A Technological and Provenance Study of Mycenean glass

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Mycenaean Glass from the Argolid, Peloponnese, Greece
A Technological and Provenance Study

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Introduction to glass

Network former: SiO_2 - quartz or quartzite sand.

+

Network modifiers:

plant ash alkali- Na_2O, K_2O or mineral source Na_2O,
to lower SiO_2 melting point from 1710- 1730 °C.

+

Network stabilizers: CaO, MgO

Either naturally occurring or deliberately added,
to stabilize the otherwise friable and soluble in water glass.

+

Network intermediates: Al_2O_3, TiO_2, ZrO_2

improve glass stability and, hence, chemical durability.

=

Glass

Coloring: Occurrence or deliberate addition: purple (Mn^{2+}, Mn^{3+}), greenish, yellowish, light blue, brown (Fe^{2+}, Fe^{3+}), dark blue (Co^{2+}), turquoise (Cu^{+}), red (Cu^{2+}) etc.

Decolorizers: Sb_2O_3- deliberately after 7th BC, MnO after 1st BC.
Opacifiers: Calcium antimonate -16th – 4th BC/ Pb, Sn- after 4th BC

Primary plant alkali source:
Chenopodiaceae family (until 800 BC).

Primary mineral alkali source: **natron**- Egypt ($Na_2CO_3\ 10H_2O$), hydrated sodium carbonate, Wadi Natrun Lake (after 800 BC).

Influence on the **ratios of Na, K, Mg oxides**: harvesting season, part of the plant, ashing, harvesting location etc.

Introduction to glass

- First glass artifacts: 3rd millennium BC- Anatolia (c. 2300 BC)
- First regularly sustained glass

Vessels production: 16th century BC. Mesopotamia and maybe in Egypt

Why glass?

Imitation of precious and semi precious stones

- Precious material
- Vast quantities
- Great color variety

+ beauty, clarity, brilliance= luxury material

Occurrence in the Aegean

First reference to glass: *κύανος*
Linear B tablets (PY TA 714)
ku-wa-no and *ku-wa-no-wo-ko*

↓

indication for mass production

- LBA II: increased number of finds
- Secondary glass production alongside with foreign imports

Mycenaean Glass Industry

- Phase I: LBI- LBII (1680- 1425/1390 BC.)
- Phase II: LBIIIA- LBIIIC (1425/1390- 1065/1060 BC.)

- ➢ Standardization and Conservatism over vast chronological periods and geographical areas.
- ➢ Preference for blue color.
- ➢ Typical Mycenaean and Minoan motifs associated with varied forms of art.
- ➢ Almost exclusive production of jewelry and decorative elements.
- ➢ Peak: LBIIIA- LBIIIB (1425/ 1390- 1190/ 1180 B.C.).
- ➢ Evidence for Glassworking: Tyrins, Thebes, Mycenae, Knossos

Glassmaking/ primary glass production

Crushed quartz pebbles/ quartz sand + alkali source + metallic oxides

A two stage model:

- semi- finished glass at relatively low temperatures (800- 900 ^{o}C)- «frit».
- glass batch = remelted at higher temperatures (1000- 1100 ^{o}C).

Glassworking/ secondary glass production

Sticks, chunks or cullet

↓

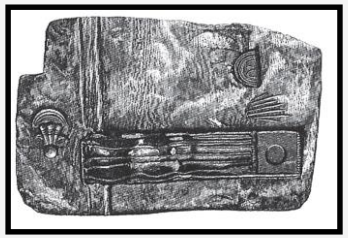
softening at workable state or melted

↓

Bead making or entering the crucibles

→ heated glass/ chipped glass- placed-pressed in molds

→ Annealing follows to avoid glass collapse



Glass chemical types

Soda Lime Silica (SLS- HMG)

(MgO: 3- 7 wt% + plant ash alkali source = marine plant /desert plant)

Occurrence: 1500- 800 BC.

Mesopotamia, NW Iran, Anatolia, Central Asia, Egypt, Mycenaean Greece and Crete Western Europe

Soda Lime Silica (SLS- LMG)

(MgO: 0.5- 1 wt% + mineral alkali source =natron)

Occurrence: 800 BC-

14th century Tell Brak in Syria, Minoan Crete

13th and 12th century Pella, Jordan.

