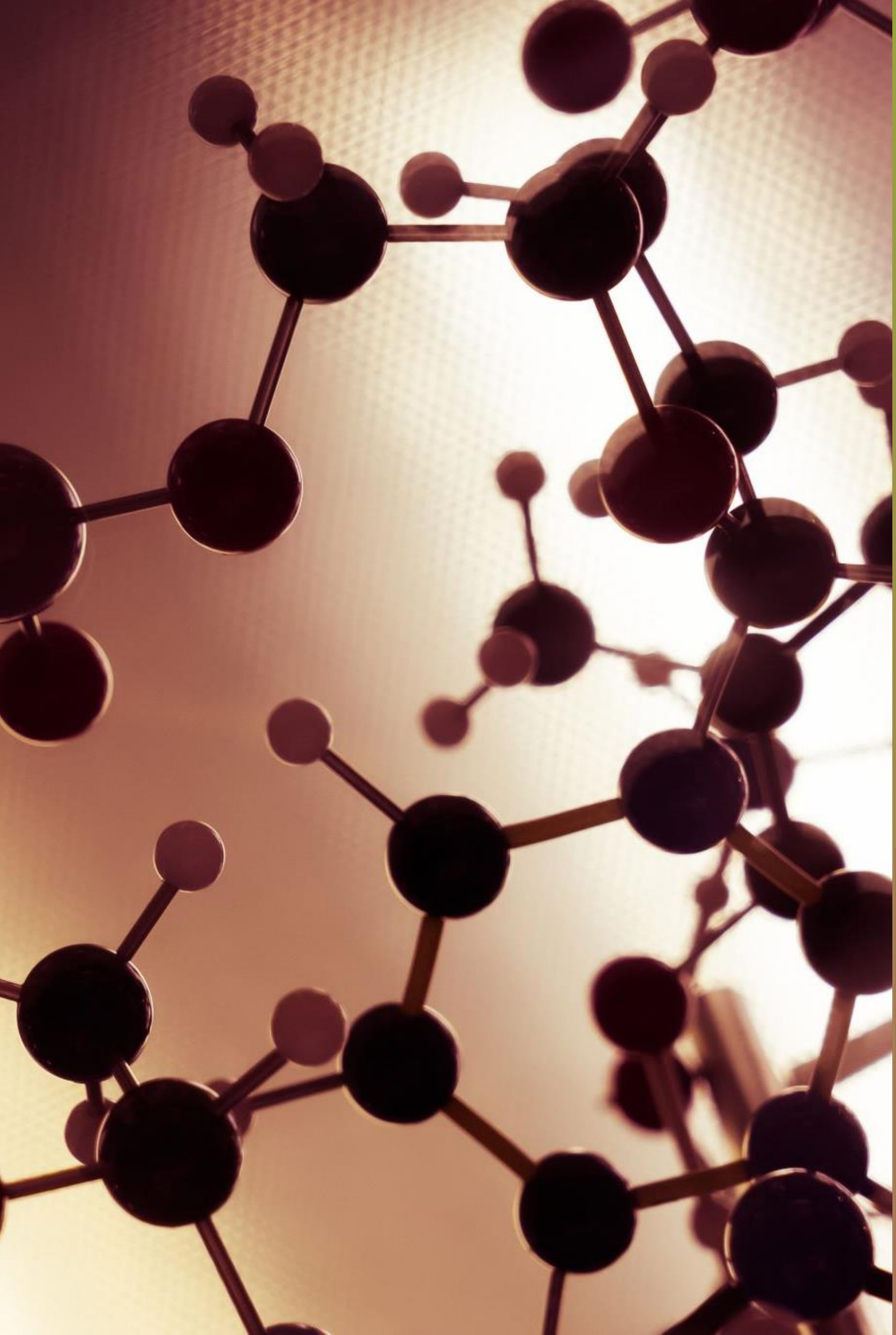


RAW MATERIALS IN CERAMIC INDUSTRY

DR. FARAH DIANA

OUTLINE OF THE TOPIC

- Geology , mineral and ores
- Mineral formation
- Beneficiation
- Silica
- Silicates
    - Clay and Kaolin, Mica, Mullite
- Oxides
    - Alumina, Magnesia, Zirconia, Zincite, Rutile and anatase
- Nonoxides
    - Silicon carbide, Titanium carbide, Aluminum Nitride, silicon nitride, zirconia diboride, tungsten carbide, carbon

