Nature’s Glass

Obsidian

First used 75,000 B.C. for tools and weapons
Discovery of Glassmaking

- Phoenicia or Mesopotamia (modern day Lebanon, Iraq and Syria)
- ~4,000 B.C.
- Possibly an accidental discovery — heating of sand, lime and natron
- May have been observed as a by-product of metallurgy
Birthplace of Glassmaking

Egyptians developed the art.
Early Glassmaking Methods

- Egyptians developed several methods for making beads and vessels with glass
  - Beadmaking
  - Casting
  - Core forming

- Slow methods

Wound glass beads, Iran, 1st millennium B.C.
Core forming

Core-formed fish vessel, Egypt, 1353-1336 B.C.

Core-formed vessel
Egypt, 1360-1240 B.C.
11.5 cm high
Core-formed Jar

- Egypt
- 1295-1186 B.C.
New, Faster Methods in 50 B.C.

- Romans and Phoenicians developed
  - Glassblowing
  - Multi-layered colored glass — *millefiori*
  - Glass carving

*Millefiori Dish* — 3rd century A.D.  
East London excavation

*Blue Blown Flask* — 5th Century A.D., Mediterranean

*The Morgan Cup* — Roman cameo  
Glass from 1st century A.D.
Blown Glass

- Roman glass from 750-550 B.C.
Roman Blown Glass

Glass perfume pot or oil flask. (London, 2nd Century A.D.)

Glass jug with chain handle (Essex, 3rd Century A.D.)
Fancy Mediterranean Glass

Mosiac glass plate
Mediterranean (220-200 B.C.)
Venice — Glassmaking Center

- Renaissance 13th - 15th centuries
- Secret techniques
- Glassmaking slowly spread to other European countries.
- brought to America in 1608
Modern Production Methods

Blowing

Empty Mold
Blank Ready
Blank Blown
Untrimmed Piece
Trimmed Piece

Pressing

Empty Mold
Loaded Mold
Glass Pressed
Finished Piece

Float Casting

Glass melt
Molten tin
Stained Glass

- Beginnings in 10-12th centuries
- Colored glass held together with lead strips
- Painted and fired to fuse paint to glass.

Virgin Annunciate, 1340, Worcestershire, England

15th century roundel
Aesop’s Reynard the Fox
Painted Glass

- 2-3rd Century A.D.
- The Yorks
Reims Cathedral (French 1211 A.D.)

- **Vitreous painted glass — 1275-1299 A.D.**
Reims Cathedral (French 1211 A.D.)

- Marc Chagall’s stained glass (1974)
Prince Rupert Drops

- Drop melted glass into cold water
- Outside of glass cools rapidly to form tough “skin”

Stress, stress, and temper
What is Glass?

- A non-crystalline solid
- An inorganic product of melting which has cooled to a rigid condition without crystallizing
- An amorphous solid - no long-range order
- Intermediate state between crystalline and liquid
- flows and glows upon heating
Quartz — a Crystalline Solid

Quartz or SiO$_2$ (silica)

All the atoms are arranged in a regular, repeating pattern called a **crystal lattice**.
Formed by slow cooling of melted **silica**.
Glass — an Amorphous Solid

- **Silica** is the basic ingredient of glass but its crystalline order has been disrupted due to rapid cooling of the melted silica.
Composition of Glasses

Three essential categories of oxides

- **Glass Forming Oxides**
  - $\text{RO}_2$ and $\text{R}_2\text{O}_3$

- **Fluxing Oxides**
  - $\text{RO}$, $\text{R}_2\text{O}$

- **Stabilizing Oxides**
  - $\text{R}_2\text{O}_3$

$R = \text{a metal ion}$
Glass Forming Oxides

- Major ingredient of a glass
- Most commonly used is SiO$_2$ (silica, sand)
- Also can use B$_2$O$_3$ (boric oxide)
Glass Network

- SiO$_4$ units linked in 3-D network by bridging the oxygen atoms
- pockets are present which can encapsulate cations in order to maintain neutral charges
- disordered array
Fluxing Oxides (Fluxes)

- Used to lower the melting point of silica
- Lowers the viscosity of molten glass
- Alkali oxides (R$_2$O)
  - Na$_2$O (soda), K$_2$O (potassa), Li$_2$O (lithia)
- Alkaline Earth oxides (RO)
  - CaO (calcia), MgO (magnesia)
- Others
  - PbO, ZnO
Sources of Fluxing Oxides

- **Aluminosilicate** rocks and minerals
  - Soda feldspars
    \[ \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \]
  - Potash feldspars
    \[ \text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \]
  - Calcium feldspars
    \[ \text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \]
Nepheline Syenite

