

# Archaeological Glass: History, Analysis, Technology and Provenance Studies

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ΠΑΝΕΠΙΣΤΗΜΙΟ ΠΕΛΟΠΟΝΝΗΣΟΥ  
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# Technical glasses

## typical glass components:

Function	raw material	oxide
<b>Network former</b>	silica sand borax, $\text{Na}_2\text{O} \times 2\text{B}_2\text{O}_3$	$\text{SiO}_2$ $\text{B}_2\text{O}_3$
<b>Network modifier</b>	soda, $\text{Na}_2\text{CO}_3$ potash, $\text{K}_2\text{CO}_3$ lime, $\text{CaCO}_3$ dolomite, $\text{CaCO}_3 \times \text{MgCO}_3$	$\text{Na}_2\text{O}$ $\text{K}_2\text{O}$ $\text{CaO}$ $\text{MgO}, \text{CaO}$



Oppenheim 1966 in (Schweizer)

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

$\text{SiO}_2$

$T_m \sim 1800^\circ\text{C}$



Salsola

Kali

$\text{K}_2\text{O}$

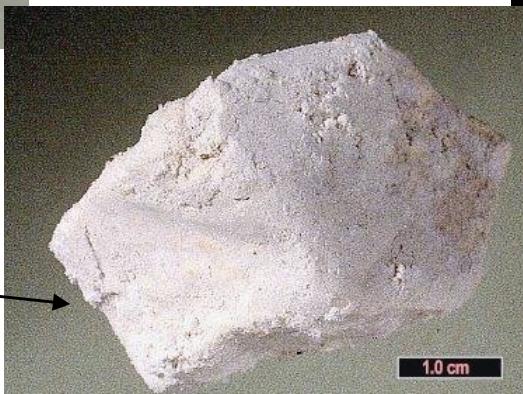


$\text{CaO}$



Natron

$\text{Na}_2\text{O}$



# Definition glasses and other vitreous materials:

[www.museums.org.za/sachm/egypt/images/fig\\_e\\_e.jpg](http://www.museums.org.za/sachm/egypt/images/fig_e_e.jpg)

- **Glass** melted, thoroughly fused
- **Faiience**: sintered fine granular  $\text{SiO}_2$ , with some alkali (5-15%) as flux and most often  $\text{H}_2\text{O}$  as binder, during heating fuse the grains on the surfaces, resulting in a hard body, the binder moves to the surface, where 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 2<sup>nd</sup> millennium 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



Satzinger, Kunsthistorisches Museum Wien 1994  
(Schweizer)

# Origin of technical Glass preparation?

Still under discussion, sometime/somewhere in Mesopotamia

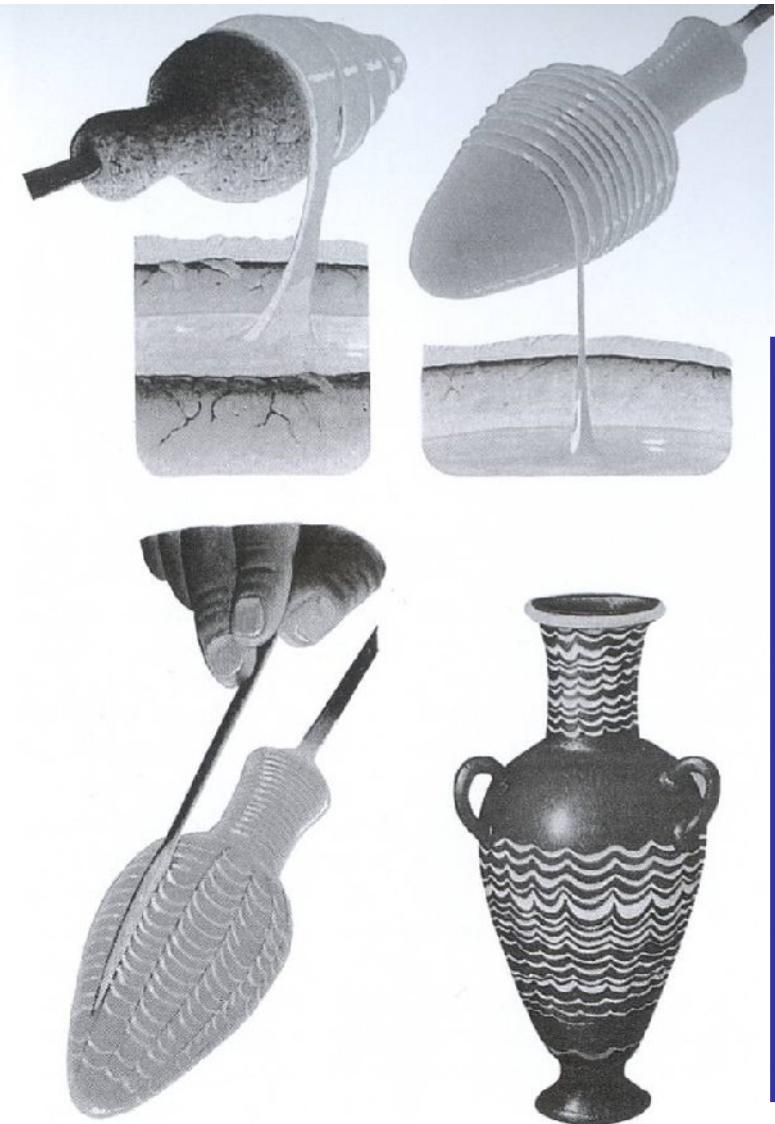
First vitreous materials probably accidentally produced in ceramic or metal workshops

