materials, energy minerals, gemstones, & aggregates

Example	Uses
Bauxite	Ore for aluminum & alumina compounds
Titanium	Ore for Ti, TiO_2, & white pigments (اصباغ)
Sulfur	From pyrite, by-product of Cu-Pb-Zn mining
Diamond	Gemstone, & used in industrial applications
Garnet	Gemstones, & used in abrasive (الجلخ)

- **Aggregate**: materials that used in construction, such as sand, gravel, crushed stone, slag, or recycled crushed concrete, fillers & extenders to a certain degree
- **Importance of the industrial minerals:**
  1. Our world is made of the industrial minerals!
  2. Building blocks of our way of life
- **Green technology (environmental technology or clean technology):** technology that conserve energy & natural resources, reduce the -ve impacts of human activities (i.e. environmental friendly) & includes the following
  1. *Alternative power*: wind turbines, & solar energy
  2. *Hybrid & electric cars, Batterie, & Magnets*
  3. *H_2O purification, Desalination, C-capture & storage*
  4. **Critical Minerals**: required for national defense, & we export >75% of these minerals (e.g. Al & Be from Beryl, Bismuthinite, & Beryllium tuff)

Industrial Minerals Classification	
Alphabetical	Obscures links between commodities
Geologic processes	Igneous, Sedimentary, or Metamorphic Misses waste & processes materials
Tectonics	Important properties, & chemicals



- Without a market, industrial mineral deposit is merely a geological curiosity. Demand feeds back from the end-use market, to the end product, to the intermediate end product, & finally back to the mineral supplier
- Most industrial minerals are widespread, have enormous reserves, easy accessible, & mined by small operations
- **Economics development needs** less investment, cheaper to obtain (closer to market, & some minerals demand a higher market price than metals), & are more effective
- **Technological needs** less processing, less energy, less environmental effects, & possess exceptionally attractive properties for the industry
- **challenges in producing industrial materials:**
  1. **Sustainable development**: Provide society with its needs, protect future sources, limit landscape alteration & affect local community as little as possible
  2. **How much of industrial minerals do we need? Are there enough materials to meet demand for technologies?**
  3. **Can by-product be recycled?**
  4. **Are these minerals environmental friendly? & What are reclamation challenges?** (REE & Be associated with U-Th, mining REE will accommodate radioactivity & radon)
  5. **Conflict minerals**: Conflict Minerals Trade Act & provide major revenue to armed fraction for violence (e.g.Congo)

Uses & Technologies of Industrial Minerals																							
	As	Bu	Ba	Br	Cl	Di	Dim	Do	Gyp	Gra	Gar	Lim	Mg	Pu	Pe	Ph	Py	Pa	Si	So	Ti	Ta	Ze
Construction					✓	✓	✓		✓			✓			✓								
Metallurgical	✓	✓	✓					✓		✓	✓		✓	✓					✓				
Chemicals		✓	✓	✓				✓				✓	✓	✓		✓							✓
Agricultural				✓	✓			✓							✓	✓		✓				✓	
Glass & Ceramics		✓		✓	✓												✓		✓	✓		✓	
Fillers & Extenders			✓		✓	✓			✓			✓								✓	✓		
Energy					✓					✓			✓										
Environment	✓	✓						✓	✓			✓	✓		✓		✓						✓

As = Asbestos, Bu = Alumina & Bauxite, Ba = Barite, Br = Borates, Cl = Clay & Mud & Clays minerals, Di = Diatomite, Dim = Dimension stone (Granite, Marble…), Do = Dolostone & Dolomite, Gyp: Gypsum, Gra = Graphite, Gar = Garnet, Lim = Limestone, Mg = Magnesite, Pu = Pumice, Pe = Perlite, Ph = Phosphate, Py = Pyrophyllite, Pa = Peat, Si = Silica & Quartz, So = Soda Ash, Ti = Titanium minerals, Ta = Talc, & Ze = Zeolite

MINING & HISTORIC CULTURE

Important Cultural Eras	
4000 BC	**Stone Age**
4000 - 5000 BC	**Bronze Age**
1500 BC - 1780 CE	**Iron Age**
1780 - 1945	**Steel Age**
1945 - present	**Nuclear Age**

- **Uses of industrial minerals in ancient societies:**
  1. Egyptians replaced water clocks with sand hours
  2. Greek & Romans made concrete-like structures
  3. Building stones used in many ancient cultures

When was the first mine?	
Prehistory	Mining began in prehistory, ancient cultures settled around areas to provided raw materials
450Ka	Prehistoric man used chert & flint as tools
300-100Ka	Mining of flint in France & England
40Ka	**The first underground main (Hematite)** Bomvu Ridge, Swaziland
33Kyr	Nazlet Khater, Nile Valley, Upper Egypt
4500 B.C.	Krzemionki Opatowskie,Southern Poland 1. Upper Palaeolithic 2. Middle and Neolithic (4500 B.C.) 3. Early Bronze Age
4Ka	Soapstone using, Maritime Archaic peoples
	Old Testament recognized the land of Ophir (Zimbabwe) in Africa, as a source of gold African mine: Zimbabwe 26Ka, Swaziland 50Ka

TABLE SALT (HALITE)

- **Table salt (NaCl) or halite** is essential to life (man requires 2-5 gr/day of salt)
- **was used as**
  - a preservativ (مواد حافظة) tanning (الدباغة)
  - Was used to preserve Egyptian mummies
  - Trade in salt (تجارة الملح) was very important: valuable to be used as currency (Salt cakes)
- **Uses in Religions:**
  1. Greek worshippers consecrated salt, covenants were sealed with salt Jewish tradition & law, involves dehydration of meat for its preservation
  2. Catholic Church used salt in purifying rituals
  3. Buddhist believed salt repeals evil spirits
  4. Pueblo people worship the Salt Mother
- **Salt in Austria:** Heilbad Durrnberg, 750-150 BC
- **Estancia Basin in central New Mexico**
  - Salt basin important in trade by 13th century
  - Spanish conquest, built churche, & demanded salt
  - Spanish shipped salt to Mexico for processing silver
- **Salt & Silver Processing** by ***Patio process*** (1557)
  - silver ores crushed to a fine slime & mixed with salt; water; Cu-sulfate; & Hg, then spread into a patio & allowed to dry in the sun light. silver could then amalgamate with mercury
- **End of an Era**: by the late 1670s the entire Salinas District, as the Spanish had named it, was depopulated
  - Apache raids increased, Famine, Poor harvests, Pueblo revolt in 1680

