CERAMIC MATERIALS I

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CLASSIFICATION OF CERAMICS

Ceramic Materials

Advanced Ceramics

Made from artificial or chemically modified raw materials.

Traditional Ceramics

Mainly made from natural raw materials such as kaolinite (clay mineral), quartz and feldspar.
Advanced versus Traditional Ceramics

**Advanced Ceramics**

Chemically prepared powders
Precipitation, spray drying, freeze drying, vapor phase, sol-gel

Slip casting, injection molding, sol-gel, hot-pressing, HIPing, rapid prototyping,

Electric furnace, hot press, reaction sintering, vapor deposition, plasma spraying, microwave furnace

Erosion, laser machining, plasma spraying, ion implantation, coating

Light microscopy, X-ray diffraction, electron microscopy, scanned probe microscopy, neutron diffraction, surface analytical methods

**Raw Materials Preparation**

**Forming**

**High temperature processing**

**Finishing**

**Characterization**

**Traditional Ceramics**

Raw minerals
- Clay
- Silica

Potters wheel, slip casting, pressing

Flame kiln

Erosion, glazing

Visible examination, light microscopy

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# Raw Material Selection Criteria

<table>
<thead>
<tr>
<th>Raw material cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Market factors</td>
</tr>
<tr>
<td>Technical process parameters</td>
</tr>
<tr>
<td>Performance of the desired product</td>
</tr>
<tr>
<td>Market price of the product</td>
</tr>
</tbody>
</table>
CERAMIC RAW MATERIALS

Ceramic Materials

Naturally occurring minerals

- their origin
- locations in which they can be found
- their relative abundance

Naturally occurring minerals require extraction, which is often a regional industry located close to abundant quantities of the natural deposit.

Most minerals need to go through some form of physical or chemical processing before use. The collective term for these processes is *beneficiation*.

*When you understand* how oxides are manufactured, it will be clear why they are often impure and why Si, Na, Ca are the major impurities.

Synthetic materials

- borides (TiB$_2$, BN, etc.)
- carbides (SiC, B$_4$C, TiC, etc.)
- nitrides (AlN, Si$_3$N$_4$, TiN, etc.)
- oxides (TiO$_2$, Al$_2$O$_3$, etc.)

These ceramics are becoming more common, but are generally expensive and desire special processing environments.

For many nonoxides the main impurities are often components of the starting material which was not reacted, e.g., Al in AlN or Si in Si$_3$N$_4$.
<table>
<thead>
<tr>
<th>Category</th>
<th>Purity, %</th>
<th>Materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crude materials</td>
<td>Variable</td>
<td>Shales, stoneware clay, tile clay, crude bauxite, crude kyanite, natural ball clay, bentonite</td>
</tr>
<tr>
<td>Industrial minerals</td>
<td>85-98</td>
<td>Ball clay, kaolin, refined bentonite, pyrophyllite, talc, feldspar, nepheline syenite, wollastonite, spodumene, glass sand, potter’s flint (quartz), kyanite, bauxite, zircon, rutile, chrome ore, calcined kaolin, dolomite</td>
</tr>
<tr>
<td>Industrial inorganic chemicals</td>
<td>98-99.9</td>
<td>Calcined alumina (Bayer process), calcined magnesia (from brines, seawater), fused alumina, fused magnesia, aluminum nitride, silicon carbide, silicon nitride, barium carbonate, titania, calcined titanates, iron oxide, calcined ferrites, zirconia, stabilized zirconia, calcined zirconates</td>
</tr>
<tr>
<td>Special inorganic chemicals</td>
<td>&gt; 99.9</td>
<td>Various materials (Si₃N₄, TiB₂, SiC, BN, etc)</td>
</tr>
</tbody>
</table>
Synthetic materials

OXIDES

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

NON-OXIDES

Most of the important non-oxide 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.
Natural Raw Materials

The Rock Cycle

Weathering and erosion of all rocks (sedimentary, igneous, metamorphic)

Deposition of sediment

Compaction and cementation

SEDIMENTARY ROCK

Melting magma

METAMORPHIC ROCK

Metamorphism (heat and pressure)

IGNEOUS ROCK

Crystallizing

Lava

IGNEOUS ROCK

Melting magma

Metamorphism (heat and pressure)
• **Minerals** are defined as (1) *naturally occurring*, (2) *inorganic substances with a narrow range of (3) chemical composition and (4) characteristic physical properties.