GEOLOGY , MINERAL AND ORES

- Major elements in the continental crust -O, Si, and Al almost 90 wt%

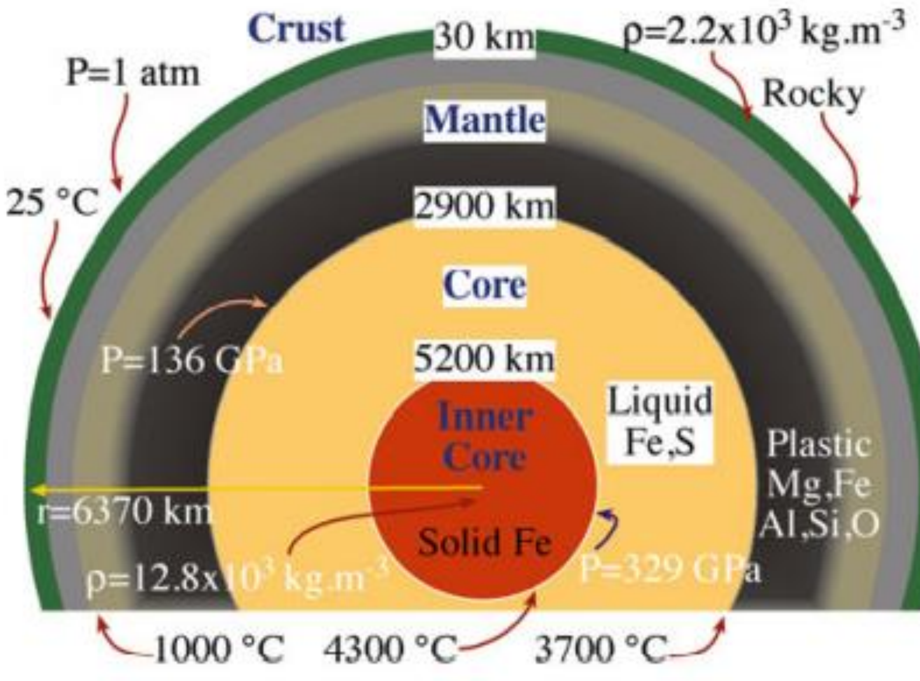


FIGURE 19.1. Cross section of the Earth.

TABLE 19.1 Abundances of the Major Elements in the Continental Crust

Element	*wt%*	*at%*	*vol% of ion*
Oxygen	47.2	61.7	93.8
Silicon	28.2	21.0	0.9
Aluminum	8.2	6.4	0.5
Total iron	5.1	1.9	0.4
Calcium	3.7	1.9	1.0
Sodium	2.9	2.6	1.3
Potassium	2.6	1.4	1.8
Magnesium	2.1	1.8	0.3
Hydrogen	Trace	1.3	0.0

MINERAL FORMATION

- Minerals - constituents of rocks, which make up the entire inorganic, solid portion of the earth.
- Rocks - not composed of a single mineral - aggregate of two/more minerals.
- 3 types of rocks: igneous, metamorphic, & sedimentary

TABLE 19.2 Major Oxides in Igneous Rocks and Their Ranges of Composition

Constituent (oxide)	*Concentration (wt%)*
SiO_2	30–78
Al_2O_3	3–34
Fe_2O_3	0–5
FeO	0–15
MgO	0–40
CaO	0–20
Na_2O	0–10
K_2O	0–15

IGNEOUS ROCK

Granite: magma cooled near earth's surface
Rhyolite: fine grain granite
Obsidian, pumice and scoria: vocanic origin
Basalt: very small grains usually rapidly cooled lava
Gabbro: like basalt but larger grains
Mafic: dark igneous (e.g., basalt)
Intermediate: e.g., diorite. Mg- and Fe-rich
Felsic: light igneous (e.g., granite). Quartz-rich