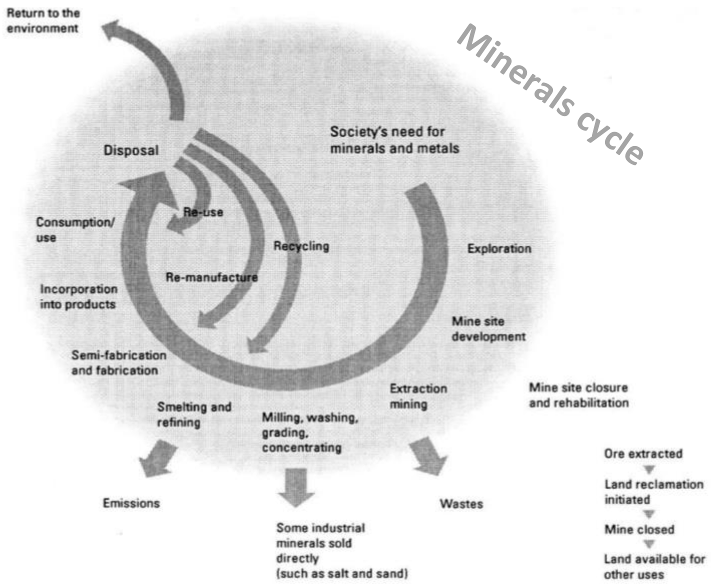
TURQUOISE (TURKEYSTONE)

- **Turquoise $CuAl_6(PO_4)_4(OH)_8H_2O$** believed to bring good fortune, success, health, protect from danger, & disease
- **Properties**: Isn't a hard (hardness = feldspar), brittle & susceptible to fracture (similar to ivory), may discolor from heat, oils, soaps, chemicals, perfume, & exposure to the sun & air. So employed in jewelry is treated to enhance color or to seal it against contaminats

- **Sources of turquoise** are differentiate using isotopes, & **Found near** Cu-deposits in arid to semiarid environments near the surface
- **Localities**:
  1. Egyptians some 70 centuries ago the oldest mine on Sinai Peninsula evidence is bracelet of turquoise & gold found on the mummified arm of queens
  2. Burro Mountains, New Mexico
  3. Cerrillos mining district, New Mexico
  4. Kingman, Arizona
  5. Morenci, Arizona
  6. Conejos, Colorado
- Mines on Turquoise Mountain, Cerrillos: the oldest known source of turquoise in the Southwest. Spanish noted that Native Americans were mining about 1500AD, probably began 700AD, found as far as Oaxaca, Mexico & eastern United States. kings and emperors of the Mixtec & Aztecs wore crowns & pendants of turquoise for good fortune and long life

CHANGES FROM PREHISTORY

Need for more commodities, Technology, Global market, & Environmental concerns



CHAPTER TWO

RESOURCES, RESERVES, & AGGREGATES

Shaas N Hamdan

RESOURCES & RESERVES

- **Resources**: any valuable inorganic or organic materials, that possible to mine & can be extracted at a profit from crust (Lithosphere, hydrosphere, & Atmosphere) whose use may impact these parts of the crust

Classification of Natural Resources	
Renewable	**Materials that replenished on short time scale (during Human life)** e.g. solar, plants, Water…
Non renewable	**Fixed quantity & not replenished by on short scale** (e.g. oil, mineral deposits, etc…)

- **Mineral resources**: non living N.O. substances, or is the concentration of natural solid, liquid, or gas within crust, that could be extracted economically

Resources Groups	
Energy resources	**Petroleum (oil & natural gas):** major for human **Alternative energy:** wind, tidal, & solar **Other fuel resources:** Coal, & Uranium
Metallic resources	Chemical element of single or alloys (valuable) Fe, Cu, Al, Pb, Zn, Au, Ag…
Nonmetallic resources	Is a natural resource that is very important 1. **Sandstone, Granite** used for construction 2. **Calcite** main ingredient in cement 3. **Red clay** used to make bricks 4. **Sand, Gypsum, & sulfur** in everyday items 5. **Halite** used as chemical fertilizers 6. **Soil & Water:** used by plants (for life)

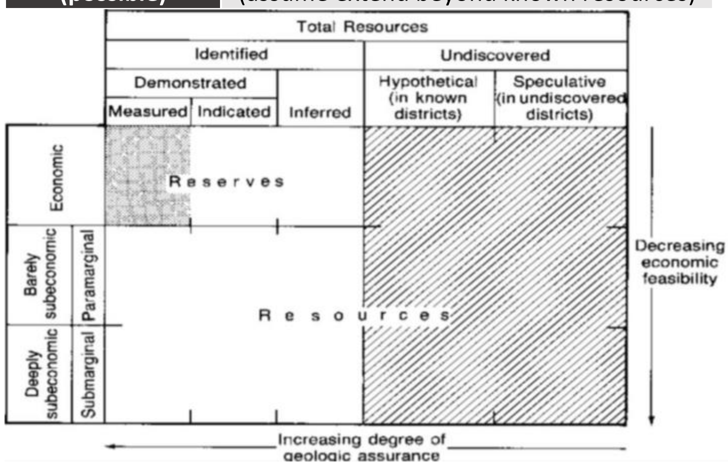
- **Petroleum**: material forms within Earth, can be burned to produce heat & electricity or made into gasoline

Types of Non-fuel Mineral Resources	
Metals	1. **Precious metals:** Au, Ag, platinum group 2. **Non-ferrous (base) metals:** Cu, Pb, Zn, Tn, Al 3. **Ferralloy (Iron):** Fe, Mn, Ni, Cr, Mo, Tn, V, Co 4. **Minor metals & non-metals:** An, Ar, Be, Bi, Cd, Mg, Hg, REE, Se, Ta, Te, Ti, Zn 5. **Fissionable metals:** uranium
Gemstone	Diamonds, emeralds, rubies, garnet, etc.
Industrial Minerals	**Any rock, mineral or naturally inorganic substance of economic value,** exclusive of metallic ores, mineral fuels, & gemstones • **Include** minerals such as barite, halite, gypsum, phosphate, diamonds, & garnet; in addition to aggregate & dimension stone