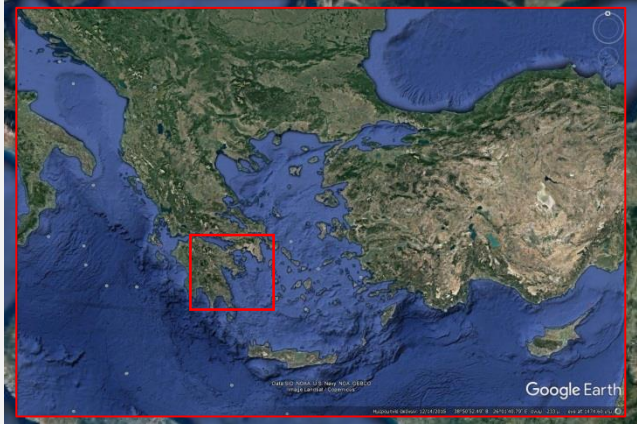
Mixed alkali glass (LMHK)

(K2O c. 6,50 -14 wt% + MgO c. 0,40- 1,00 wt% + Na2O: 5-13 wt% total amount of alkalis is around 14- 16 wt.%)

Occurrence: LBA end- beginnings of Iron age

Italian sites, W. Ireland, Switzerland, Germany, Thasos in the Aegean and Elateia

The Argolid area



Athens

Mycenae

Palaia Epidavros

Kazarma

Asine

Image Landsat / Copernicus
Data SIO, NOAA, U.S. Navy, NGA, GEBCO

Google Earth

Ημερομηνία εικόνων: 12/14/2015 37°28'28.64" Β 22°44'12.04" Ε ανύψ 48 μ eye alt 316.79 χλμ

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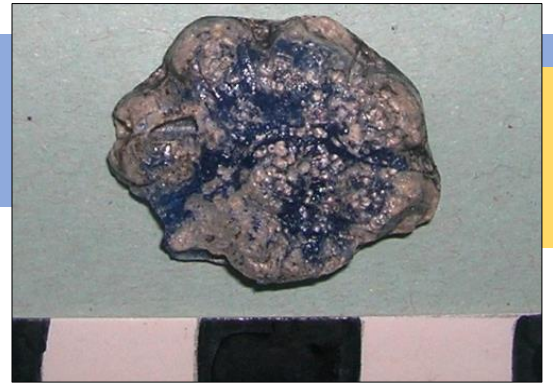
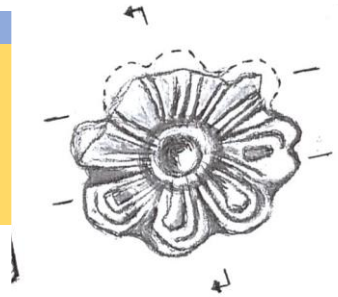