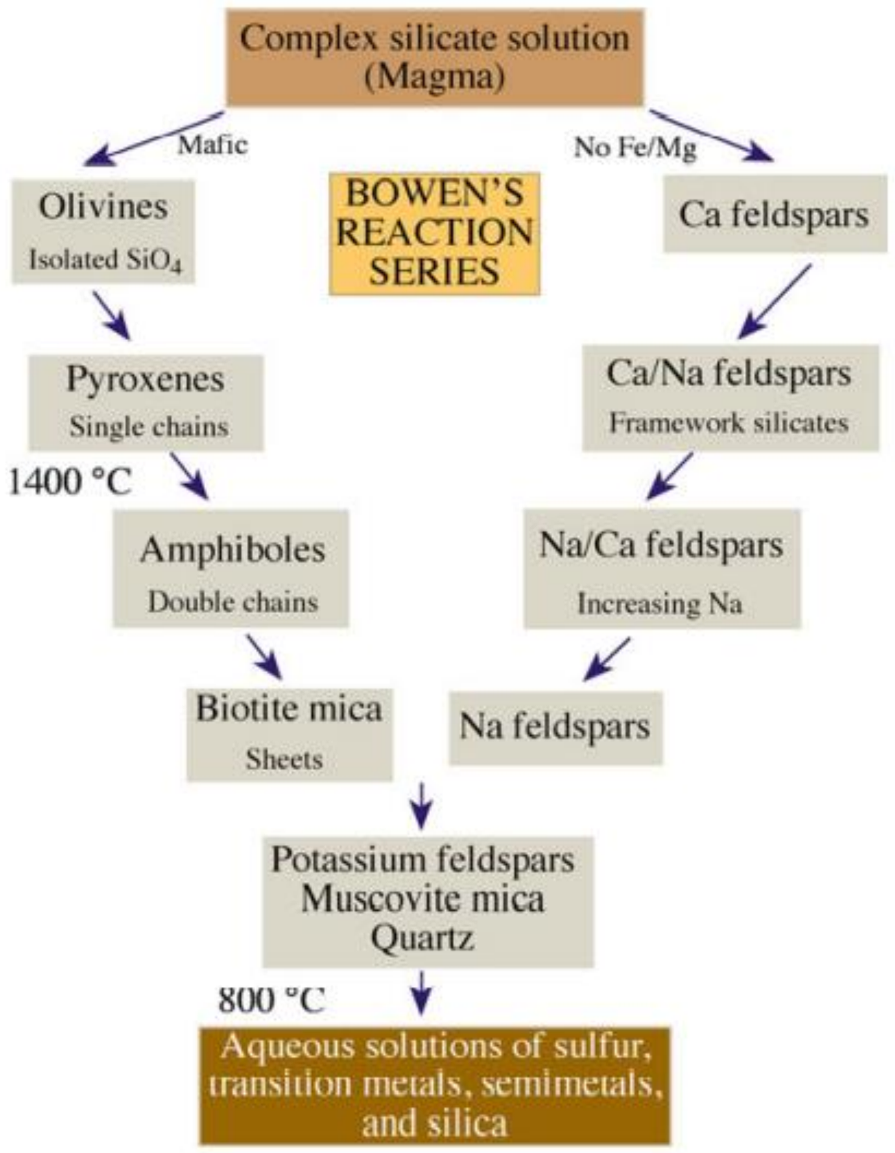


FIGURE 19.2. Bowen's reaction series.