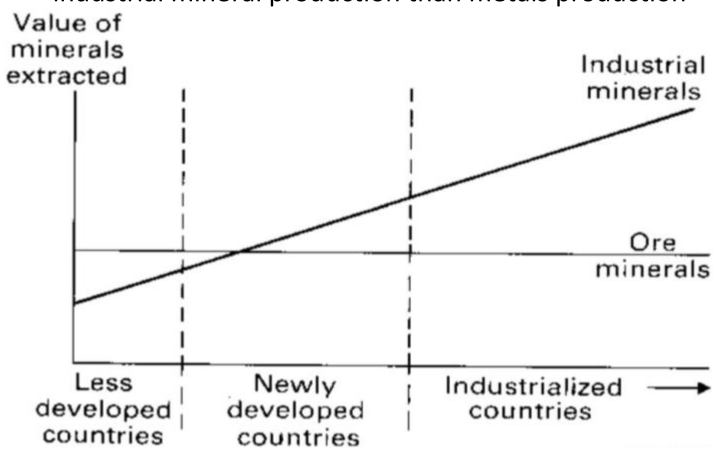
- **Dimensional stone:** is the rock that is cut & can be used as a building materials
- **Sustainable development:** هي التنمية التي تلبي احتياجات الحاضر دون التأثير على قدرة الاجيال القادمة من تلبية احتياجاتها الخاصة

- **For best comparisons on the resources, the classification scheme of the resources is based on:**
  1. **Geological characteristics**: grade & tonnage of the deposits, thickness & depth of the deposits
  2. **Profit assessment:** Prices, Values, & Extraction cost
- **Resources classification**: may be _identified or undiscovered_, & classified based on the _degree of certainty_ that it actually exists

Classification	Definition
Measured (Proven)	Material sampled so that we are certain of outline, tonnage, & grade
Indicated (Probable)	Materials sampled to some degree, giving confidence that we are reasonably certain of tonnage & grade
Inferred (possible)	There is some basis for believing it exist. (assume extend beyond known resources)



- **Relative Importance of Industrial Minerals & Metals Exploitation in Evolving Economies:** Mature economies are characterized by a greater economic importance of industrial mineral production than metals production



- **Economically**: larger sector of mineral productivity, require little or no processing (can be sold directly) & may require firing processing (command higher prices)
  - **Aggregates demand controlled by** market & source
  - **USA & Europe** lack of aggregate sources (Import)
  - **Aggregate sources in Jordan**: Gravel, Sandstone, Igneous Rocks (Dolerite, Granite), Limestone, Dolomite, Railway Ballast (Igneous & Metamorphic)

Aggregate Sources	Used in
Igneous Rock	**Construction industry**
Sand & Sandstones	**Glass industry**
Limestone & Dolomite	**Construction industry**

- **What is Required of an Aggregates? (requirements)**
  1. **Provide strength & bulk, Land fill-strength & shape**
  2. **Tarmac or concrete**
  3. **Properties of construction material, cement or asphalt** depend on the properties of the aggregates
  4. **Density, Grading, Shape, Texture, Reactivity, & Water Absorption are taken into account**
- **Concrete**: cement acts as a binder to hold aggregates & must be stable under conditions of use
  - **Consist of** 1:5 cement & aggregates (course & fine) respectively mixed in different proportions
  - **Concrete strength are measured for** finished material & raw aggregates
  - For concrete using, Aggregate are routinely tested as for road (Especially 10% fines value & AIV)
- **Aggregate Reactivity:** problems of concrete apparent after constructions, some materials prone to reactivity
  - **Alkali-silica reactivity (ASR):** reaction with quartz, glass, or amorphous silica
  - **Alkali-carbonate (ACR):** not problem in limestone aggregates & restricted to dolomite crystals that set within finer grained clay carbonate mixture
- **Road construction method** (RCM, Macadam): method of bind aggregate with bitumen to produce tarmacadam

Aggregate for Tarmac & Road (RCM)		
Sub-base	**6-38 mm** 0.5 m **4.25 mm**	**Crushed rock** Aggregate that must be Frost resistant **Materials that must be Non-plastic**
Road-base	<38 mm	Coarse aggregate bound by bitumen that should be Frost Resistance
Base-course	<38 mm	Coarse aggregate bound by bitumen that should be Frost Resistance
Wearing-course	19-25 mm	Rolled asphalt with 30% coarse aggregate & covered by bitumen

- **Structure of roads must be**:
  1. Layered to provide layers with differing property
  2. Strong enough to take traffic weight
  3. Must be resist wear & provide frictional resistance

Assessment of Aggregates for road constructions	
Shape & Size	**Rough & Poorly Sorted** grains maximize bonding **Roundness & smoothness** are important in unbound material (Eliminate <0.075mm fraction)

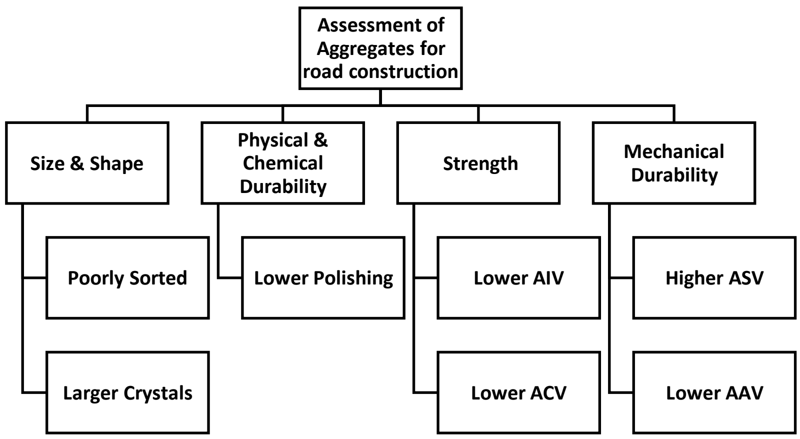
Size assessed by sieving (British Standard BS)	
>5mm	**Coarse aggregate**
<5mm	**Fine aggregate**

Physio-chem-durability	**Frost resistance** is important under prevailing climatic conditions in Northern Hemisphere **Ability of aggregates to respond to volume changes associated with** water ingress or freeze or T change must be assessed petrographically **To asses weathering index or to testing resistance:** 1. **Moisture**: must be low with no variations 2. **Bonding ability:** must bond well with bituemen **Highr polishing resistance** → lower strength
Strength	**Measured by cmbination of 3 tests that assessed according to guidelines laid down under BS**

Strength tests	
Aggregate impact (AIV)	**Assessing** intermittent load **Low AIV <20** → high resistance
Aggregate crushing(ACV)	**Assessing** continuous load **Low ACV** → high resistance
10% fines values	**Assessing** load required to yield 10% of the material <2.36 mm **variation of ACV test**

Mechanical durability	
	Aggregate durable in service under ambient climatic conditions (to effect of water & frost)
Polished stone value (PSV)	**Polishing provides low resistance** **Higher PSV** → Higher resistance **Minimum acceptable PSV depends:** 1. Traffic density 2. Type of roads & junctions
Aggregate abrasion (AAV)	**Measure wear of aggregate surface** **Lower values** → greater resistance **Acceptable Values range:** 1-15