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 copper / bronze ores / melts)

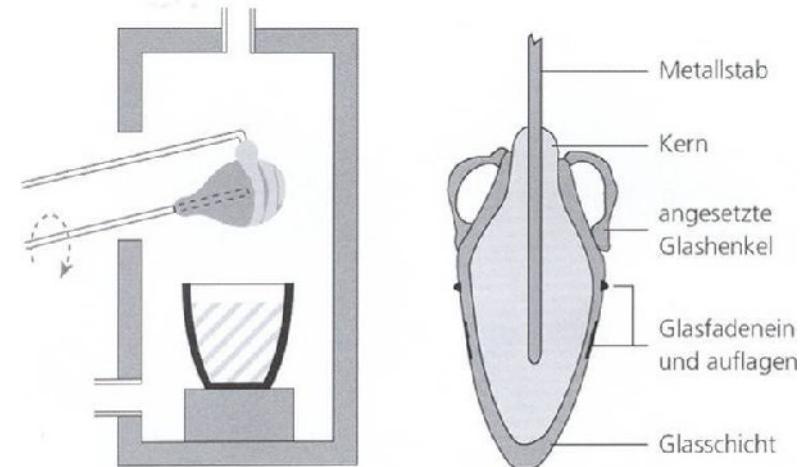
# Making of glass container glass – sand core technique



Earliest container glass in Mesopotamia and Egypt (1400 BC)

## sand core and band technique:

- form (sand / clay)
- wrapping with hot glass bands
- melting/fusing of glass bands
- decorative linings by colored glass bands
- annealing



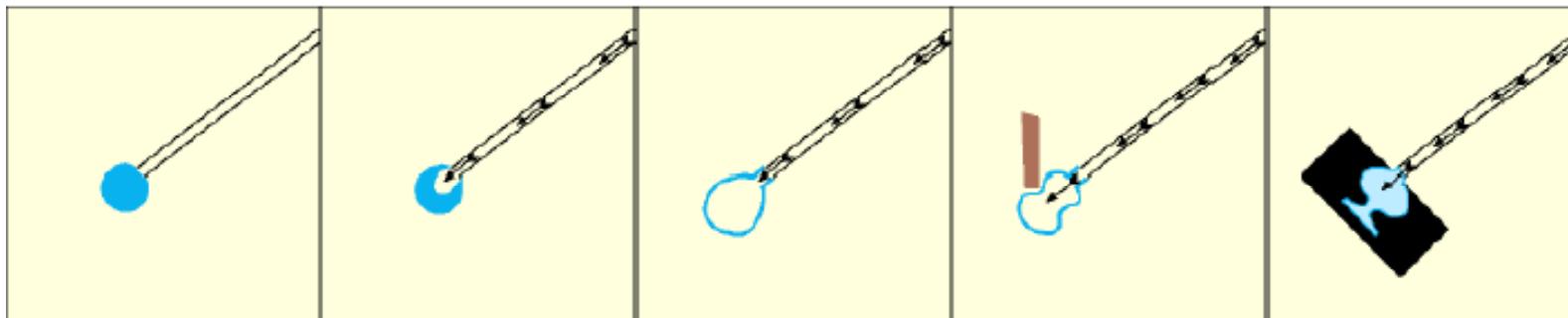
Schematics in Schweizer, according to Bass 1997 and Stern/Schlick-Nolte 1994



Sand core vessels, 6.-4. ct BC, Gordion Türkei , Toledo Museum of Art

# Making of glass

## Invention of the glass makers pipe



[www.petrie.ucl.ac.uk/digital\\_egypt/glass/blow1.gif](http://www.petrie.ucl.ac.uk/digital_egypt/glass/blow1.gif)



Syrien (Sidon) 100 v.u.Z

- 30 000      -2000      -1400      -200

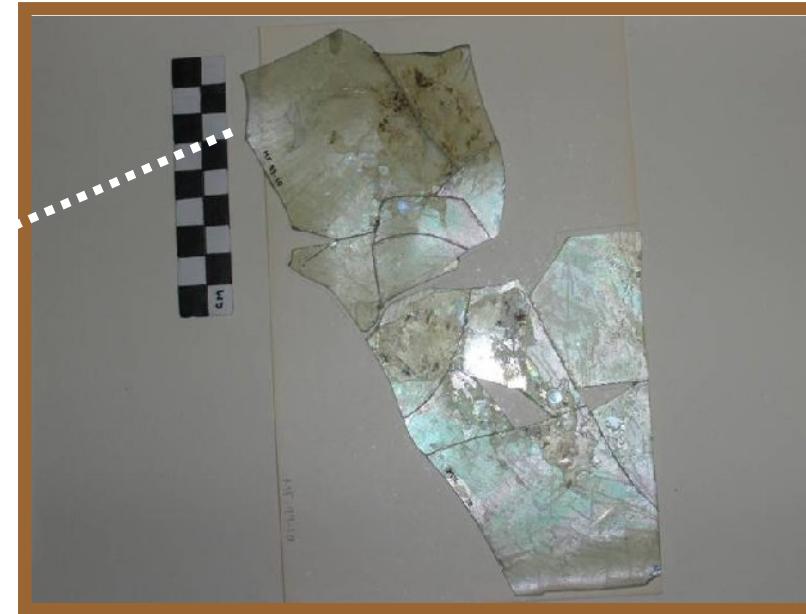
[www.romanglassmakers.co.uk/articles/blower.gif](http://www.romanglassmakers.co.uk/articles/blower.gif)