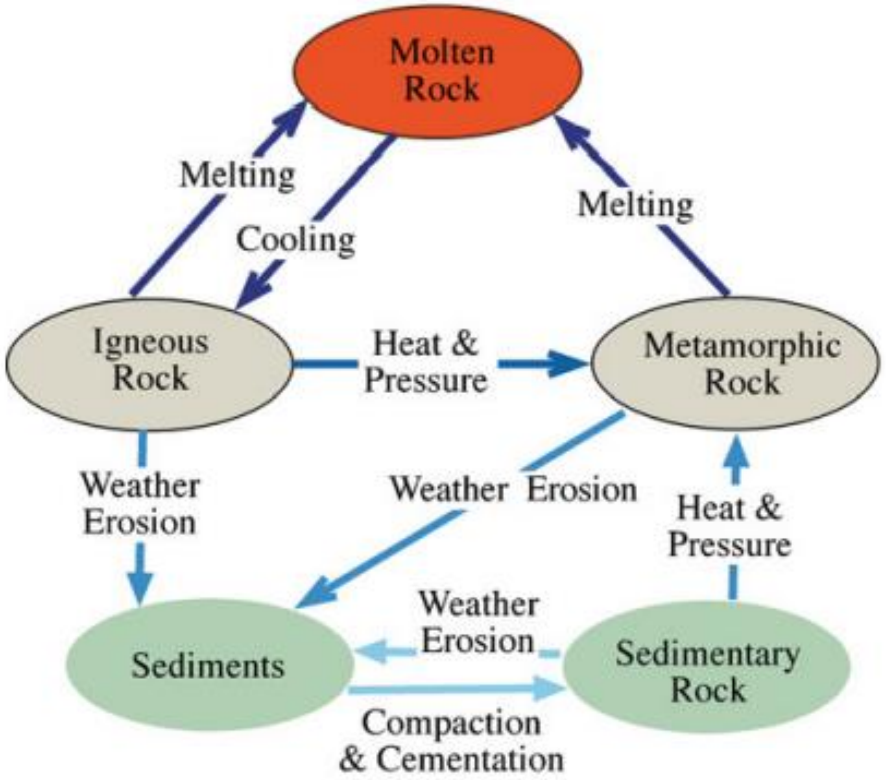
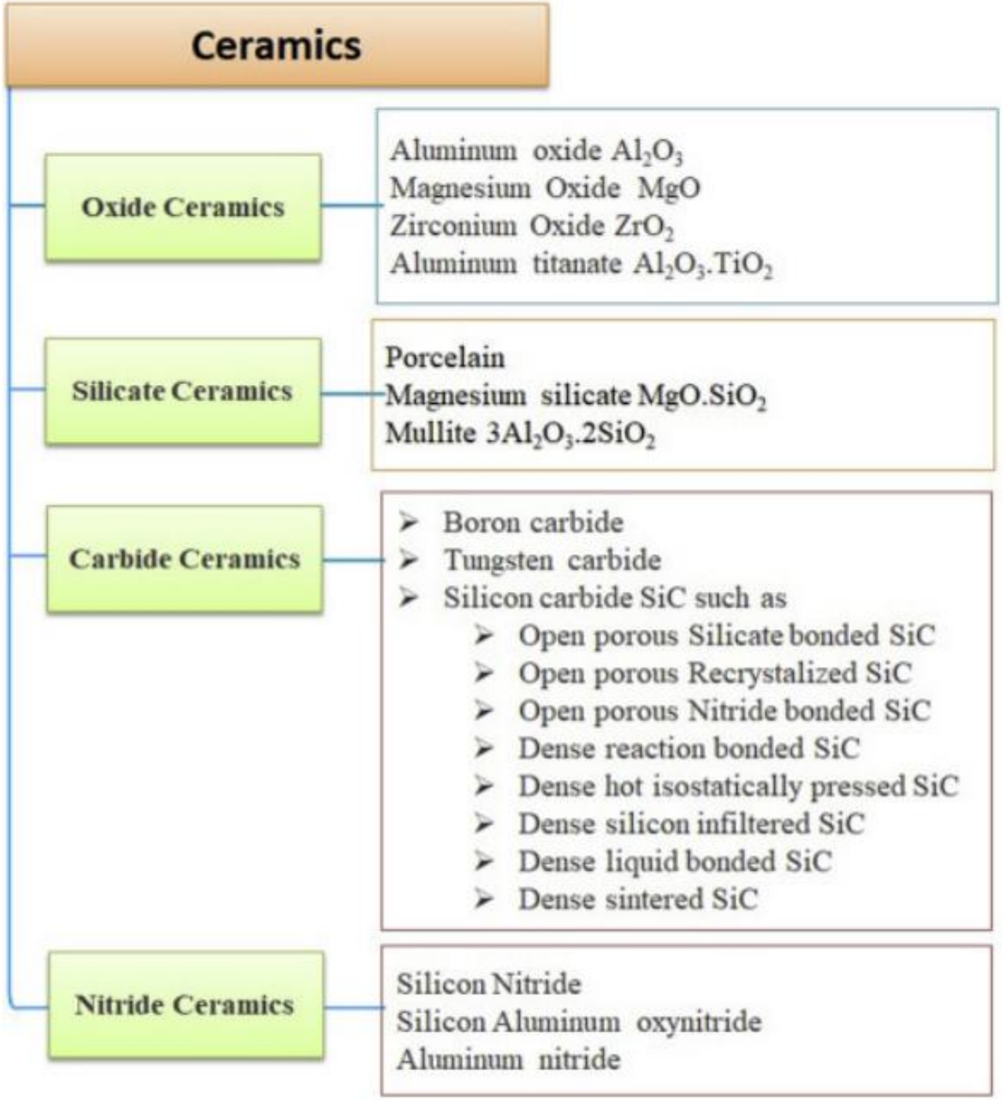


FIGURE 19.3. Simplified diagram of the rock cycle.

Igneous	Rocks formed by cooling and solidification of magma
Metamorphic	Rocks that have undergone structural and/or chemical transitions
Sedimentary	Rocks formed when smaller particles become cemented

- The traditional ceramics industry is largely based on various combinations of clay minerals, feldspar and silica.
- The mineral raw materials used in the ceramic industry are mainly inorganic, nonmetallic, crystalline solids formed by complex geologic processes.
- Oxygen, silicon, and aluminum together account for 90% of the elements in the earth's crust , These, together with other minerals compounds of oxygen, constitute the greatest bulk of naturally occurring ceramic raw materials.