SUMMARY



CHAPTER THREE

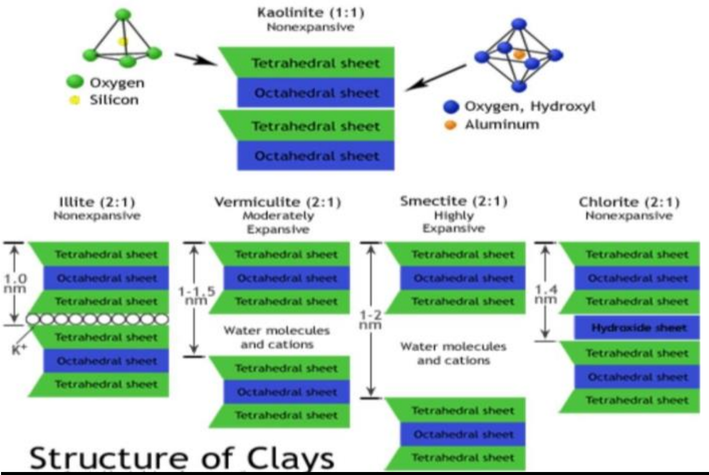
INDUSTRIAL CLAYS

Shaas N Hamdan

CLAY MINERALS

- **Clays**: hydrous aluminosilicate minerals, with <2µm crystal sizes & formed by combination T & O layers

Group	T:O	O	Interlayer Cations	Basal Spacing
Kaolinite	1:1	Di	No	<10Å
illite	2:1	Di	K	10Å
Vermiculite	2:1	Tri	Water + Various Cation	10-15Å
Smectite	2:1	Di,Tri	Water + Ca or Na	10-20Å
Chlorite	2:1	Tri	OH	14Å



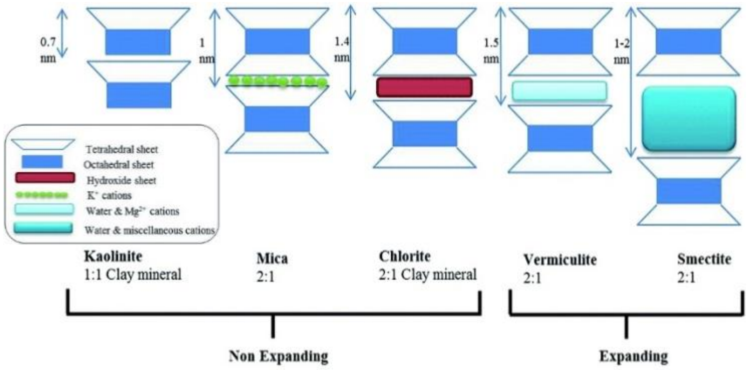
Clay structures or Clay Layers		
Tetrahedral layer or Siloxane sheet	T	$[Si_2O_5]^{-2}$
Di Octahedral (Gibbsite)	O	$Al_2(OH)_6$
Tri Octahedral (Brucite)	O	$Mg_3(OH)_6$

- **Bonds**: The different groups are joined by weak van der Waals bonds (i.e. between T-O; or T-O & another T-O) or by hydrogen bonds from intersheet water molecules

Compositions of Phyllosilicates		
Str.	Dioctahedral	Triocatehdral
T-O	$Al_2Si_2O_5(OH)_4$ **Kaolinite**	$Mg_3Si_2O_5(OH)_4$ **Lizardite**
T-O-T	$Al_2Si_4O_{10}(OH)_2$ **Pyrophyllite**	$Mg_3Si_4O_{10}(OH)_2$ **Talc**
With substitution of Mg or Fe in Talc		
T-O-T	**Chlorite**: $(Fe,Mg)_3(Si,Al)_4O_{10}(OH)_2$	
T-O-T	**Vermiculite**: $(Mg,Fe^{2+},Fe^{3+})_3(Al,Si)_4O_{10}(OH)_2{\cdot}4H_2O$	
With substitution of K, Na, or Ca in Pyrophyllite or Talc		
T-O-T	$KAl_2(AlSi_3)O_{10}(OH)_2$ **Muscovite**	$K(Fe,Mg)_3(AlSi_3)O_{10}(OH)_2$ **Biotite**
T-O-T	$NaAl_2(AlSi_3)O_{10}(OH)_2$ **Paragonite**	$KMg_3(AlSi_3)O_{10}(OH)_2$ **Phlogopite**
T-O-T	$CaAl_2(Al_2Si_2)O_{10}(OH)_2$ **Margarite**	$CaMg_3Al_2Si_2O_{10}(OH)_2$ **Clintonite**
T-O-T	**Smectite**: with 0.3Al interlayer cation $X_{0.3}Al_2(Al_{0.3}Si_{3.7})O_{10}(OH)_2$ or $X_{0.3}Mg_3(Al_{0.3}Si_{3.7})O_{10}(OH)_2$	
T-O-T	**Illite:** $K_{0.8}Al_2(Al_{0.8}Si_{3.2})O_{10}(OH)_2$	

Mg adsorpe water so nH_2O may add to compound with Mg

KAOLINITE GROUP



Minerals	**Kaolinite minerals differ by Stacking sequence of layers** **Kaolinite**: occur as plate, **Dickite**: occur as plate **Halloysite**: can have single H_2O layer, & occurs as a tubular
Formed by	**Kaolinization**: chemical change of feldspar $KAlSi_3O_8$ or muscovite into kaolin (Weathering, Diagenesis, alteration) • **Kaolinite & Halloysite** are formed in soil • **Dickite** replaces kaolin at depth 3.1-3.2Km (120-130°)
Used in	Ceramic, Paint, Filling, Coating, Surface pigment on high quality glossy paper (30%)

- **Kaolinite differentiate from tri-O member (chlorite) by**
  1. **Heating**: Di-O minerals become amorphous to X-ray as heating up to 550°C. But heating alone will not distinguish kaolinite from chlorite because 002, 003, 004 chlorite peaks are also weakened by heat
  2. **Intercalation complex**: Kaolin react with K-acetate & dehydrated halloysite react with formamide

Kaolin (China Clay, White Hill, Kaolinite deposits)	
Composed	Kaolinite, illite, & other impurities
Properties	White powder, whitness, brightness, valuable
Uses	Yield pure white clays & chemically simplicity Used as filler or coating for paper