Syrian balsam bottles 2<sup>nd</sup> ct AD



[www.museesdegrasse.com/MIP/Data/Images/A4c\\_012.gif](http://www.museesdegrasse.com/MIP/Data/Images/A4c_012.gif)

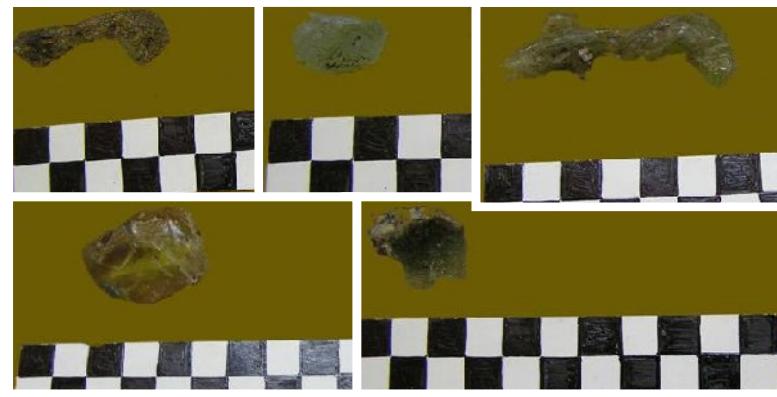
# Window glass and glass tesserae



# GLASS MAKING



droplet



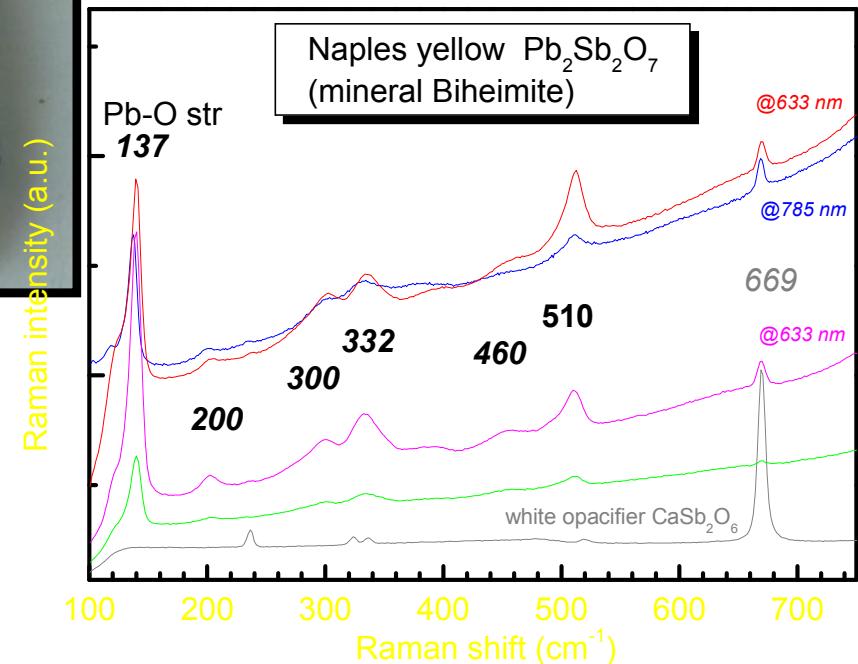
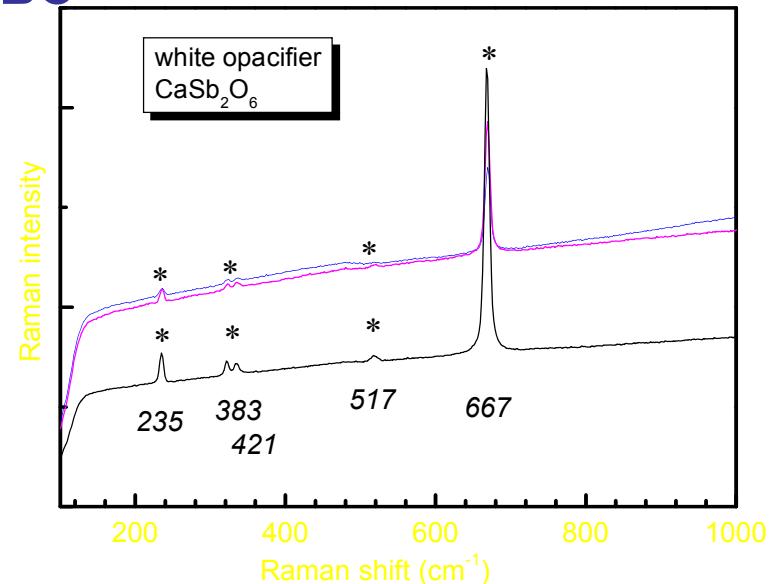
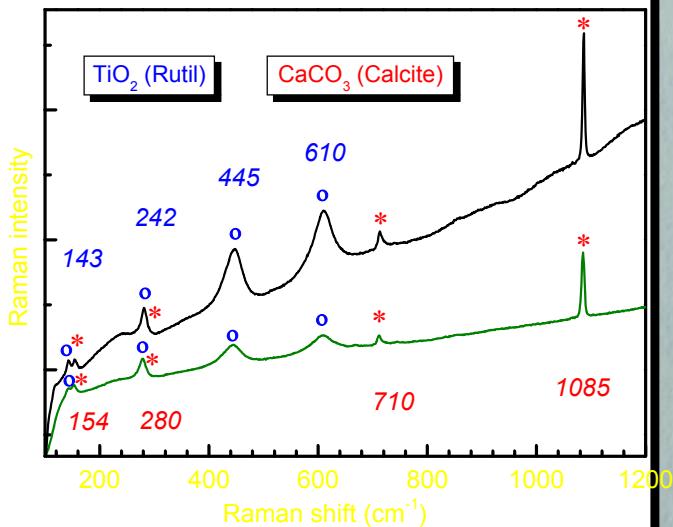
tests