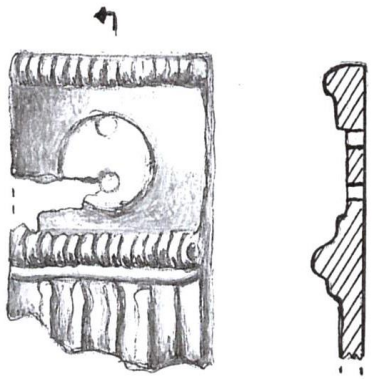

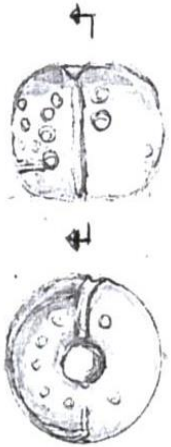


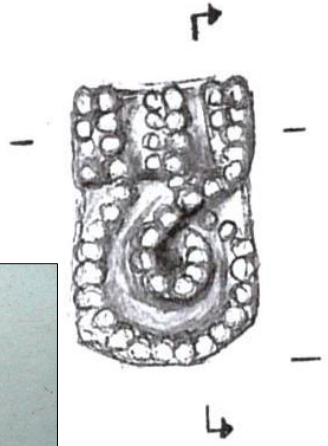
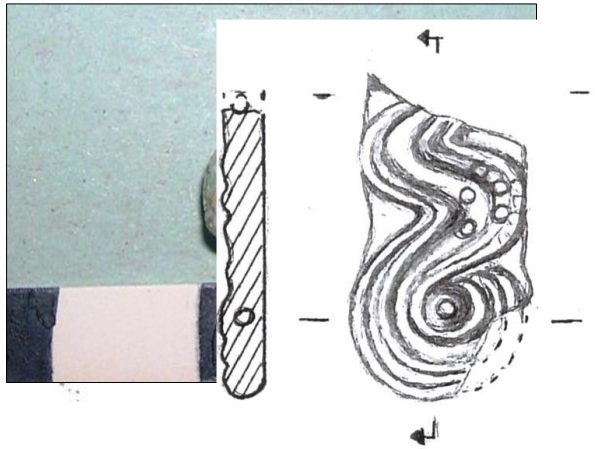
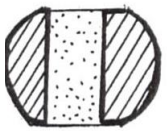

Samples

Two types of glass:
- Glass plaques (n=14)
- Glass beads (n=21)

35 glass fragments
- Mycenae (n=6)
- Palaia Epidavros (n=27)
- Kazarma (n=1)
- Asine (n=1)

Coloration
- Blue (n=28)
- Purple-violet (n=3)
- Turquoise (n=1)
- Unknown (n=3)

Dating of the samples
- Between 1600-1060 BC (LBII-LBIIIC)
- Funerary archaeological context

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Objectives of the study

- Application of a wide range of techniques
- Identification of the technology of the glass
- Isolation of groups of the same technology
- Provenance study
- Pinpointing trading routes

Experimental Techniques

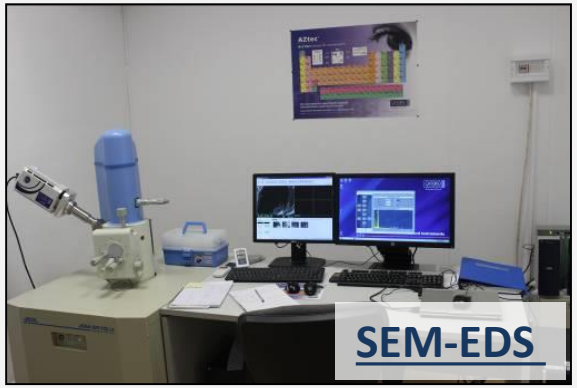
Fiber Optics Microscopy - FOM: for a first characterization of the glass beads preservation state.

Scanning Electron Microscopy coupled with an Energy Dispersion Analyser: for surface microtopography and characterization of major and minor elements.

Prompt-Gamma Activation Analysis – PGAA: for a bulk analytical examination of the glass matrix to evaluate the SEM analytical data on selected samples.

X-Rays Fluorescence - XRF: for the surface compositional analysis and identification of trace elements on selected samples.


FOM


SEM-EDS


PGAA


XRF

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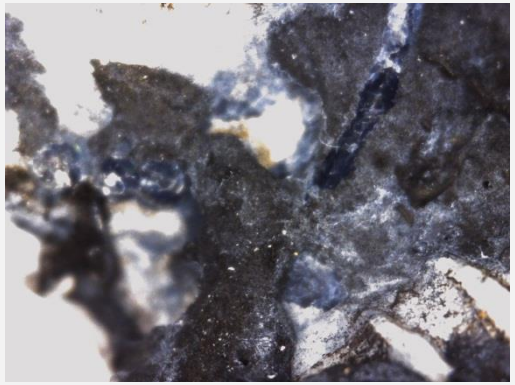
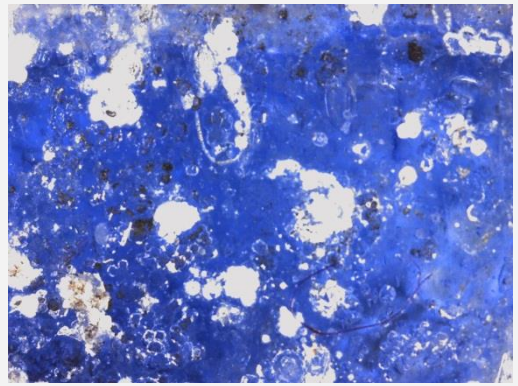
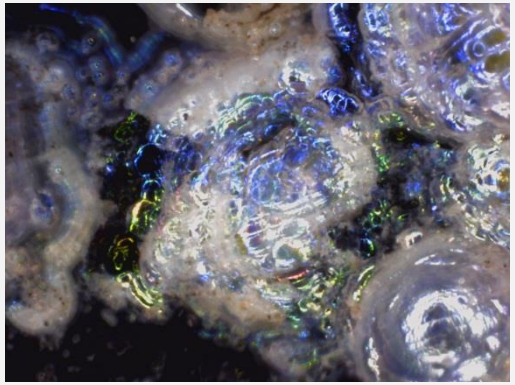
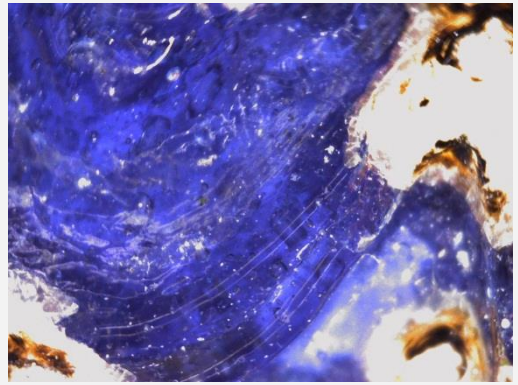
Experimental Techniques