- igneous rock composed of a silicate mineral called orthoclase ($\text{KAlSi}_3\text{O}_8$)
- granite-like appearance with little or no quartz content (free SiO2)
- used to lower the melting temperature of glass and ceramic, promoting faster melting and fuel savings
Melting Point of Silica and Flux

- mp. of potash feldspar = 1686°C
- mp. of SiO₂ = 1723°C

Diagram:
- 1686°C
- 1723°C
- 990°C
- Eutectic point
- 100% Potash feldspar
- 100% SiO₂
Stabilizing or Adhesive Oxides

- Used to control viscosity, inhibit flow of molten glass, retard crystal formation
- Lower thermal expansion of glass — resistance to cracking under changing temperatures
- \( R_2O_3 = Al_2O_3, B_2O_3 \)
Opacifying Oxides

- Compounds with a high refractive index added to make glass opaque

\[
\begin{align*}
\text{SnO}_2 &= 2.04 \\
\text{TiO}_2 &= 2.55-2.75
\end{align*}
\]

Milk glass
Coloring Glass

- Transition metal ionic compounds of iron, manganese, copper, cobalt, silver, gold, and uranium

http://1st-glass.1st-things.com/articles/glasscolouring.html
Glass Coloring Agents

- Iron salts - ubiquitous
  Fe$^{2+}$
  Fe$^{3+}$

- Manganese
  Mn$^{3+}$ (Mn$_2$O$_3$)
Glass Coloring Agents

- Copper
  $\text{Cu}^{2+}$

- Cobalt
  $\text{Co}^{2+}$

- Chromium
  $\text{Cr}_2\text{O}_3$
Glass Coloring Agents

- Nickel
  Ni$^{2+}$

- Gold
  Au$^{2+}$

- Uranium
  U$^{2+}$
Glass Types

- Quartz Glass (fused silica)
- Soda-Lime Glass (window glass)
- Borosilicate Glass (scientific, Pyrex®)
- Leaded Crystal
- Specialty Glasses
Quartz glass

- Also called “fused silica”
- pure SiO$_2$
  - high mp = 1723°C, high viscosity
  - chemical and physical durability
  - transparent to visible and UV light
  - many scientific applications
Soda-Lime Glass

- Used to make windows, mirrors, bottles.
- \( \text{SiO}_2 + \text{Na}_2\text{O} + \text{CaO} \)
  - m.p. lowered to 1300\(^\circ\)C
  - can be attacked by strong acids (H\(^+\))
  - can be attacked by strong bases (OH\(^-\))
  - high “thermal expansion” — cracks easily when heated and cooled
Borosilicate Glass

- Brand names of Pyrex®, Kimax®
- $\text{SiO}_2 + \text{Na}_2\text{O} + \text{B}_2\text{O}_3$
  - boron lowers thermal expansion of glass
  - lower m.p. and lower viscosity
  - durable, chemically resistant glass
  - used in scientific glassware
  - used in household cook ware
Leaded Glass

- Misnomer of “leaded crystal’
  - cut to look like crystals
- \( \text{SiO}_2 + \text{Na}_2\text{O} + \text{K}_2\text{O} + \text{PbO} \)
  - lowers m.p. and viscosity of glass
  - highly refractive and reflective glass
  - PbO is an historically important flux
  - poisonous in glass and unfired and fired pottery — can be leached by acids
  - used to shield from radiation (eg. TVs)
Special Glass

- Photochromic Glass
  - mid-1960’s innovation out of Corning Glass
  - Contains 0.01-0.1% AgCl and CuCl
  - UV light decomposes AgCl to produce silver atoms and glass darkens (similar to photographic film)
  - In the dark the reaction is reversed by the Cu$^+$ in the glass
Gorilla Glass 1962-2010!
Iridescence on Glass

- Multiple layers produced through weathering and corrosion
- Cause refraction of light and production of interference colors
- Seen in ancient and antique glass
- Carefully reproduced in art glass
Other Uses of Glassy Materials

- **Glazes**
  - Applied to surface of ceramics

- **Enamels**
  - Applied to surface of metals

18th century bottle, Chinese
Glaze

- Turquoise Matte
  - Nepheline Syenite 1725
  - Strontium Carbonate 597
  - OM-4 Ball Clay 187
  - Flint 213
  - Lithium Carbonate 81
  - Copper Carbonate 81
Enamels

- British Museum study
Glaze and Enamel Composition

- Similar to glass
- Glazes usually contain more components
- Formulated to melt at lower temperatures (about 1000ºC)
- Glass former is silica
- Fluxing Oxides - to lower m.p.
- Stabilizing Oxides - to control fluidity
Application of Glaze and Enamel

- Glazes are usually applied as slurries or suspensions.
- Can be applied by dipping, spraying, or painting.
- Must be thixotropic (what???)
- Must match thermal expansion and contraction characteristics to those of clay body or metal surface.