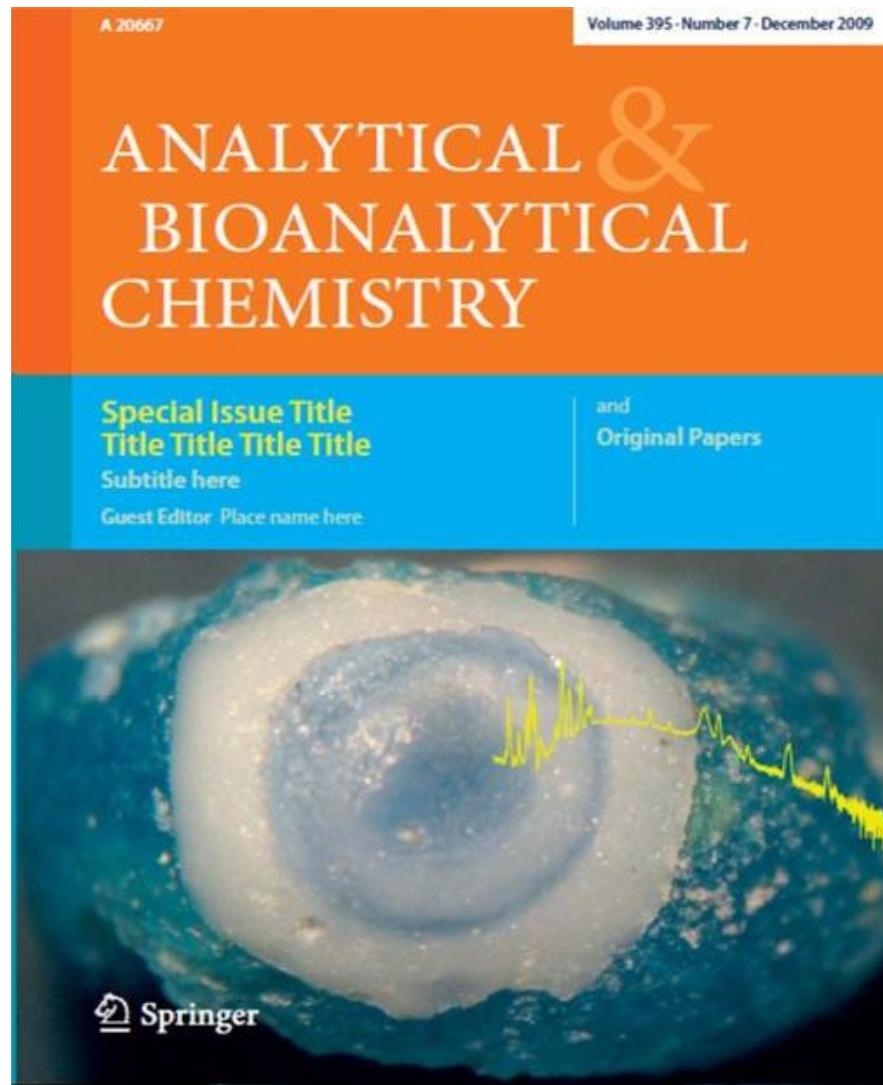
Tools and waste material

# Colors due to crystalline Pigments not transparent translucent / opaque $\Rightarrow$ RAMAN

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



# Blue – White Colorations within a 5<sup>th</sup> c BC bead from Thebes

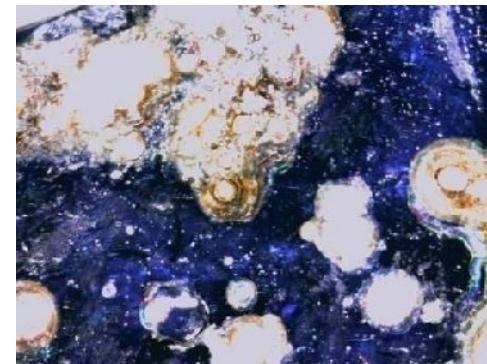
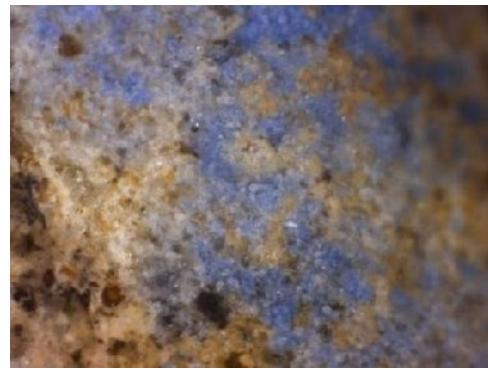


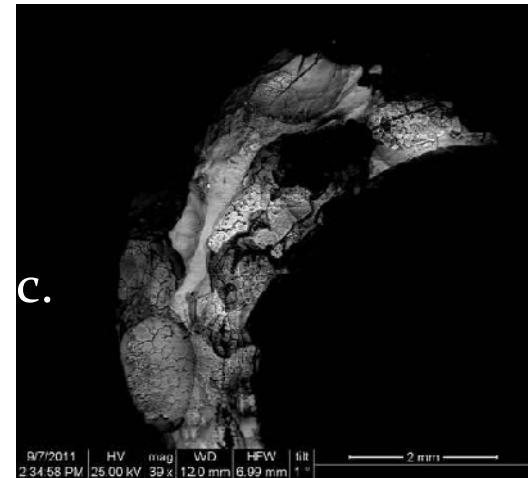
# Mycenaean Glass (1.400 BC) from the Peloponnes