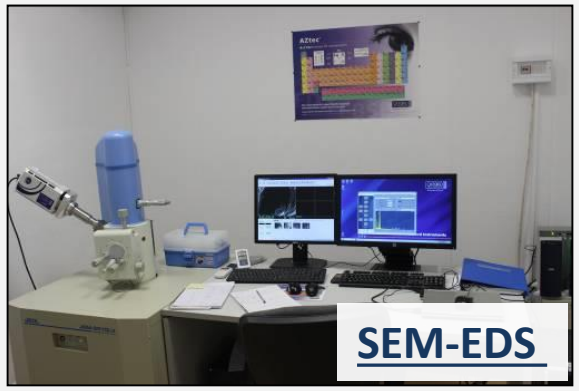








Experimental Techniques



- Philips (FEI, Quanta Inspect D8334).
- Voltage 25kV.
- Acquisition time (live time): 250sec.
- Three measurements on each sample.
- Accuracy - precision with NIST 620-621.

NIST 620	SiO_2	Na_2O	CaO	MgO	Al_2O_3	K_2O	SO_3	BaO	As_2O_3	Fe_2O_3	TiO_2	Zr
Certified composition	72.08	14.39	7.11	3.69	1.80	0.41	0.28	-	0.056	0.043	0.018	-
SEM/EDX	71.14	14.01	7.27	3.81	1.67	0.51	0.21	0.11	0.049	0.041	0.011	-

NIST 621	SiO_2	Na_2O	CaO	MgO	Al_2O_3	K_2O	SO_3	BaO	As_2O_3	Fe_2O_3	TiO_2	Zr
Certified composition	71.13	12.74	10.71	0.27	2.76	2.01	0.13	0.12	0.03	0.04	0.018	0.001
SEM/EDX	70.89	12.11	11.11	0.32	2.59	1.95	0.11	0.12	0.03	0.048	0.011	-

Experimental Techniques

- External cold neutron beam of 108 $cm^{-2} \cdot s^{-1}$.
- The spectra were collected by Compton-suppressed HPGe detector and were evaluated using the Hypermet-PC program.

	SEM	PGAA	SEM	PGAA	SEM	PGAA	SEM	PGAA	SEM	PGAA	SEM	PGAA	SEM	PGAA	SEM	PGAA	SEM	PGAA
Sample	SiO2		Na2O		CaO		MgO		K2O		Fe2O3		Al2O3		CoO		CuO	
PE21	64.75	66.3	18.29	17.2	6.03	6.65	3.84	3.14	2.54	1.82	0.71	0.452	2.31	1.12	0.2	0.05	0.5	0.2
PE33	63.88	62.8	17.02	18.3	8.16	8.06	3.72	4.27	1.36	1.43	0.82	0.763	2.49	2.13	0.1	0.09	0.3	0.1