- Clay Minerals
- Talc and Related Minerals
- Silica and Silicate Minerals
- Feldspars and related minerals.
- Refractory Raw Materials

Talc

Silica

Clay

BENEFICIATION

- Beneficiation - process that most minerals need to go through before they can be used in producing ceramics.
- Physical beneficiation - crushing + grinding of coarse rocks.
- The particle size of the raw material may affect subsequent steps in the production process
- Chemical beneficiation
  - processes of separating the desired mineral from unwanted waste products
  - by dissolution in a suitable solvent followed by filtration.
- The purity of the raw materials is reflected in the composition of the final product.
- For ceramics -control over purity is required- the raw materials are synthesized.
- Several important ceramics do not occur naturally in mineral form & must be fabricated chemically.
- Synthesis of ceramic powders can have advantages
  - purity
  - generation of fine particle sized powders - well-defined morphology

SILICA

- Silica (SiO_2) is an important raw material for ceramics- glass manufacture.
- The SiO_2 content of high quality optical glasses can be as high as 99.8 wt%.
- A major source of silica is sand.
- **Industrial sand** and **silica sand** -used by the ceramics industry for sands that have a high SiO_2 %.
- In some of the high quality silica sand sources mentioned below the SiO_2 content is >99.5%

Silica and Silicate Minerals

- Silica is a major ingredient in glass, glazes, enamels, refractories, abrasives, and whiteware compositions.
- It is widely used because it is inexpensive, hard, chemically stable

- The major source of silica for the ceramic industry is sandstone, consisting of lightly bonded quartz grains.
- The sand is frequently mined by loosening the quarts grains with a stream of high-pressure water.

Feldspars and Related Minerals

- Feldspar are anhydrous aluminosilicates containing K+, Na+, and Ca2.; they are present in virtually all igneous rocks.
- Most production comes from pegmatites which are coarsely crystalline rock formed in the later stages of crystallization of a magma

Feldspars and Related Minerals

- Nepheline syenite
- Wollastonite
- Sillimanite


Sillimanite


Nepheline syenite


Wollastonite

SILICA IN MALAYSIA

The Department of Mineral and Geoscience Malaysia (JMG) has estimated that there are approximately **148.4 million tonnes of silica sand reserves located in the states of Johor, Perak, Terengganu, Kelantan, Sabah and Sarawak**. Presently, Malaysia is the world's sixth largest exporter of processed silica sand.

27 Nov 2020

https://www.mida.gov.my/diversifying-investment-opportunities-in-silica-sand-in-malaysia/#:~:text=The%20Department%20of%20Mineral%20and,exporter%20of%20processed%20silica%20sand.

The term of silica is used to describe a mineral commodity which contains a high proportion of silica in the form of rock and sand. In Malaysia, the source of silica is solely from the mining of silica sand. Most of the silica produced are from the mining of natural beach ridges, tin mine tailing sand and some from amang retreatment plants. The silica sand is processed using a variety of steps involving drying, screening, scrubbing, flotation, sizing, iron removal, grinding and acid leaching.

Malaysia has a large amount of silica sand resources. The Minerals and Geoscience Department has estimated about 141.8 Mt of silica sand resources occurs throughout the country. The reserves are located in Sarawak (45.7 Mt), Terengganu (45.6 Mt), Sabah (29.9 Mt), Perak (10.9 Mt), Selangor (8.4 Mt), Johor (1.0 Mt) and Kelantan (0.3 Mt).

In 2013, there were 34 silica sand producers compared with 32 in the previous year, with 20 producers in Perak, 11 in Johor, two in Sarawak and one producer in Selangor. In Sarawak, silica sand was produced from the mining of natural raised beach sand deposits whilst in Perak, Johor and Selangor it was produced both from natural raised beach sand and tin mine tailing sand.

During the year, the total production of silica increased slightly by 9% to 1.2 Mt with an estimated value of RM52.8 million from 1.1 Mt produced in 2012. Johor was the largest producer with a production of 655,924 tonnes, followed by Perak (376,248 tonnes), Sarawak (203,854 tonnes) and Selangor (7,634 tonnes). The bulk of the domestic silica produced went into the manufacturing of glass products. It is also consumed in ceramics, foundries, water treatment, glass wool and other related industries.