- **Major impurities that reduce value of Kaolin deposits**:
  1. **Fe-oxides & hydroxide**: discoloured fired products
  2. **Smectite**: influence behaviour, for paper coating
  3. **Contaminant (e.g. silica & fine feldspar):** produce abrasive slurry, that causes wear
- **Kaolin may be discolord due to** the existence of other decomposed phases as biotite

BALL CLAY (PLASTIC CLAY)

Composition	Kaolinite & illite, with traces of smectite, quartz, anataze, Fe-oxide, & organic matter
Used in	**Ceramic industry:** provide strength & malleability **Cement:** binding non shrinking component in firing In **Moulding**

ILLITE GROUP

- **Illite group:** non-expanding, clay-sized, dioctahedral, micaceous minerals, similar to muscovite (T-O-T) but has more Si, Mg, Fe, & water & less Al & interlayer K, considered as alkali-deficient, Si & OH rich muscovite

Composition	$K_{0.5-0.8}Al_2(Al,Si)_4O_{10}(OH)_2$ If **4> Si >3** (3.2) & **1> Al >0** (0.8)
Minerals	**Illite** (with 0.8-0.9K), **Hydromuscovite** **Glauconite** (green Fe-rich member)
Formed by	**Alteration of mica** (alkaline condition) & **feldspars** (in acidic conditions)
Occurrence	Common constituents of shales

- **Illite mineral:** dominant in argillaceous rocks (mudrock), forms by weathering of feldspar, alteration of other clays, or degradation of muscovite under alkaline conditions & high concentrations of Al & K
- **Glauconite:** Fe-member of illite group formed in marine & occurs in pelletal form. ethylene glycol, K-saturation, & heating to 550°C have no effect on their X-ray peaks

SMECTITE (BENTONITE)

- **Smectite group**: is a very soft phyllosilicate group, consists of 2T:1O (di or tri) in which interlayer Al is 0.3, The particles are plate-shaped with diameter ≈ 1 μm

Cations	Ca & Na (In case of Na, adsorp larger water)
Minerals	Beidellite, Montmorillonite (Mg- & Al-rich), Nontronite (Fe-rich), Saponite, Palygorskite
Occurrence	• Acidic conditions with poor drainage • Low K^+, & high Ca^{2+}, Mg^{2+}, Na, & SiO_2 • Parent rock must be enriched in Ca or Na • Smectite stability expressed as function of acitivity-activity or activity-T diagrams
Formed by	**Chemical precipitate** from solution **Hydrothermal alteration** at high T & high K/H ratio with silica contents exceed Qz saturation
Used in	Drilling muds, construction, & fertilizers
Properties	high exchange capacity, & high ability to absorb H_2O (2 layer) that lead to expand

- **Bentonite (Montmorillnite)**: clays of smectite group
  1. **Sodium bentnite**: Wyoming or Swelling bentonite
  2. **Calcium Bentonite**: non swelling bentonite
  3. **Engineering Bentonite**: Ca-bentonite convert to Na-bentonite by ion exchange (swelling capabelity)

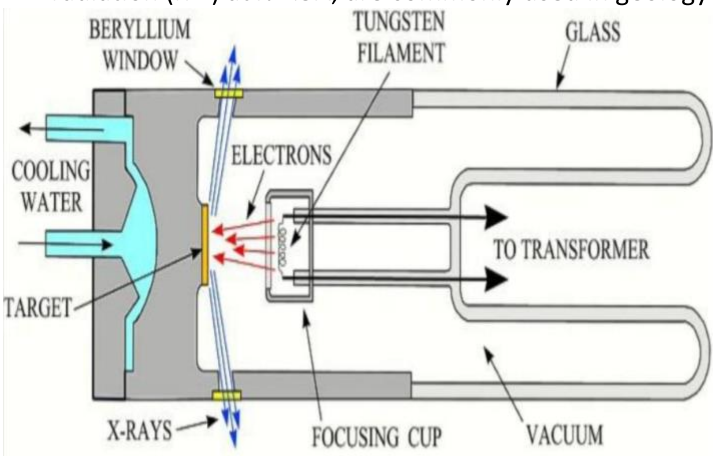
Bentonite: most dominant industrial clay minerals	
Composition	Smectite (Montmorillonit, shrink or swell water layer), Volcanic Ash, & organic matter
Properties	CEC & chemical sorption properties, Chemically & Physically reactive
Factors required to form a bentonite deposits	1. Source of volcanic ash 2. Depositional basin in which the ash accumilated by sorting processes & react with seawater to yield smectite 3. Deposit must protected from erosion (no further change in clay occurs)

ILLITE-SMICTITE LAYER

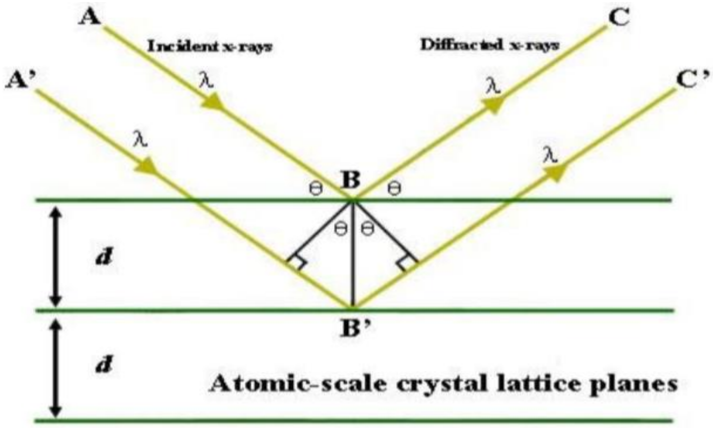
- **Illite-Smictite Mixed layer (I/S):** 80%illite : 20%smectite
- **I/S reaction** course as mudrock buried to depth 3700km

X-RAY DIFFRACTION

- **X-rays**: are electromagnetic radiation with low λ, & produced when charged particles are deacelerated
- In X-ray tube, high voltage in electrodes draws electrons toward a target (anode) & if incident X-ray encounters crystal lattice scattering occurs & X-rays are produced
  - **Destructive interference**: if waves come together in such a manner that they cancel each other
  - **Constructive interference**: if waves add together (superposition) so that a new wavefront is created
- Tubes with Cu-target, produce strongest characteristic radiation (K 1) at λ 1.5Å, are commonly used in geology



- Each crystalline material has a characteristic atomic structure, so it will diffract X-rays in a unique pattern