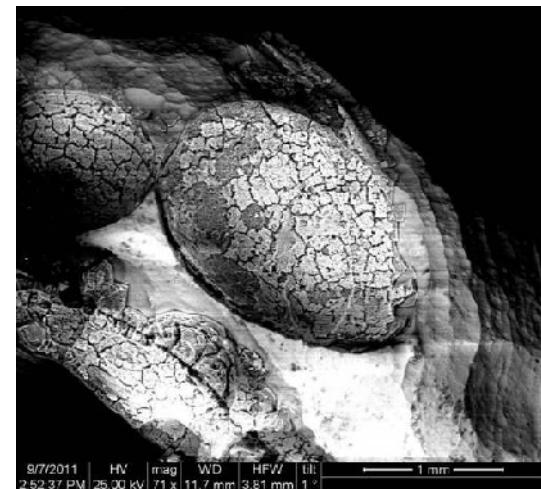
# techniques

## 1) Optical LED Microscopy (OM)

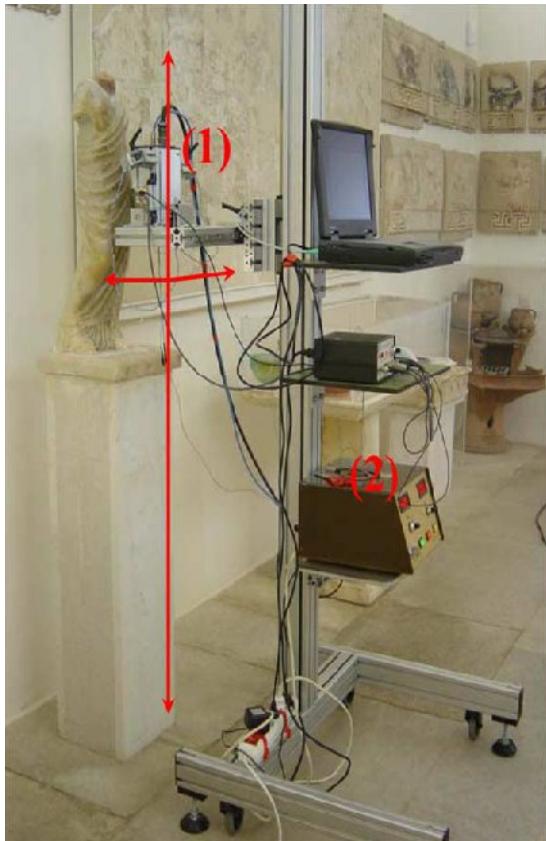




# Scanning Electron Microscopy SEM / EDAX



# Portable and hand-held XRF (milli-XRF)

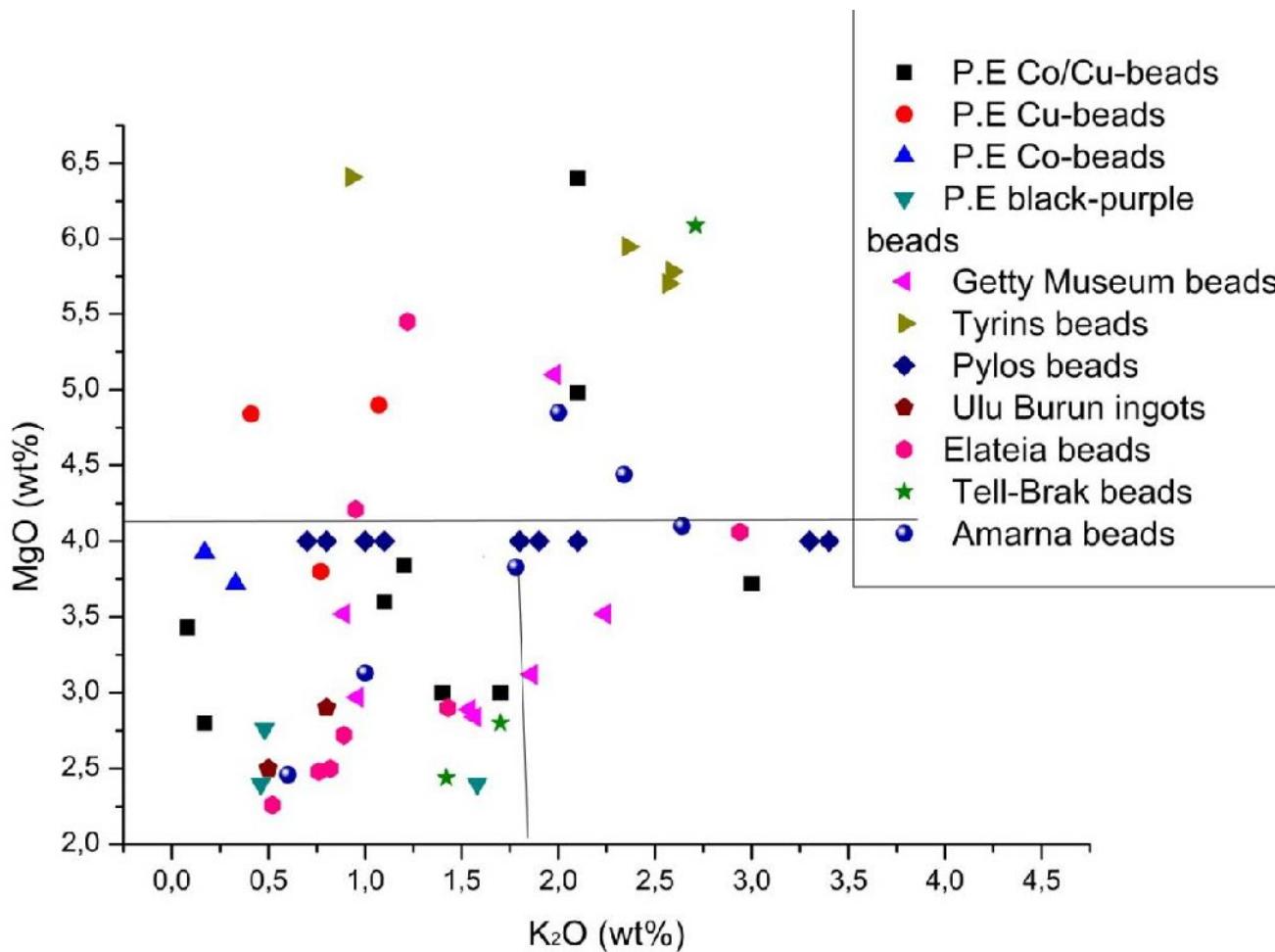


Major oxide / wt%	Appr. Det. Lim. / wt%
H <sub>2</sub> O	0,09
Na <sub>2</sub> O	0,01
MgO	1
Al <sub>2</sub> O <sub>3</sub>	0,5
SiO <sub>2</sub>	0,1
K <sub>2</sub> O	0,1
CaO	1
Minor oxide / wt%	
TiO <sub>2</sub>	0,05
MnO	0,02
Fe <sub>2</sub> O <sub>3</sub> t	0,05
CoO	0,01
NiO	0,05
CuO	0,05
SbO <sub>2</sub>	0,1
Trace elements / wt%	
B	0,00003
S	0,1
Cl	0,003
Ag	0,01
Sm	0,00005
Gd	0,00005

## X-RAY FLUORESCENCE

1. Liritzis, I., Zacharias, N., 2011. [Portable XRF of Archaeological Artifacts: Current Research, Potentials and Limitations](#), in S. Shackley (ed.) X-Ray Fluorescence Spectrometry (XRF) in Geoarchaeology, Springer, 109-142.
2. D. Sokaras, A.G. Karydas, A. Oikonomou, N. Zacharias, K. Beltsios, V. Kantarelou, *Combined elemental analysis of ancient glass beads by means of ion-beam, portable XRF and EPMA techniques*, [Analytical Bioanalytical Chemistry](#) 395, 199–2209, 2009.

# EPIDAUROS (35 samples, dark blue MgO vs. K<sub>2</sub>O)



# Rhodes



Kamiros Acropolis 625-600 B.C.