• An example: The naturally occurring form of the **compound** sodium chloride is the **mineral** halite.
Mohs' scale of mineral hardness quantifies the scratch resistance of minerals by comparing the ability of a harder material to scratch a softer material. The Mohs scale was invented in 1812, by the German mineralogist Friedrich Mohs. Mohs based his scale on ten minerals.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Talc</td>
<td>1</td>
</tr>
<tr>
<td>Gypsum</td>
<td>2</td>
</tr>
<tr>
<td>Calcite</td>
<td>3</td>
</tr>
<tr>
<td>Fluorite</td>
<td>4</td>
</tr>
<tr>
<td>Apatite</td>
<td>5</td>
</tr>
<tr>
<td>Feldspar</td>
<td>6</td>
</tr>
<tr>
<td>Quartz</td>
<td>7</td>
</tr>
<tr>
<td>Topaz</td>
<td>8</td>
</tr>
<tr>
<td>Corundum</td>
<td>9</td>
</tr>
<tr>
<td>Diamond</td>
<td>10</td>
</tr>
</tbody>
</table>

http://www.allaboutgemstones.com/mohs_hardness_scale.html
Mohs Hardness Scale

1. Talc
Talc is the world's softest mineral and the lowest mineral on the Mohs scale. Talc is a hydrated magnesium sheet silicate which is highly insoluble in water. Talc is translucent to opaque with an iridescent or pearly luster. Talc is used in cosmetics such as talcum powder, as a lubricant, and in paper manufacturing.

**Absolute Hardness: 1**
**Chemical Composition: Mg$_3$Si$_4$O$_{10}$(OH)$_2$**

2. Gypsum
Gypsum is a soft mineral composed of calcium sulfate dihydrate. Gypsum occurs in nature as flattened or twinned crystals and transparent cleavable masses called selenite. When Gypsum has a silky and fibrous texture it is called Satin Spar.

**Absolute Hardness: 2**
**Chemical Composition: CaSO$_4$·2H$_2$O**

3. Calcite
Calcite is an anhydrous carbonate, and one of the most widely distributed minerals on the Earth's surface. It is a common constituent of sedimentary rocks. In crystallized form, Calcite has a vitreous luster.

**Absolute Hardness: 9**
**Chemical Composition: CaCO$_3$**
4. Fluorite
Fluorite (fluor-spar) is a mineral composed of calcium fluoride. It is an isometric mineral with a cubic crystal habit. Fluorite is named for its property of fluorescence, or its ability to fluoresce under ultraviolet light.

**Absolute Hardness:** 21  
**Chemical Composition:** $\text{CaF}_2$

5. Apatite
Apatite (hydroxylapatite, fluorapatite, chlorapatite) is a group of phosphate minerals and is one of few minerals that are produced by biological organisms. Hydroxylapatite is the major component of tooth enamel.

**Absolute Hardness:** 48  
**Chemical Composition:** $\text{Ca}_5(\text{PO}_4)_3(\text{OH},\text{Cl},\text{F})$

6. Orthoclase
Orthoclase (aka feldspar) in an igneous rock forming tectosilicate (silicate) mineral and is a key component in granite. Orthoclase derives its name form the Greek word for "straight fracture" because of its two cleavages at right angles to each other. Orthoclase crystallizes in the monoclinic crystal system.

**Absolute Hardness:** 72  
**Chemical Composition:** $\text{KAlSi}_3\text{O}_8$

http://www.allaboutgemstones.com/mohs_hardness_scale.html
Mohs Hardness Scale

7. Quartz
Quartz is one of the most common minerals found in the Earth's crust. It has a hexagonal crystal structure made of trigonal crystallized silica (silicon dioxide). The typical shape of a Quartz crystal is a six-sided prism that ends in six-sided pyramids.

**Absolute Hardness:** 100  
**Chemical Composition:** SiO₂

8. Topaz
Topaz is a silicate or "nesosilicate" mineral created from a combination of aluminium and fluorine. It crystallizes in the orthorhombic system and it's crystals are prismatic in form.

**Absolute Hardness:** 200  
**Chemical Composition:** Al₂SiO₄(OH-,F-)₂

http://www.allaboutgemstones.com/mohs_hardness_scale.html

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Mohs Hardness Scale

9. Corundum
Corundum is the crystalline form of aluminium oxide and one of the basic rock-forming minerals. Corundum is naturally clear or colored by impurities. Due to its hardness, Corundum is used as an abrasive in sandpaper. Emery is an impure and less abrasive variety of Corundum.