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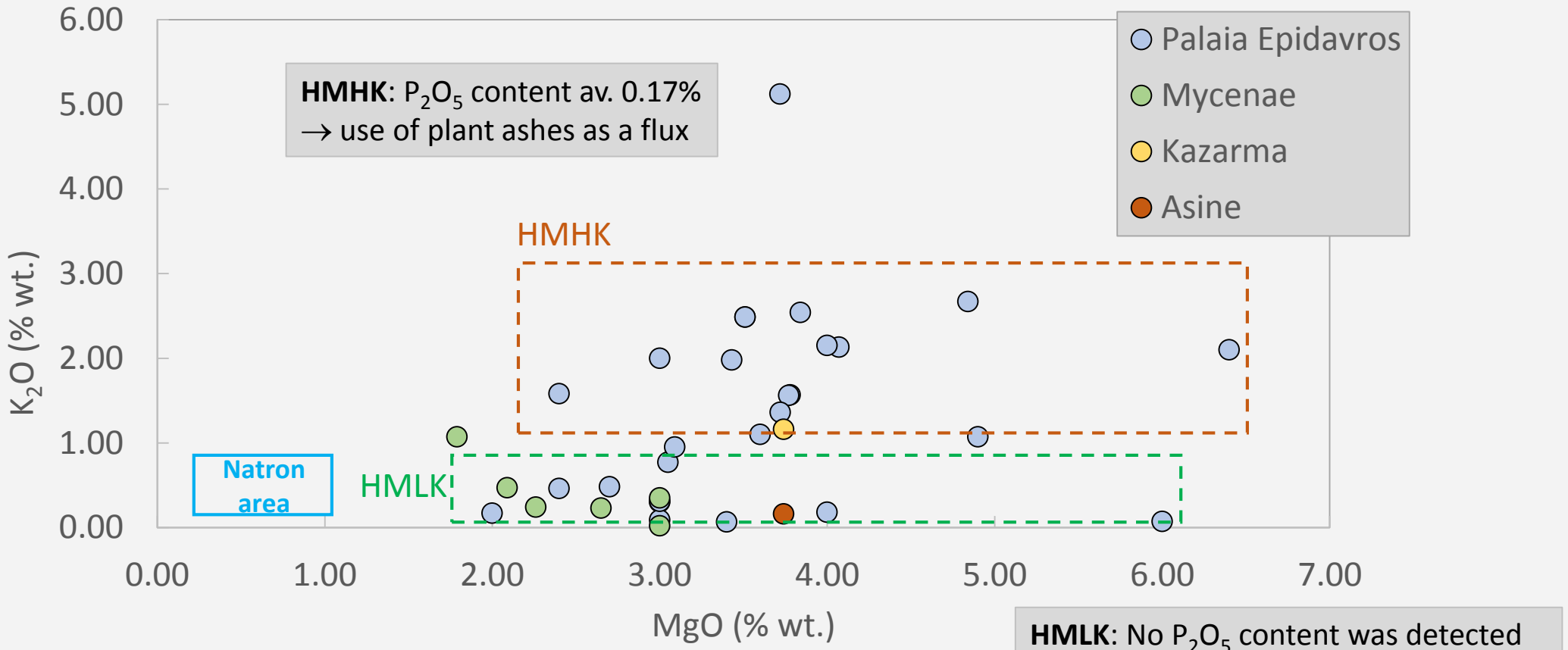
Experimental Techniques

- HH-XRF, Bruker (Tracer IV).
- Silicon SSD detector.
- Quantitative analysis was performed with S1 PXRF software based on FP approach.

NIST 620	SiO_2	Na_2O	CaO	MgO	Al_2O_3	K_2O	SO_3	BaO	As_2O_3	Fe_2O_3	TiO_2	Zr
Certified composition	72.08	14.39	7.11	3.69	1.80	0.41	0.28	-	0.056	0.043	0.018	-
XRF	71.87	13.99	7.02	3.55	1.69	0.39	0.21	0.11	0.065	0.032	0.014	0.001

NIST 621	SiO_2	Na_2O	CaO	MgO	Al_2O_3	K_2O	SO_3	BaO	As_2O_3	Fe_2O_3	TiO_2	Zr
Certified composition	71.13	12.74	10.71	0.27	2.76	2.01	0.13	0.12	0.03	0.04	0.018	0.001
XRF	72.01	13.01	10.09	0.19	2.93	1.96	0.18	0.11	0.039	0.039	0.014	0.001