# Thebes



Image of 6 samples from Thebes

**The 29 Thebian samples to be analyzed in this study have been dated as follows:**

**Archaic (n = 16)**

**Late Archaic (n = 2)**

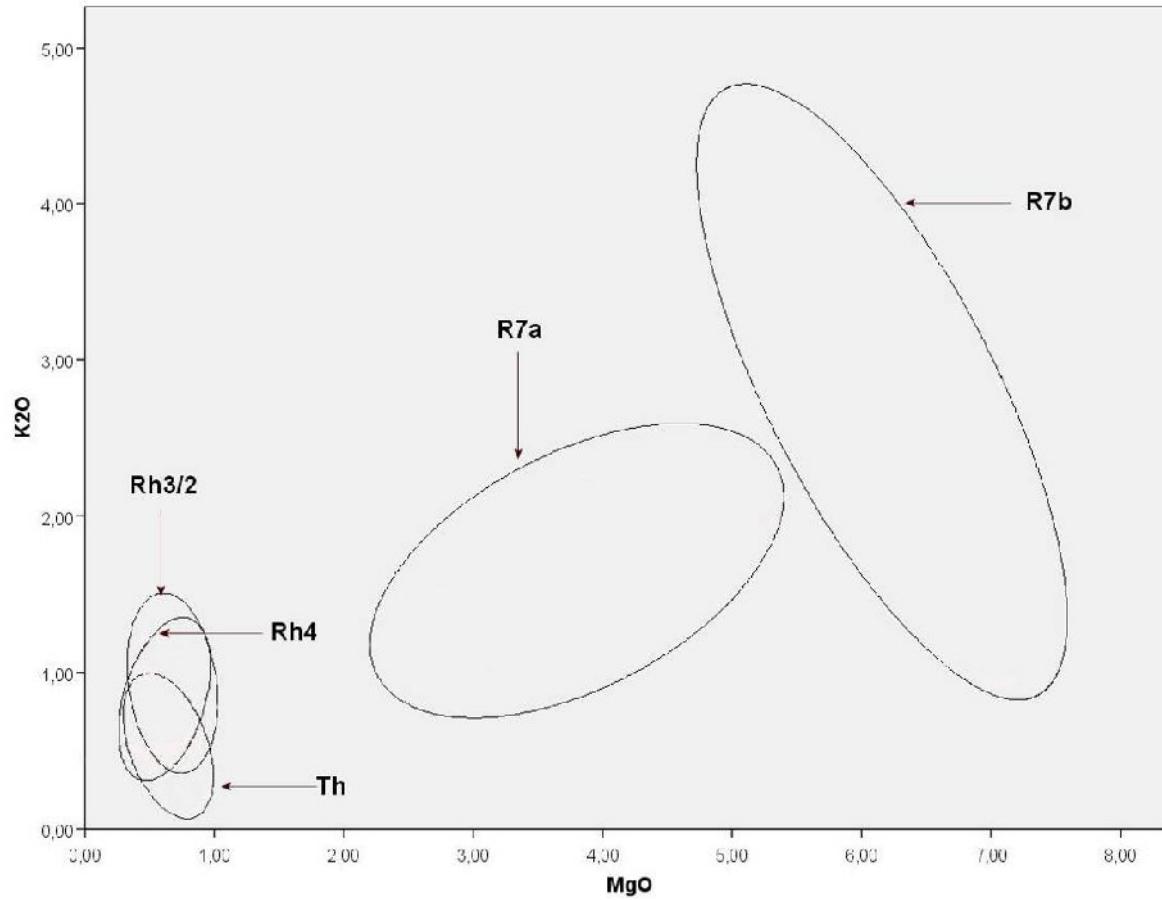
**Late Archaic/Classical (n = 1)**

**Classical (n = 6)**

**Classical/Hellenistic (n = 3)**

**Hellenistic (n = 1).**

# $K_2O$ - $MgO$



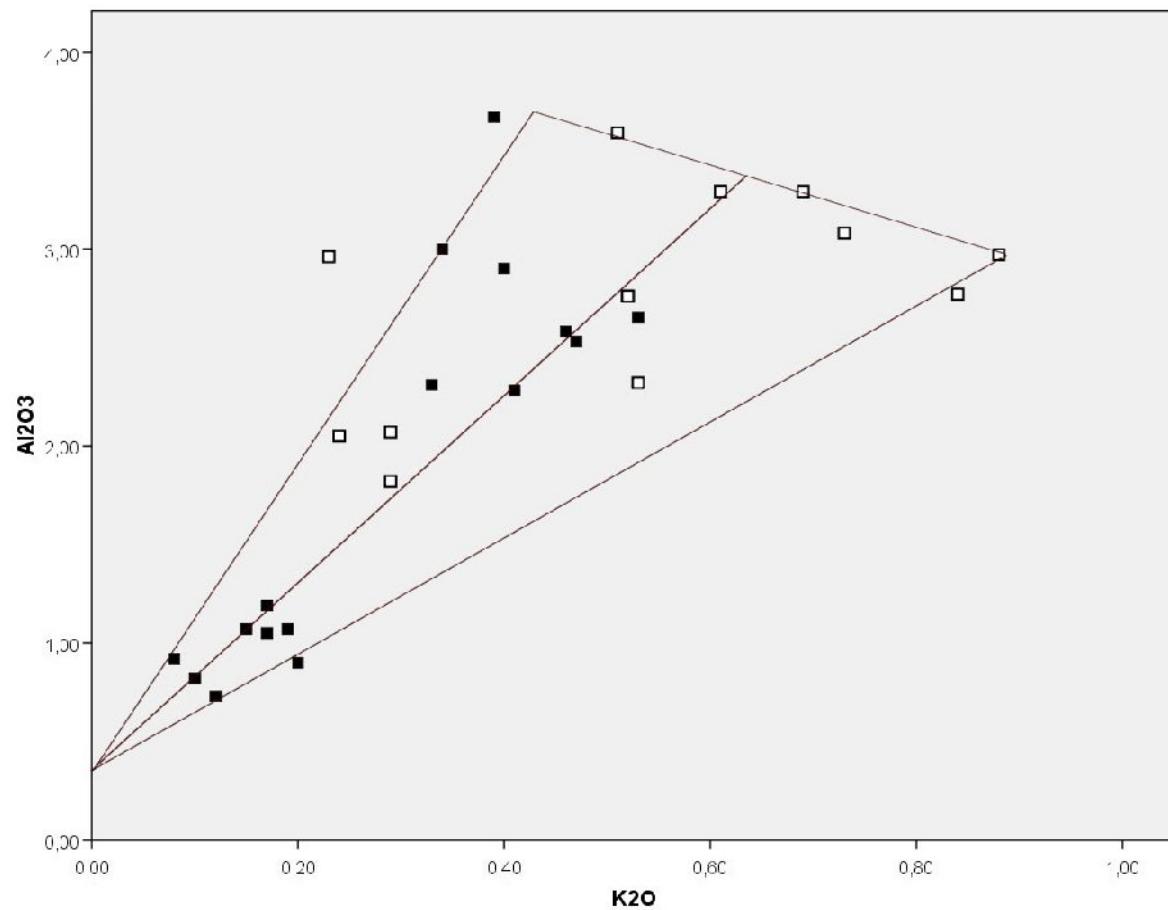
**R7a,b= Rhodes 7<sup>th</sup> c. B.C.**