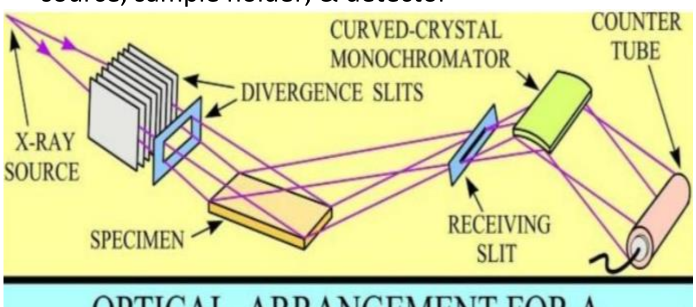


- **Bragg's law**: relationship between λ of incident X-rays, angle of incidence, & spacing between the crystal planes

$$n\lambda = 2d\sin\theta$$

n: order of reflection, λ: wavelength of the incident X-rays, d: interplanar spacing of the crystal, & θ: angle of incidence

- **Components of powder X-ray diffractometer:** X-ray source, sample holder, & detector



OPTICAL ARRANGEMENT FOR A PHILLIPS X-RAY DIFFRACTOMETER

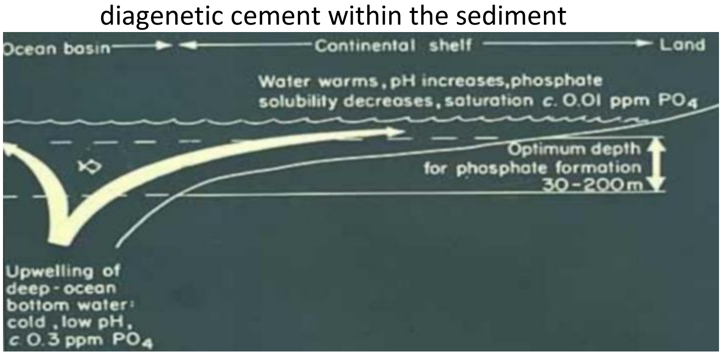
CHAPTER FOUR

MINERALS FOR CHEMICAL INDUSTRY & AGRICULTURE

Shaas N Hamdan

PHOSPHATE ROCK

- **Phosphate** row material for fertilizer industry, extracted from phosphate (predominantly marine biochemical rock & formed by fossils of animal bone & bird dropping)
  - Are economically viable if contain >20%P_2O_5
- **The dominant phosphate mineral is Apatite**
  - **Apatite** $Ca_5(PO_4)_3(OH, F)$ is common in Igneous rock
  - **C-fluorapatite (francolite)** $Ca_5(PO_4, CO_3, OH)_3(OH,F)$ is common in sedimentary rock (42%wt P_2O_5)
- **Impurities**: silicates & carbonates
- **Carbonates** must be reduced from phosphates to give 27-40%P_2O_5 & dissolved in sulphuric acid to produce superphosphate (with 32%Ca) the result is that insoluble apatite is converted to acid Ca-phosphate that able to enter soil solutions to uptake by plants
  - Further treatment with sulphuric & phosphoric acid yield a highly concentrated soluble superphosphate $CaH_2(PO_4)_2H_2O$ with 56%P_2O_5
- **Beneficiation**: involving crushing, sizing, & flotation & used to remove carbonate impurities from phosphate rocks in order to increase concentration of P_2O_5
- **Formation of phosphate minerals** relates to biological productivity of the oceans, formed as concretionary horizons in response to the upwelling of phosphate-rich cold water from the deep ocean (Namebia & Morocco)
- **Conditions required in the formation of phosphate:**
  1. The upwelling current must enter a shallow water
  2. High organic productivity & Little terrigeneous input
  3. Warm & Arid climate: 40° latitude from the Equator
  4. Anoxic bottom in apatite precipitating as a nodular diagenetic cement within the sediment



- Phosphate minerals may be rich in fluorine up to 6%, which effect groundwater quality near mining operation as in Gaza Strip (10mg/L). 1mg/L is beneficial to health, while >3mg/L are hazardous

PHOSPHATES IN JORDAN

(عابد، 2000، جيولوجيا الاردن وبيئته ومياهه)

Age: Upper Cretaceous – Cenozoic (Tertiary)

Groups, Formations, Units, Associations

مجموعة عجلون Ajlone Group

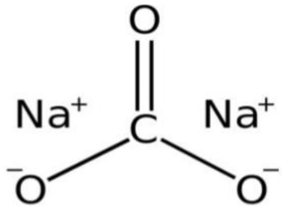
تكوين شعيب توروني كريتاسي	هي وحدة الحجر الجيري الاكونويدي تتكون من جبس عقيدي، رقائقي، جيد التطبق مع الدولومايت وطين اخضر واحمر ومارل اصفر والحجر الجيري **فوسفات صويلح:** يتواجد في حزام ضيق وهو فوسفات طري ولم يتم تحليله لمعرفة كميته

مجموعة البلقاء Belqa Group

تكوين الغدران كمباني كريتاسي	يمتد من شمال غرب الاردن وحتى مادبا ومن مادبا الى وادي الحسا، يحتوي فوسفات وطباشير كتلي، وكوكينا واويستر المتعاقب مع الطباشير **يضم فوسفات الصحراء الجنوبية الشرقية:** يتعاقب مع الصوان ويقع تحت عمان الصواني **نسبة P_2O_5 فيه:** (24.9)
تكوين عمان كمباني كريتاسي	قسم لجزئين وهما جزء سفلي كثير الصوان وعلوي كثير الفوسفيت
تكوين الحسا او وحدة الفوسفوريت ماسترختي كريتاسي	وهو التكوين الحامل لصخور الفوسفات القيمة ويشمل صخور الفوسفات من تكوين عمان، المتعاقب مع المارل، طباشير، صخر زيتي **الرصيفة**: من تركيب عمان الحلابات، مكون من الفوسفات الحبيبي، الحجر الجيري والحجر الجيري المارلي والدولوميت والصوان **تل السور**: من تركيب عمان الحلابات، يكثر به الصوان العدسي وشعاب الاويستر **الجيزة**: تعاقب فوسفات وشعاب الاويستر كالموجود بالحسا والابيض ولم يتم دراستها حتى اليوم **الحسا، القطرانة، جرف الدراويش، والابيض**: فوسفات عدسي متعاقبة مع الاوستر والصوان والكوكينا والحجر الجيري والمارل والدولومايت **ذيبان (الشقيق):** متعاقب مع الاوستر ويشبه خامات الحسا والابيص ولم يتم دراسته **لواء الكورة:** طبقة فوسفات طري خالص سمكه ومتعاقبة مع الصوان في اسفلها، 19.4٪P_2O_5 **الشدية/معان:** بين جرف بطن الغول والجفر، متعاقب مع الاويستر والكوكينا والمارل والتربة ويوجد في 4 مستويات عامودية(26-27٪ فوسفات)
تكوين الموقر ماسترختي-باليوسن	صخوره طرية ومكونة من المارل والطباشير وجزؤه السفلي اسود من الصخر الزيتي، ويزداد الفوسفات به بالجزء السفلي القريب من الحسا
تكوين الرجام باليوسين-ايوسين	يتكون من الصوان الطبقي والطباشير والحجر والفوسفات ويتميز عن تكوين عمان برقة طبقات الصوان المتعاقبة مع الصخور الكربونية