Results-Biplots



HMLK: No P_2O_5 content was detected with none of the techniques

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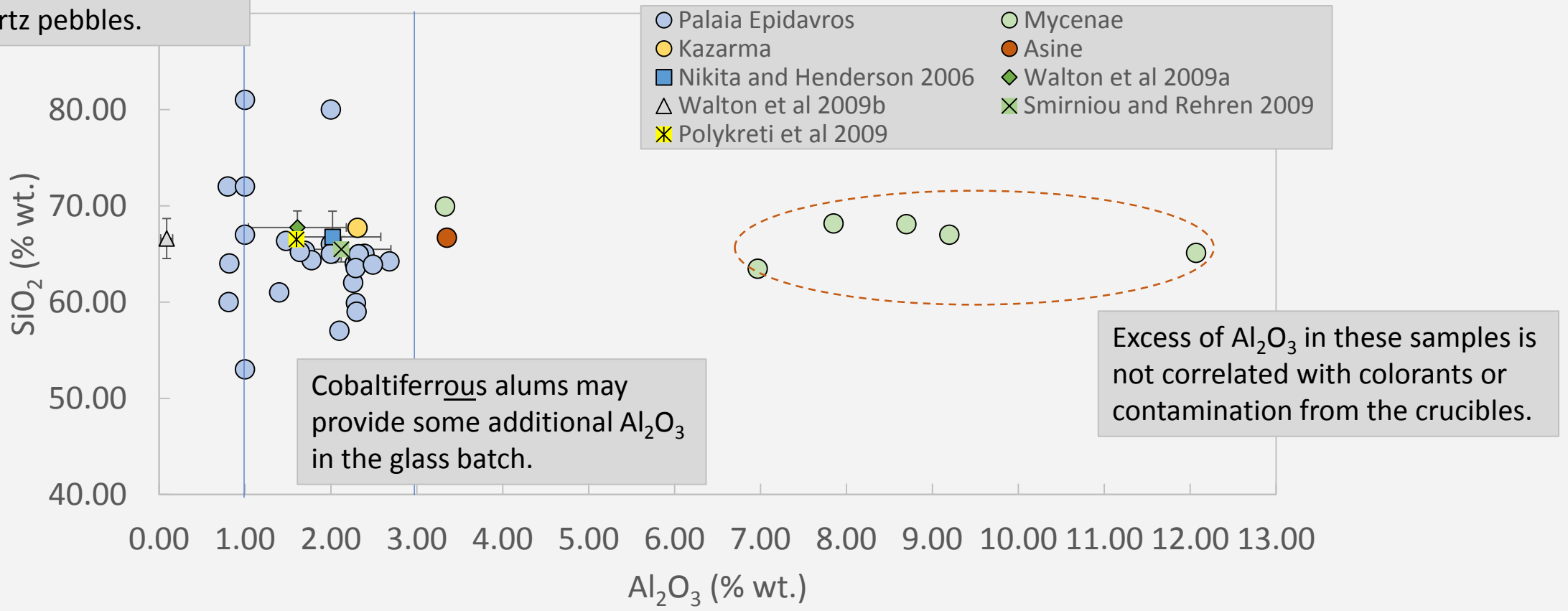
Results-Biplots

Low Al_2O_3 indicates a pure source of silica which most likely is quartz pebbles.



Cobaltiferrous alums may provide some additional Al_2O_3 in the glass batch.

Excess of Al_2O_3 in these samples is not correlated with colorants or contamination from the crucibles.