Absolute Hardness: 400  
Chemical Composition: $\text{Al}_2\text{O}_3$

10. Diamond
Diamond is the hardest natural occurring material. Diamond is a natural allotrope of carbon. The crystal bond structure of diamonds give the stone its hardness and differentiates it from graphite, which is the main allotrope of carbon.

Absolute Hardness: 1500  
Chemical Composition: C
WEATHERING

- **Mechanical Weathering**
  - Physical disintegration of rock (with no chemical alteration)

- **Chemical Weathering**
  - Chemical alteration of minerals within the rock
  - Usually softening or dissolving the minerals
  - Forming clays, oxides and solutes
WEATHERING

- The result of mechanical weathering
  - Rock falls and slides
  - Crushing and abrasion

Rocks physically broken apart into sediment (but composition does NOT change)

Increases surface area
(lots of crushed broken pieces)
WEATHERING

MECHANICAL WEATHERING ABRASION

WATER

WIND

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Animals that burrow in ground can cause weathering
WEATHERING

• Sediments of:
  – Parent rock
  – Mineral particles
  – Angular fragments

Sediments from Mechanical Weathering
WEATHERING

What is Chemical Weathering?
Breakdown of rocks by chemical reactions that change the composition of rocks

Hydrolysis
Feldspar + Water = Clay
OCCURS WHEN Water combines with minerals most often in granite (mica and feldspars) to form CLAY
What is Chemical Weathering?
Breakdown of rocks by chemical reactions that change the composition of rocks

CARBONATION (causes dissolving)

Rainwater containing carbon dioxide dissolves minerals
(all rain water is slightly acidic)

Most strongly affected are calcite minerals:
Limestone and marble
WEATHERING

What is Chemical Weathering?
Breakdown of rocks by chemical reactions that change the composition of rocks

**RUSTING-OXIDATION**

OXIDATION OCCURS when oxygen combines chemically with iron to form iron oxide
What is Chemical Weathering?

Breakdown of rocks by chemical reactions that change the composition of rocks

Dissolving-ACID RAIN

sulfuric acid-pollution in air dissolves in rainwater and eats away at buildings & rocks
• Chemical Weathering
  – Dissolving → Dissolved ions
  – Oxidation → Iron in Ferromag. Minerals → Iron Oxides (e.g., Hematite)
  – Formation of Clays from silicates (e.g., Feldspar)
WEATHERING

- Chemical Weathering
  - Dissolving → Dissolved ions
  - Oxidation → Iron in Ferromag. Minerals → Iron Oxides (e.g., Hematite)
  - Formation of Clays from silicates (e.g., Feldspar)

### Oxidation:
\[ 4\text{FeSiO}_3 + \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{FeO(OH)} + 4\text{SiO}_2 \]

### Hydration:
\[ \text{CaSO}_4 + 2\text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \]
WEATHERING

CLIMATE CONTROLS WEATHERING

- PHYSICAL WEATHERING:
  COLD AND MOIST
  ALTERNATE FREEZE / THAW

- CHEMICAL WEATHERING:
  WARM AND MOIST (just like a chemical reaction)

IN BOTH CASES – WATER IS THE PRIMARY INGREDIENT THAT PROMOTES WEATHERING
Soil Formation and Weathering Related to Climate
## Weathering Products of Common Rock-Forming Minerals

<table>
<thead>
<tr>
<th>Original Mineral</th>
<th>Under Influence of CO₂ and H₂O</th>
<th>Main Solid Product</th>
<th>Other Products (Mostly Soluble)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feldspar</td>
<td>→</td>
<td>Clay mineral</td>
<td>Ions (Na⁺, Ca⁺⁺, K⁺), SiO₂</td>
</tr>
<tr>
<td>Ferromagnesian minerals</td>
<td>→</td>
<td>Clay mineral</td>
<td>Ions (Na⁺, Ca⁺⁺, K⁺, Mg⁺⁺), SiO₂, Fe oxides</td>
</tr>
<tr>
<td>(including biotite mica)</td>
<td></td>
<td>Clay mineral</td>
<td></td>
</tr>
<tr>
<td>Muscovite mica</td>
<td>→</td>
<td>Quartz grains (sand)</td>
<td>Ions (K⁺), SiO₂</td>
</tr>
<tr>
<td>Quartz</td>
<td>→</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcite</td>
<td>→</td>
<td></td>
<td>Ions (Ca⁺⁺⁺, HCO₃⁻)</td>
</tr>
</tbody>
</table>
Minerals may be subdivided into two majors groups:

- **Silicates** (most abundant)
- **Non-silicates** (~8% of Earth’s crust):
  - Oxides \( \text{O}^{2-} \)
  - Carbonates \( (\text{CO}_3)^{2-} \)
  - Sulfides \( \text{S}^{2-} \)
  - Sulfates \( (\text{SO}_4)^{2-} \)
  - Halides \( \text{Cl}^-, \text{F}^-, \text{Br}^- \)
  - Native elements (single elements; e.g., Au)
Minerals

- Plagioclase feldspars 39%
- Potassium feldspars 12%
- Quartz 12%
- Pyroxenes 11%
- Micas 5%
- Clays 5%
- Amphiboles 5%
- Other silicates 3%
- Nonsilicates 8%
- Oxides
- Carbonates
- Sulfides/sulfates
- Native elements
- Non-ferromagnesian Silicates (K, Na, Ca, Al)
- Ferromagnesian Silicates (Fe, Mg)

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Minerals

- **Silicates**
  - **Tetrahedron**
    - fundamental building block
    - 4 oxygen ions surrounding a much smaller silicon ion

Silicates are by far the most abundant mineral group accounting for more than 90% of the Earth's crust. Silicates are the major rock-forming minerals. It follows that **oxygen** and **silicon** are the most abundant elements in the crust.
Non-Silicates

- Usually form at low temperatures
  - Carbonates
    - Calcite - Ca CO₃
    - Dolomite - CaMg(CO₃)₂
  - Evaporite Minerals
    - Gypsum - CaSO₄·2H₂O
    - Halite - NaCl
  - Oxides
    - Hematite
<table>
<thead>
<tr>
<th>Group</th>
<th>Member</th>
<th>Formula</th>
<th>Economic Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxides</td>
<td>Hematite</td>
<td>Fe₂O₃</td>
<td>Ore of iron, pigment</td>
</tr>
<tr>
<td></td>
<td>Magnetite</td>
<td>Fe₃O₄</td>
<td>Ore of iron</td>
</tr>
<tr>
<td></td>
<td>Corundum</td>
<td>Al₂O₃</td>
<td>Gemstone, abrasive</td>
</tr>
<tr>
<td></td>
<td>Ice</td>
<td>H₂O</td>
<td>Solid form of water</td>
</tr>
<tr>
<td></td>
<td>Chromite</td>
<td>FeCr₂O₄</td>
<td>Ore of chromium</td>
</tr>
<tr>
<td></td>
<td>Ilmenite</td>
<td>FeTiO₃</td>
<td>Ore of titanium</td>
</tr>
<tr>
<td>Sulfides</td>
<td>Galena</td>
<td>PbS</td>
<td>Ore of lead</td>
</tr>
<tr>
<td></td>
<td>Sphalerite</td>
<td>ZnS</td>
<td>Ore of zinc</td>
</tr>
<tr>
<td></td>
<td>Pyrite</td>
<td>FeS₂</td>
<td>Sulfuric acid production</td>
</tr>
<tr>
<td></td>
<td>Chalcopire</td>
<td>CuFeS₂</td>
<td>Ore of copper</td>
</tr>
<tr>
<td></td>
<td>Bornite</td>
<td>Cu₅FeS₂</td>
<td>Ore of copper</td>
</tr>
<tr>
<td></td>
<td>Cinnabar</td>
<td>HgS</td>
<td>Ore of mercury</td>
</tr>
<tr>
<td>Sulfates</td>
<td>Gypsum</td>
<td>CaSO₄ · 2H₂O</td>
<td>Plaster</td>
</tr>
<tr>
<td></td>
<td>Anhydrite</td>
<td>CaSO₄</td>
<td>Plaster</td>
</tr>
<tr>
<td></td>
<td>Barite</td>
<td>BaSO₄</td>
<td>Drilling mud</td>
</tr>
<tr>
<td>Native elements</td>
<td>Gold</td>
<td>Au</td>
<td>Trade, jewelry</td>
</tr>
<tr>
<td></td>
<td>Copper</td>
<td>Cu</td>
<td>Electrical conductor</td>
</tr>
<tr>
<td></td>
<td>Diamond</td>
<td>C</td>
<td>Gemstone, abrasive</td>
</tr>
<tr>
<td></td>
<td>Sulfur</td>
<td>S</td>
<td>Sulfur drugs, chemicals</td>
</tr>
<tr>
<td></td>
<td>Graphite</td>
<td>C</td>
<td>Pencil lead, dry lubricant</td>
</tr>
<tr>
<td></td>
<td>Silver</td>
<td>Ag</td>
<td>Jewelry, photography</td>
</tr>
<tr>
<td></td>
<td>Platinum</td>
<td>Pt</td>
<td>Catalyst</td>
</tr>
<tr>
<td>Halides</td>
<td>Halite</td>
<td>NaCl</td>
<td>Common salt</td>
</tr>
<tr>
<td></td>
<td>Fluorite</td>
<td>CaF₂</td>
<td>Used in steelmaking</td>
</tr>
<tr>
<td></td>
<td>Sylvite</td>
<td>KCl</td>
<td>Fertilizer</td>
</tr>
<tr>
<td>Carbonates</td>
<td>Calcite</td>
<td>CaCO₃</td>
<td>Portland cement, lime</td>
</tr>
<tr>
<td></td>
<td>Dolomite</td>
<td>CaMg(CO₃)₂</td>
<td>Portland cement, lime</td>
</tr>
<tr>
<td></td>
<td>Malachite</td>
<td>Cu₂(OH)₂CO₃</td>
<td>Gemstone</td>
</tr>
<tr>
<td></td>
<td>Azurite</td>
<td>Cu₃(OH)₂(CO₃)₂</td>
<td>Gemstone</td>
</tr>
<tr>
<td>Hydroxides</td>
<td>Limonite</td>
<td>FeO(OH) · nH₂O</td>
<td>Ore of iron, pigments</td>
</tr>
<tr>
<td></td>
<td>Bauxite</td>
<td>Al(OH)₃ · nH₂O</td>
<td>Ore of aluminum</td>
</tr>
<tr>
<td>Phosphates</td>
<td>Apatite</td>
<td>Ca₅[PO₄]₃(PO₄)₃</td>
<td>Fertilizer</td>
</tr>
<tr>
<td></td>
<td>Turquoise</td>
<td>CuAl₆(PO₄)₄(OH)₈</td>
<td>Gemstone</td>
</tr>
</tbody>
</table>
NATURAL RAW MATERIALS