SODIUM CARBONATES

- **Sodium-carbonate (Na_2CO_3)** Washing soda; Soda ash; or soda crystal & is Na-salt of carbonic acid characterize by white color, alkaline taste, very soluble in water (generates alkaline solution), & have odourless powder that is hygroscopic (absorbs moisture from the air)



- **Produced by** evaporitic deposits or alkaline brines or lakes in solvay plants near salt & limestone deposits

Locality	Discovery in N-America of Na-carbonate The largest deposits in Wyoming Green River Formation, African Rift Valley (Lake Magadi)
Uses	Well known compound for water softener Food additive (E500), & Acidity regulator Anti-caking agent, Raising agent, & Stabilizer

- **Solvay (Ammonia soda) process:** is the major industrial process in production of Na-carbonate that requires limestone & halite as raw materials, in which limestone & salt released, Na-carbonate & Ca-chloride formed, water & ammonia recycled
  - Used in glass & laundry deteragent manufacturing

<u>*Began with halite reaction*</u>

$$NaCl_{(s)} + H_2O_{(l)} + NH_{3(aq)} + CO_{2(g)} \rightarrow NH_4Cl_{(s)} + NaHCO_{3(s)}$$

<u>*Remove $NaHCO_3$ precipitate by filtration, heat $NaHCO_3$*</u>

$$2NaHCO_{3(s)} \rightarrow NaHCO_{3(s)} + H_2O_{(l)} + CO_{2(g)}$$

<u>*Prepare hydrated lime from Calcine Limestone*</u>

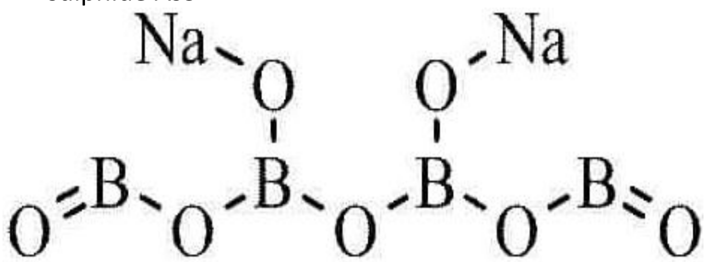
$$CaCO_{3(s)} \rightarrow CaO_{(aq)} + CO_{2(g)},\ CaO_{(aq)} + 2H_2O_{(l)} \rightarrow Ca(OH)_{2(aq)} + 2H^+_{(aq)}$$

<u>*Regenerate ammonia*</u>

$$2NH_4Cl_{(s)} + Ca(OH)_2 \rightarrow 2NH_3{}^+_{(aq)} + CaCl_{2(s)} + 2H_2O_{(l)}$$

BORATES

- **Borates minerals** (e.g. borax $Na_2B_4O_5(OH)_48H_2O$): is the evaporates with limited number of boron composition & different water content, associated with arsenic-sulphide AsS



Formation	**Formation**: B & As (components of gaseous volcanic emissions) affects evaporitic water bodies with which they interact & leds to the formation of Na-borates & Ca- borates
Environment	Controlled by ***degree of weathering, diagenesis, & amount of water available*** So susceptible to dehydration & rehydration during burial & structural deformation
Procedures, & Locality	**Turkey:** Ca-borate interbedded with volcanic **USA**: Na-borate
Uses	Raw material for ***glass industry*** (Pyrex) ***Cleaning agents***, in soaps as a surfactant **Fire retardants, agriculture & metallurgy** Used in ***preparation of Egyptian mummies***

EVAPORATES

- **Evaporitic rocks:** occurs in sequences with gypsum & anhydrite, very important because of their mineralogy, physical properties, & behavior within the subsurface
- **Used:** used in production of fertilizers & explosives, & in produced of salt cake (Na-sulphate) by reaction with sulphuric acids in addition to more uses

Mineral class	Mineral name	Composition
Chlorides	Halite	$NaCl$
	Sylvite	KCl
	Carnallite	$KMgCl_3.6H_2O$
	Kainite	$KMg(SO_4)Cl.\ 3H_2O$
Sulfates	Anhydrite	$CaSO_4$
	Gypsum	$CaSO_4.2H_2O$
	Kieserite	$MgSO_4.H_2O$
	Langbeinite	$K_2Mg_2(SO_4)_3$
	Polyhalite	$K_2Ca_2Mg(SO_4)_6H_2O$

Evaporitic Sequence 1km water evaporate generate 17m evaporites minerals			
1Km Water Evaporation	**Mineral Precipitation**	**Vol% of total evaporates**	**Mass of 17m**
50% (500m)	**Calcite**	**0.6%**	**0.102m**
85% (850m)	**Gypsum**	**3.6%**	**0.612m**
90% (900m)	**Halite**	**78.2%**	**13.29m**
95% (950m)	**K- & Mg-salt**	**17.6%**	**2.992m**

- **Mining Processes for Evaporates:**
  1. **Solution Mining**: Potash, Salt, & Sulfur ores are soluble in water & we remove ores from solution by pumping compressed air to trapped in air bubbles & rise to surface or by water evaporation process
  2. **Solar Evaporation**: by evaporation of sea water (30% of world salt produced in this way)

Halite	**Occurrence**: occurs in sequences (100m) interbedded with clays or other sediments or as salt domes **Halite** are ideal for trapping petroleum deposits, & play important role in the subsurface stability **Uses**: 1. Raw material in **chemical industry** (e.g. solvay process & production of NaOH or chlorine by electrolysis) 2. Used on roads in winter to **prevent icing** 3. **Essential for life** (2-5g/day) & **chemical fertilizers** **Mining processes**: 1. **Solution mining**: yielding solution with 99.5%NaCl 2. **Underground mining**: carried as controlled producing from salt beds deep to prevent surface subsidence 3. **Solar evaporation**: in salt pans by evaporitic seawater
Salt Dome	Structural dome formed when a thick bed of evaporite minerals found at depth forming a diapir • **Impermeable (stratigraphic trap)** for petroleum & gas • **Used for underground storage due to their stability, physical behaviour, & ability to protect groundwater**: important for disposal of nuclear waste
K-Salt	**Occur** as thin seams comparing to thickness of surrounding evaporite (3-6m, up to 10m), yield 25-35%K_2O equivalent **Mining**: require separation of ore minerals from evaporite, by means of flotation, electrostatic or solution methods **Potash fertilizers**: dominant end use of K-minerals, express in K as equivalent to K_2O