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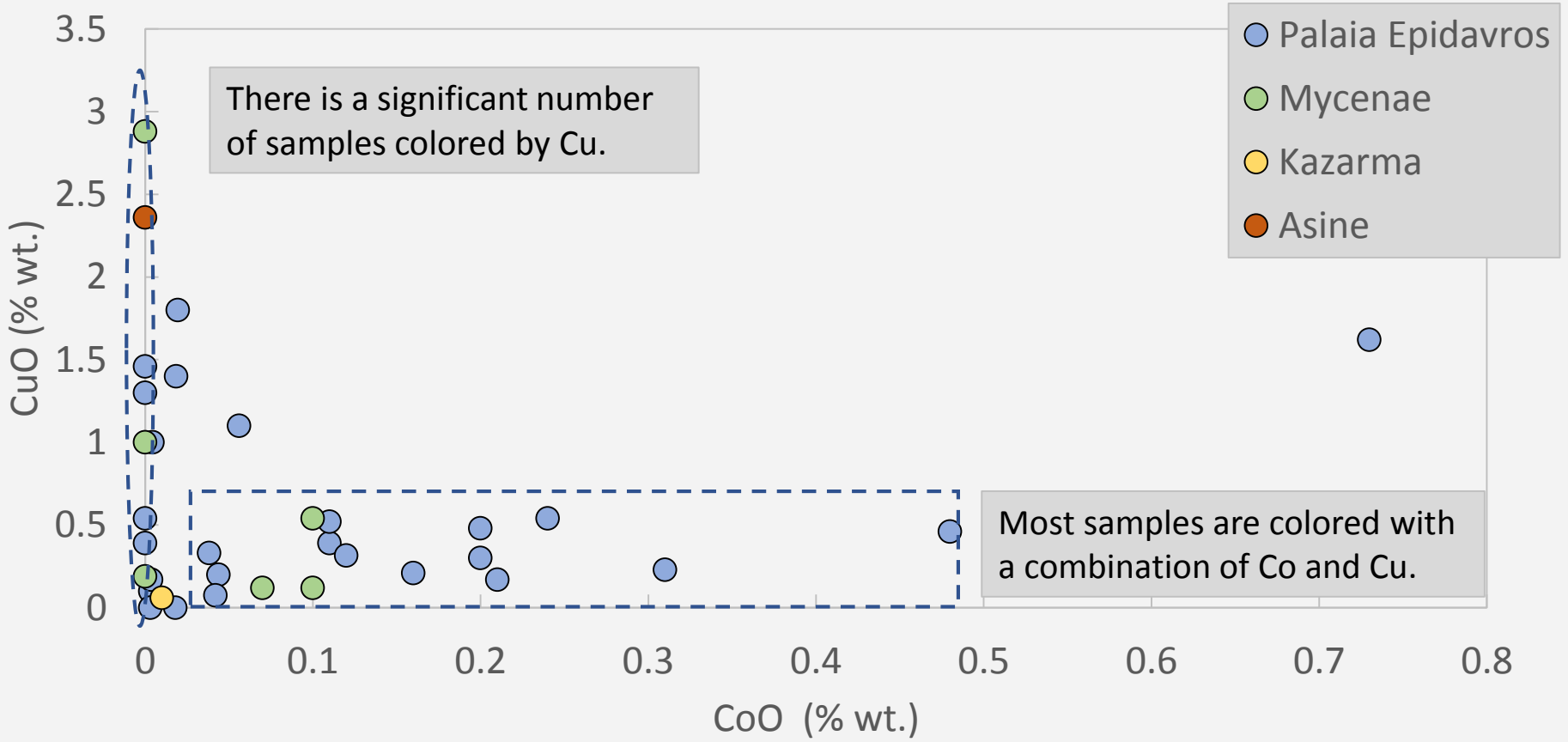
Results-Biplots