Export of silica sand in 2013 increased slightly to 376,693 tonnes worth RM44.54 million from 370,989 tonnes worth RM29.52 million recorded in the previous year. The major exporter of silica sand is Syarikat Sebangun Sdn. Bhd. in Bintulu, Sarawak. During the year, Malaysia exported most of the silica to Singapore, Philippines, Japan and ROK. Malaysia imported a total of 13,327 tonnes worth RM13.09 million of silica sand, an increase from the 9,682 tonnes registered in 2012. The imported silica sand was mainly from Taiwan and Australia. ■

Source: Industrial Minerals Disember 2013

https://jmg.gov.my/add_on/fb/malaysian_minerals_yearbook_2013/mobile/index.html#p=112

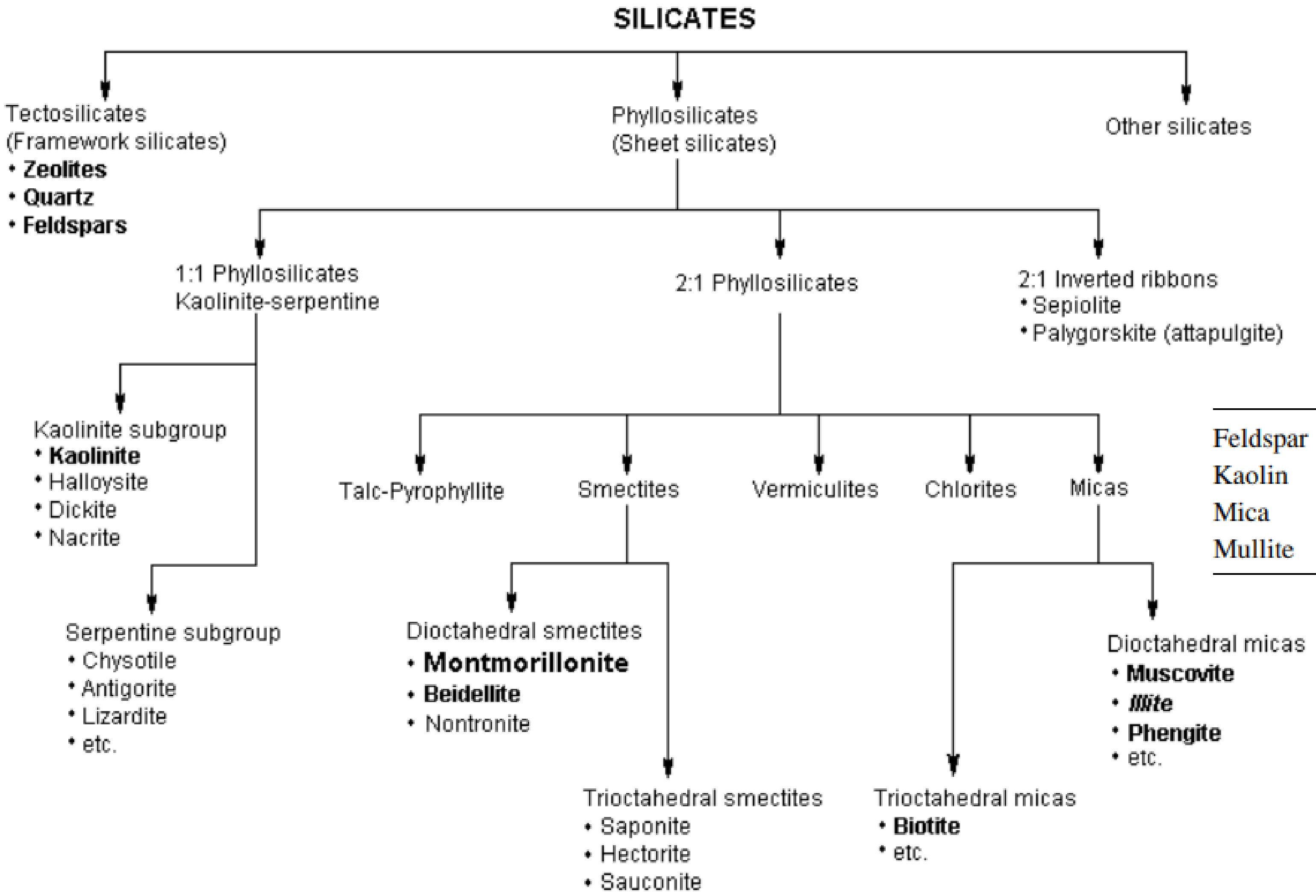
SILICA RESOURCES& SILICA BASED INDUSTRY

- The most common forms of silica sand in Malaysia:
  - Natural sand deposits made up of beach sand and ridges
  - Man-made deposits of tailing dumps from alluvial mining areas.
- In terms of industry, the silica-based industry can be divided into four categories
  - Glass industry (container, crystal, flat, funnel, tableware, insulating, laminated-tempered, optical, speciality glass)
  - Foundry industry (mould)
  - Chemical industry (sodium silicate, silicon wafer fabrication)
  - Others (water filtered sand, bunker sand, cement, construction, etc.)

Table 1. Uses of silica sand (Azimah, 2002).