**Rh4= Rhodes 4<sup>th</sup> c. B.C.**

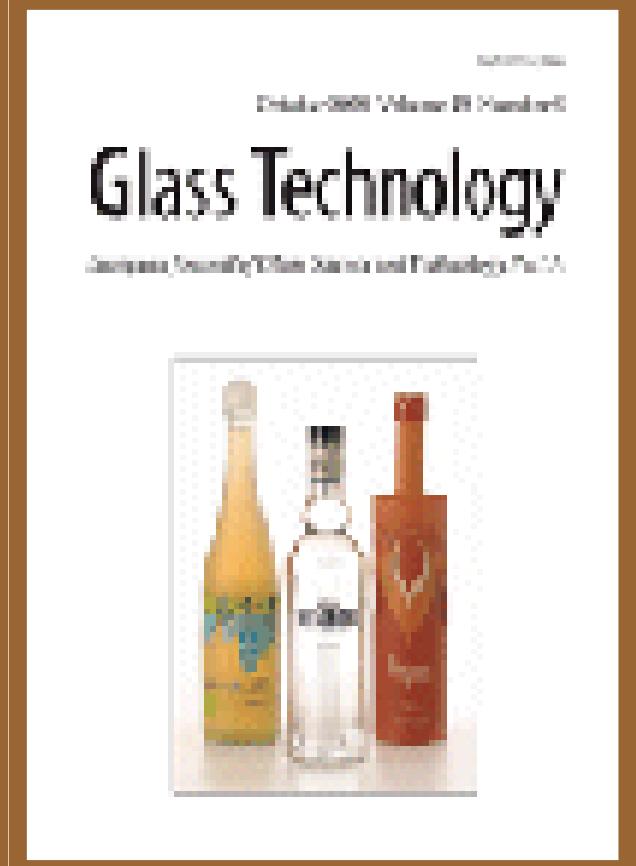
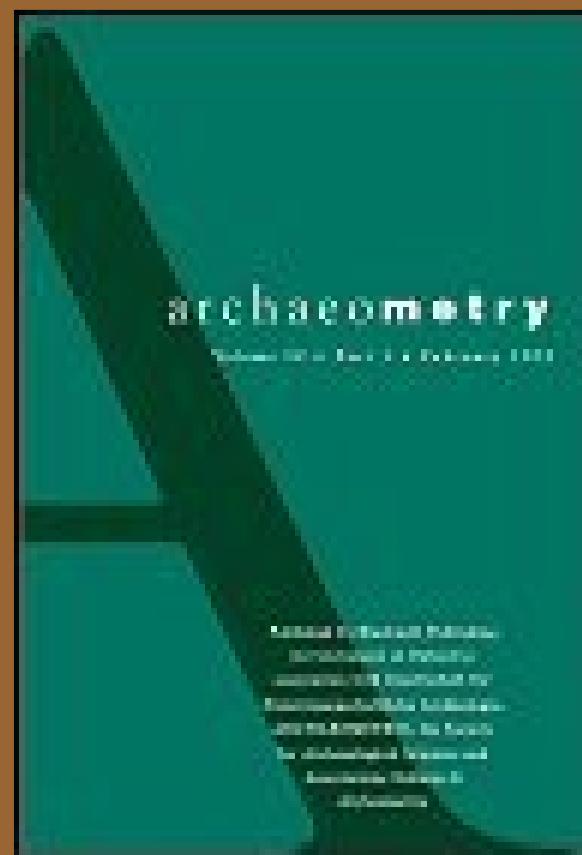
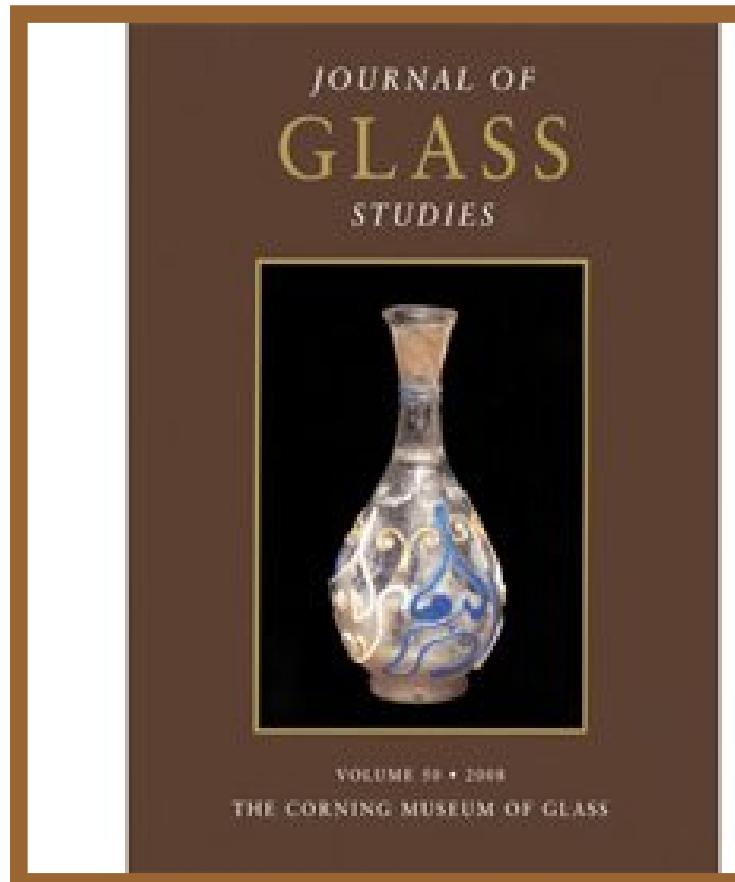
**Rh3/2= Rhodes 3<sup>rd</sup>-2<sup>nd</sup> c. B.C.**

**Th= Thebes from archaic to hellenistic times**

# $\text{Al}_2\text{O}_3 - \text{K}_2\text{O}$



# journals



## ACKNOWLEDGMENTS

**D. Moencke, M. Papageorgiou, M. Kaparou, E. Palamara**