- Clays
- Silica
- Feldspar
- Talc
- Wollastonite
- Aluminum Minerals
- Lithium Minerals
- Flourine Minerals
Non-uniform, crude materials from natural deposits clays. (Montmorillonite, illite, etc.)

Large mining trucks must carry more than 300 tons per load, and all are powered by diesel engines.
The preparation, particularly of clay, by exposure to the weather for a long period. This helps to oxidize any pyrite present, rendering it soluble, so that this and other soluble impurities are to some extent leached out; the water content also becomes more uniform and agglomerates of clay are broken down with a consequent increase in plasticity.

Weathering is simply the chemical and/or physical breakdown of a rock material. Weathering involves specific processes acting on rock materials at or near the surface of the Earth.

<table>
<thead>
<tr>
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</tr>
<tr>
<td>Calcite</td>
<td>→</td>
<td>—</td>
<td>Ions (Ca²⁺, HCO₃⁻)</td>
</tr>
</tbody>
</table>

Weathering products of common rock-forming minerals
Element Abundances

Common cations that bond with silica anions

- Oxygen (O): 46.6%
- Silicon (Si): 27.7%
- Aluminum (Al): 8.1%
- Iron (Fe): 5.0%
- Calcium (Ca): 3.6%
- Sodium (Na): 2.8%
- Potassium (K): 2.6%
- Magnesium (Mg): 2.1%
- All others: 1.5%
Abundance of Minerals in the Earth’s Crust *

<table>
<thead>
<tr>
<th>Mineral groups</th>
<th>vol%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feldspars</td>
<td>58</td>
</tr>
<tr>
<td>Pyroxenes, amphiboles</td>
<td>13</td>
</tr>
<tr>
<td>Quartz</td>
<td>11</td>
</tr>
<tr>
<td>Micas, chlorites, clay minerals</td>
<td>10</td>
</tr>
<tr>
<td>Carbonates, oxides, sulfides, halides</td>
<td>3</td>
</tr>
<tr>
<td>Olivines</td>
<td>3</td>
</tr>
<tr>
<td>Epidotes, aluminosilicates, garnets, zeolites</td>
<td>2</td>
</tr>
</tbody>
</table>

THE END

Thanks for your kind attention
Any Questions