Silica-based Industry	Uses
Glass Industry	Silica sand (SiO_2), limestone ($CaCO_3$) and soda ash (Na_2CO_3) are fused at 1,100°C to make commercial glass. Composition is usually 75% silica, 10% lime, 15% soda ash. The sand should be of even grain size and have minimum silica content of 99.5%.
Foundry sand industry	Silica sand is used for moulds and cores in metal casting. It is relatively cheap, thermally and chemically stable, and with bentonite clay as binder, is reusable for multiple casting cycles. Specifications require well sorted, subrounded grains, with minimum silica content of 98%.
Chemical industry	Sodium silicate is manufactured from silica sand. This chemical is a starting point for detergents, fillers, and extenders in paints, rubber, and plastics for use in adhesives, sealants, toothpaste applications, and in making dessicant, silica gel.
Other uses	Natural abrasives; in the making of silicon carbide, ceramic and ceramic glazes, as fused silica in optical and laboratory instrument glassware, cement manufacture, water filtration, and as proppant to increase the permeability of oil and gas-bearing rock formations, construction industry, golf bunker sand, water filter.

SILICATES
CLAY AND KAOLIN, MICA, MULLITE



Feldspar	70% used for glass
Kaolin	Used in fine china, paper, and rubber
Mica	>200,000 t of low-quality mica used each year
Mullite	600,000 t are used each year for refractory furnace blocks

CLAY& KAOLIN

- Clay is the primary ingredient in traditional ceramics and is a general name given to the layer silicates with a grain size <2 mm.
- Any of the layer silicates could qualify as a clay mineral.

TABLE 19.4 Commercial Clays, Their Main Uses, and Annual U.S. Production

Type	*Main uses*	*Annual U.S. production (Mt)*	*Comments*
Ball clay	Floor and wall tiles Sanitaryware	1.3	Also called “plastic clay” because it improves workability
Bentonite	Foundry sand bond Absorbents	4.4	U.S. imports bentonite from Canada
Common clay	Bricks Cement	26	Also called “brick clay” Red color comes from iron
Fire clay	Refractories	0.3	Fire clay refractories contain 25–45% alumina
Fuller’s earth	Absorbents	3.2	Textile workers (or “fullers”) cleaned raw wool by kneading it in a mixture of water and fine earth, which adsorbed oil, dirt, and other contaminants
Kaolin	Paper	7.2	Kaolinite is a hydrous aluminum silicate; kaolin is a white firing clay, primarily composed of kaolinite

Common Types of Clay

- ❖ Kaolin or China Clay
- ❖ Ball Clays
- ❖ Fire Clays
- ❖ Flint Clays
- ❖ Pottery Clay
- ❖ Shale
- ❖ Vitrifying Clays
- ❖ Brick Clays
- ❖ Slip Clays

Important Characteristics of Clays in Ceramic Bodies

- ❖ Clays have the ability to form clay-water composition and to maintain their shape and strength during drying and firing
- ❖ They fuse over a temperature range depending on their composition in such a way as to become dense and strong without losing their shape

Talc and Related Minerals

- Talc is a hydrous magnesium silicate which has a layer structure similar to that of the clay minerals.
- It is an important ceramic raw material for the manufacture of electrical and electronic components

Talc and Related Minerals

- Pyrophyllite
- Block talc
- Asbestos

MULLITE

- Mullite ($3Al_2O_3.2SiO_2$) does not exist in nature in large quantities & must be produced synthetically.
- Mullite has many properties that make it suitable for high-temperature applications.
- It has a very small coefficient of thermal expansion (*giving it good thermal shock resistance*) & is creep resistant at high temperature.
- It does not react readily with molten glass/with molten metal slags & is stable in the corrosive furnace atmosphere
  - used as furnace lining & in other refractory applications in the iron and steel-making & glass industries.
- There are two commercial approaches to producing mullite
  - Sintering
  - Fusing

OXIDES

ALUMINA, MAGNESIA, ZIRCONIA, ZINCITE, RUTILE AND ANATASE

- The raw materials used for oxide ceramics are produced by chemical processes
  - to achieve a high chemical purity
  - to obtain the most suitable powders for component fabrication

TABLE 19.6 Oxide Raw Materials

Alumina	Refractories, abrasives, substrates
Ceria	Catalysts, fuel cells, chemical/mechanical polishing
Ferrites	Magnets
Magnesia	Refractories
Rutile and anatase	Paints
Zincite	Rubber, adhesives, varistors
Zirconia	Additives, furnace components


Refractory Raw Materials
❖ Alumina
❖ Magnesia
❖ Dolomite
❖ Chrome Ore
Alumina
Magnesia
Dolomite
Chrome Ore