SULPHUR

- **Sulphur**: occur as solid, liquid, or gas in the form of different compound (e.g. native element, sulfates, sulfides, or petrolum liquid or gas) & transported above melting point (113°C) in thermally insulated tankers
- **Sulfur are recovered as** SO_2 that produced by oxidation roasting & used to production of sulfuric acid that is used in manufacturing of phosphate fertilizers
- **Types of sulfur:**
  1. **Bright sulphur**: contains ≤ 0.08% Ca
  2. **Dark sulphur:** <0.25%Ca, <0.25ppmAs, <2ppmSe

Sources	**Anhydrite** is an important historical source **Volcanic activity:** not major source. Only in Japan / Chile **Oil:** refining of *oil sweetened* by remove of sulfur by hydrogenation process that produce hydrogen-sulfide (sour gas) in concentration more than methane & both could be sources of sulfur (by *claus process*) **Microbes:** use sulfur as H-acceptor so producing H_2S that oxidized to forms native sulfur
Mining	a well with 4 concentric pipes drilled into sulfur-deposits & the sulfur melt by hot water at 113°C & mobilized by compressed air pressur into the surface
Location	**Mosul/Iraq or Poland** (Miocene evaporates) **Portugal & Spain** (Iberian Belt): A major source of pyrite, submarine volcanic origin
Uses	1. Used in the form of **sulphuric acid** 2. **Essential of petroleum process & many chemical industrial processes** (catalyst, acid leaching) 3. **Combustion of S bearing fuels** (in coal) & **releases** SO_2 into the atmosphere that leds to acid rain

- **Native Sulfur** (<40% of world S-production): derived by microbiological activity that affect gypsum & anhydrite
- **Pyrite** (30% of world S-production): the most important metallic S-ore, accompanied by other metals so sulfur is by-products of metal mining & smelting operations

ZEOLITES

- **Zeolite**: framework aluminosilicates or rings of $(Al,Si)O_4$ & is a microporous solids (members of molecular sieves)
- **Molecular sieves:** ability to selectively sort molecules based on the size due to very regular pore structure
- **Structure**: Al-O form -ve centers so +ve cations (e.g. Na, K, Ca, Mg) inter pores (cavities or channels) & move via channels to permitting ion exchange or dehydration
- **Channels (pores):** have sizes called *molecular sieves* & controls the adsorption & size of molecules in pores
  - Size of species < Min. dimension of widest channels
  - The more the T-layers, the longer the dimension
- **Mining Processes:**
  1. **Open Pit Mining**: by remove overburden materials
  2. **Ore blasted or stripped using tractor** which ore crushed, dried, & milled (milled ore is air-classified)

Occurrence	**Occur naturally or produced industrially**: 206 zeolite are identified (45 naturally occurring) **As volcanic ash** react with alkaline groundwate, or crystallize in post-depositional environments over Ka-Ma in shallow marine basins
Impurities	Contaminated by mineral (metal, Qz, or zeolites) so excluded from many commercial applications

- World's production is 3M tonne, in China, S-Korea, Japan, Jordan, Turkey, Slovakia, & USA (Respectively)
- **Enclosed ions effects** are related to orientation within pores (channels or cavities) or differences in strength of adsorption

Types of ions within pore spaces (channels) & their effects	
+ve ions	loosely held → easily exchanged in a solution
Soft cation (Na)	Led to water softeners (pick up hard cation such as Mg, & Ca & leaving water)
Proton	Leds to strong solid acid (used as catalysts)
Metal	Form catalysts (shape-selective catalyst)

- **Uses**: Available of zeolite at low cost & shortage of compete minerals are essential for large-uses
  1. **Prying agents**, & **Laundry Detergents**
  2. **Shape-selective catalysis**, & in **Petrochemical industry**
  3. **Production process**, & **Biogas Industry** (energy storage)
  4. **Ion-exchanger**: domestic & water purification processes
  5. **Molecular sieves:** in separation, & considered as traps
  6. **Construction**: in asphalt, concrete, or cement industry
  7. **Gemstone**, & **Fluidized bed cat-cracking refinery process**

Natural zeolites is subdivided into 6 groups

G	R	C	Structures & Common Minerals		
GA	1	0	**Fibrous with chain-like structur of T_2O_{10}**		
			Natrolite	NAT	Natrolite, Gonnardite, Scolecite
			Edingtonite	EDI	Edingtonite & Kalborsite
			Thomsonite	THO	Thomsonite-series
GB	4	1	**Single-chain of 4-rings that share 2 opposite T**		
			Analcime	ANA	Leucite, Pollucite, Wairakite
			Other		Montesomaite (MON), Laumonite(LAU), Yugawaralite (YUG), Goosecrekite(GOO)
GC	4	2	**Doubly-connected chains of 4-membere rings**		
			Phillipsite	PHI	Phillipsite & Harmotome
			Gismondine	GIS	Amicite, Garronite, Gobbinsite
			Other		Bogsite (BOG), Merlnoite (MER), Mazite (MAZ), Paulingite(PAU), Perlalite(lindeL)
GD	6	M	**Tabular with chain of 6-rings, open columnar**		
			Chabazite	CHA	Herschelite, Willhendersonite, SSZ-13
			Faujasite	FAU	Faujasite-series, Linde X, Linde Y
			Mordenite	MOR	Maricopaite, Mordenite
			Bellbergite	BEL	TMA-E, Aiello, Barrer; type EAB
			Other		Offretite, Wenkite, Bikitaite, Erionite, Ferrierite, Gmelinite, Levyne, Rpistilbite
GE	3-5	M	**Chains of $T_{10}O_{20}$ with 3 & 5 membered rings**		
			Heulandite	HEU	Clinoptilolite, Heulandite
			Stilbite	STI	Barrerite, Stellerite, Stilbite
Other	M	M	**Cowlesite, Pentasil (ZSM-5, MFI), Linde A (zeolite A, LTA), Tschernichite (β-polymorph A, disordered, BEA)**		

G = Group | R = Number of Rings | C = Number of Chains | M = Multi