Archaeological Glass: History, Analysis, Technology and Provenance Studies

N. Zacharias
Technical glasses

**typical glass components:**

<table>
<thead>
<tr>
<th>Function</th>
<th>raw material</th>
<th>oxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Network former</td>
<td>silica sand</td>
<td>SiO$_2$</td>
</tr>
<tr>
<td></td>
<td>borax, Na$_2$O×2B$_2$O$_3$</td>
<td>B$_2$O$_3$</td>
</tr>
<tr>
<td>Network modifier</td>
<td>soda, Na$_2$CO$_3$</td>
<td>Na$_2$O</td>
</tr>
<tr>
<td></td>
<td>potash,K$_2$CO$_3$</td>
<td>K$_2$O</td>
</tr>
<tr>
<td></td>
<td>lime, CaCO$_3$</td>
<td>CaO</td>
</tr>
<tr>
<td></td>
<td>dolomite,CaCO$_3$×MgCO$_3$</td>
<td>MgO, CaO</td>
</tr>
</tbody>
</table>

The Sardanapal-library of the Assyrian king Assurbanipal (700 BC) contains the oldest remaining **glass recipe** on a clay tablet:

“Take 60 parts sand, 180 parts ash from sea plants, 5 parts chalk-and you get glass.”

Invokes also the stars, prayers, sacrifices,…
Use of raw materials for glass production in ancient times

SiO$_2$
Tm~1800°C
Salsola Kali
K$_2$O
CaO
Natron
Na$_2$O
Definition
glasses and other vitreous materials:

- **Glass**: melted, thoroughly fused
- **Faience**: sintered fine granular SiO₂, with some alkali (5-15%) as flux and most often H₂O as binder, during heating fuse the grains on the surfaces, resulting in a hard body, the binder moves to the surface, were it becomes more concentrated and fusing becomes more complete, creating a vitreous outer layer on the molded body of crystalline silica „self glazing“ from the outside faience is hard to distinguish from e.g. a colored glass bead; most objects older than 2000 BC are (intentional) faience, much fewer are (accidental) glasses; oldest objects in faience from 4800-4000 BC, beads, amulets; high period 2nd millenium BC

- **Frit**: sintered polycrystalline body without glazing. fired 700-800°C < melting point, for several hours, frit is often the first step in glass production – before melting and complete fusing
Still under discussion, sometime/somewhere in Mesopotamia.

First vitreous materials probably accidentally produced in ceramic or metal workshops.

Many aspects are quite close to ceramic production and glazing.

**BUT:**

only metal workshops would provide the high temperatures that are essential for glass melting (e.g. colorful slags from cupper / bronze ores / melts)
Making of glass
container glass – sand core technique

Earliest container glass in Mesopotamia and Egypt (1400 BC)

sand core and band technique:

a) form (sand / clay)
b) wrapping with hot glass bands
c) melting/fusing of glass bands
d) decorative linings by colored glass bands
e) annealing

Schematics in Schweizer, according to Bass 1997 and Stern/Schlick-Nolte 1994

Sand core vessels, 6.-4. ct BC, Gordion Türkei, Toledo Museum of Art
Making of glass
Invention of the glass makers pipe

Syrien (Sidon) 100 v.u.Z

Syrian balsam bottles 2nd ct AD
Window glass and glass tesserae
GLASS MAKING

droplet

tests

Tools and waste material
Colors due to crystalline Pigments
not transparent translucent / opaque ⇒ RAMAN

Classical Glass Vessel - Thebes, ca. 5th century BC

- TiO$_2$ (Rutile)
- CaCO$_3$ (Calcite)
- CaSb$_2$O$_6$

Raman shift (cm$^{-1}$)

- 235
- 383
- 517
- 667

Pb-O str
t (mineral Biheimite)

@633 nm

Raman intensity (a.u.)

- 137
- 300
- 460
- 510

Raman intensity (a.u.)

- 143
- 242
- 445
- 610

Raman intensity (a.u.)

- 154
- 280
- 710
- 1085

Raman intensity (a.u.)

- 332
- 510
- 669

Raman shift (cm$^{-1}$)

- 100
- 200
- 300
- 400
- 500
- 600
- 700
Blue – White Colorations within a 5th c BC bead from Thebes
Mycenaean Glass (1.400 BC) from the Peloponnese
1) Optical LED Microscopy (OM)

- Use a system of LED light sources connected to a portable computer for digital recording and management of images.
- Magnification x15, x50, and x200: microscopic imaging of distinct phases and characteristics.
Scanning Electron Microscopy
SEM / EDAX
Portable and hand-held XRF (milli-XRF)

**Major oxide / wt%**

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Limit / wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2O</td>
<td>0.09</td>
</tr>
<tr>
<td>Na2O</td>
<td>0.01</td>
</tr>
<tr>
<td>MgO</td>
<td>1</td>
</tr>
<tr>
<td>Al2O3</td>
<td>0.5</td>
</tr>
<tr>
<td>SiO2</td>
<td>0.1</td>
</tr>
<tr>
<td>K2O</td>
<td>0.1</td>
</tr>
<tr>
<td>CaO</td>
<td>1</td>
</tr>
</tbody>
</table>

**Minor oxide / wt%**

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Limit / wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO2</td>
<td>0.05</td>
</tr>
<tr>
<td>MnO</td>
<td>0.02</td>
</tr>
<tr>
<td>Fe2O3t</td>
<td>0.05</td>
</tr>
<tr>
<td>CoO</td>
<td>0.01</td>
</tr>
<tr>
<td>NiO</td>
<td>0.05</td>
</tr>
<tr>
<td>CuO</td>
<td>0.05</td>
</tr>
<tr>
<td>SbO2</td>
<td>0.1</td>
</tr>
</tbody>
</table>

**Trace elements / wt%**

<table>
<thead>
<tr>
<th>Element</th>
<th>Limit / wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>0.00003</td>
</tr>
<tr>
<td>Cl</td>
<td>0.1</td>
</tr>
<tr>
<td>Ag</td>
<td>0.01</td>
</tr>
<tr>
<td>Sm</td>
<td>0.00005</td>
</tr>
<tr>
<td>Gd</td>
<td>0.00005</td>
</tr>
</tbody>
</table>

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**X-RAY FLUORESCENCE**


EPIDAUROS (35 samples, dark blue MgO vs. K2O)
Rhodes

Kamiros Acropolis 625-600 B.C.
The 29 Thebian samples to be analyzed in this study have been dated as follows:

Archaic (n = 16)
Late Archaic (n = 2)
Late Archaic/Classical (n = 1)
Classical (n = 6)
Classical/Hellenistic (n = 3)
Hellenistic (n = 1).

Image of 6 samples from Thebes
$K_2O - MgO$

R7a,b = Rhodes 7th c. B.C.
Rh4 = Rhodes 4th c. B.C.
Rh3/2 = Rhodes 3rd-2nd c. B.C.
Th = Thebes from archaic to hellenistic times
Al₂O₃ – K₂O
ACKNOWLEDGMENTS
D. Moencke, M. Papageorgiou, M. Kaparou, E. Palamara