Other Raw Materials
❖ Soda ash
❖ Borate minerals
❖ Fluorspar
❖ Phosphate minerals
❖ Abrasive raw materials
Soda Ash
Flourspar
Borate Minerals

NONOXIDES

SILICON CARBIDE, TITANIUM CARBIDE, ALUMINUM NITRIDE, SILICON NITRIDE, ZIRCONIA DIBORIDE, TUNGSTEN CARBIDE, CARBON

- Most of the important nonoxide ceramics do not occur naturally and therefore must be synthesized.
- The synthesis route is usually one of the following:
  - Combine the metal directly with the nonmetal at high temperatures
  - Reduce the oxide with carbon at high temperature (carbothermal reduction) and subsequently react it with the nonmetal

SiC	Abrasives, harsh-environment electronic packing
TiC	Bearings, cutting tools
AlN	Electronic packaging, crucibles
Si_3N_4	Future gas-turbine and diesel engine components
ZrB_2	Crucibles and thermowell tubes (steel)
WC	Abrasives, cutting tools
C	Graphite: solid lubricant; diamond: abrasive

Based on composition of *raw materials and type of ceramic materials:*

a) Silicate ceramics:

compounds containing the anionic complex (SiO_4) e.g. the silicate group.

- **Porcelain**
- **Magnesium Silicates ($MgO.SiO_2$)**
- **Mullite (or Porcelainite : $3Al_2O_3.2SiO_2$)**

b) Advanced ceramics:

i) Oxide ceramics:

- **Aluminum Oxide (Al_2O_3)**
- **Titanium Oxide (TiO_2);**
- **Magnesium Oxide (MgO)**
- **Zirconium Oxide (ZrO_2)**
- **Lead Zirconate Titanate ($Pb(Zr_xTi_{1-x})O_3$)**
- **Lead oxide (PbO)**
- **Aluminum Oxide -Titanium Oxide (Al_2O_3 . TiO_2)**

ii) Non-oxide ceramics:

carbides and nitrides are the most important compounds of this group.

- **Carbide ceramics**
- **Nitride ceramics**
- **Boride ceramics**
- **Silicide ceramics**

Carbide ceramics:

- Aluminum carbide (Al_4C_3)
- Silicon carbide (SiC)
- Boron carbide (CB_4)
- Calcium carbide (CaC2)
- Chromium carbide (Cr_3C_2)
- Hafnium(IV) carbide (HfC)
- Molybdenum carbide (Mo_2C)
- Niobium(IV) carbide (NbC)
- Tantalum(IV) carbide (TaC)
- Titanium carbide (TiC)
- Tungsten(IV) carbide (WC)

Nitride ceramics

- Aluminum nitride (AlN)
- Magnesium nitride (Mg_3N_2)
- Silicon aluminum oxynitride ($Al_6N_6O_2Si$)
- Silicon nitride (Si_3N_4)
- Barium nitride (Ba_3N_2)
- Boron nitride (BN)
- Calcium nitride (Ca_3N_2)
- Gallium nitride (GaN)
- Germanium(III) nitride(Ge_3N_4)
- Indium(III) nitride (InN)
- Lithium nitride (Li_3N)
- Strontium nitride (Sr_3N_2)
- Tantalum nitride(TaN)
- Titanium carbonitride (Ti_2CN)
- Titanium nitride (TiN)
- Zirconium nitride (ZrN)

Silicide ceramics

- Calcium silicide technical ($CaSi_2$)
- Magnesium silicide (Mg_2Si)
- **Molybdenum disilicide ($MoSi_2$)**
- Niobium silicide ($NbSi_2$)
- Tungsten silicide (WSi_2)

Boride ceramics

- Aluminum diboride (AlB_2)
- Aluminum dodecaboride (AlB_{12})
- Calcium hexaboride (CaB_6)
- Gadolinium boride (GdB_6)
- Hafnium boride (HfB_2)
- Lanthanum boride (LaB_6)
- Lanthanum hexaboride(LaB_6)
- Magnesium boride (MgB)
- Nickel boride (Ni_2B)
- Niobium diboride (NbB_2)
- Niobium monoboride (NbB)
- Silicon tetraboride (SiB_4)
- Tantalum boride (TaB)
- Tantalum boride (TaB_2)
- Tungsten boride (WB)
- Vanadium boride (VB_2)

ASSIGNMENT 1

- Describe the properties of the ceramic raw material, the processing/production in Malaysia and also its application. Select and present one of the ceramic raw material below:
  - Silicate & alumina
  - Magnesia & rutile & anatase
  - Zirconia and zincite
  - Silica carbide & titanium carbide
  - Silica nitride & zirconia diboride
  - Tungsten carbide & carbon.