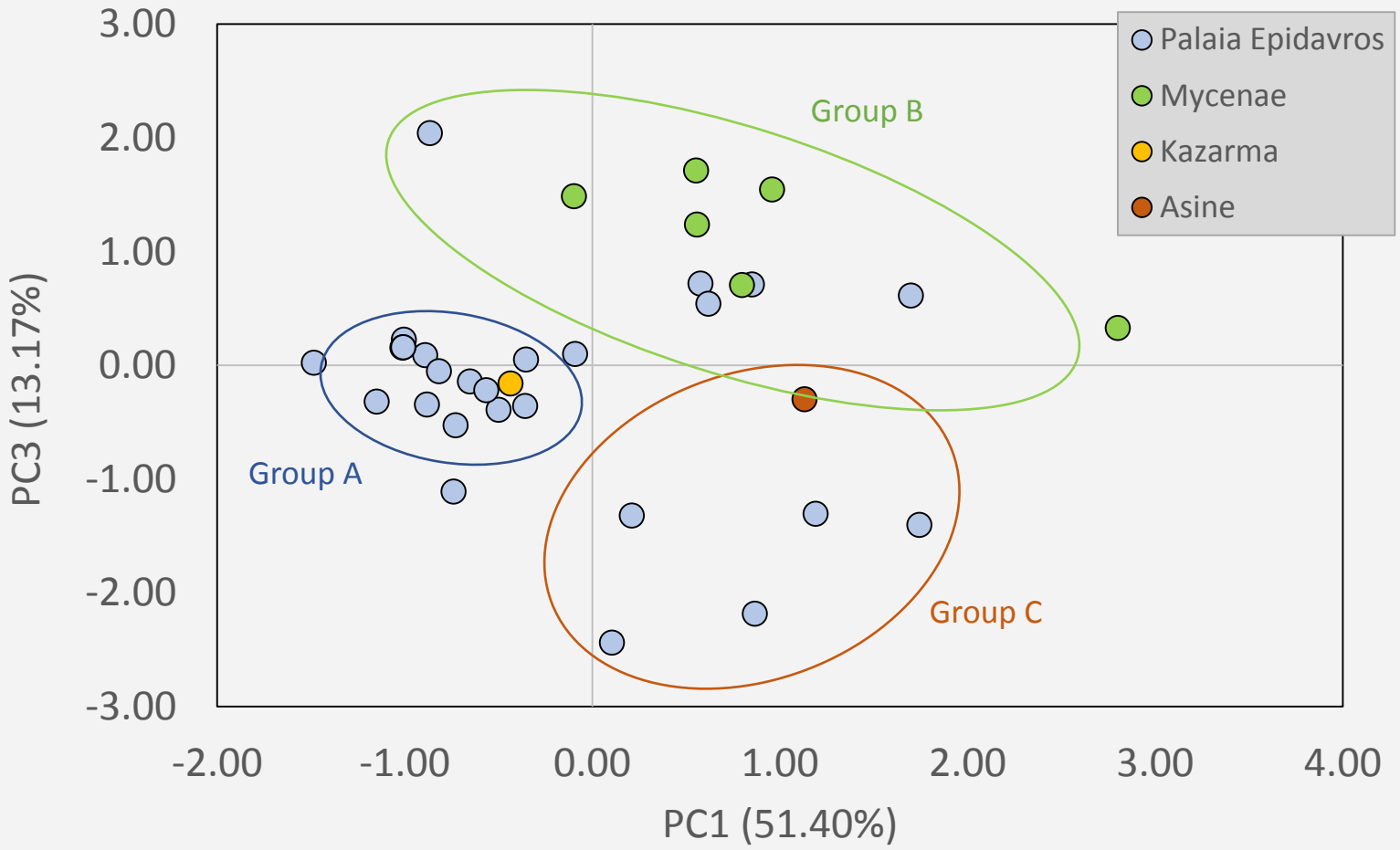
Principal Component Analysis (PCA)

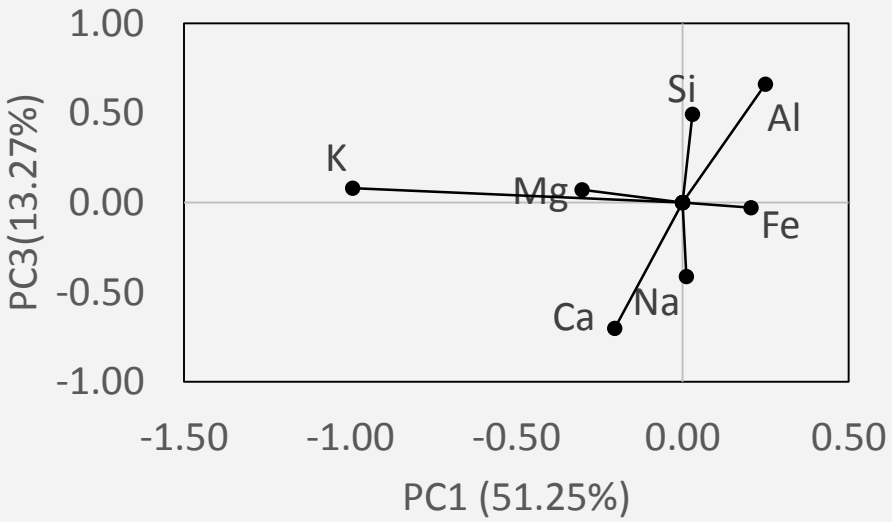
Valuable tool for studying large number of samples containing several variables of numerical data such as chemical compositions.

Data treatment

- SiO_2, Na_2O, Al_2O_3, MgO, K_2O, Fe_2O_3 and CaO
- The elemental data were normalized in 100% and transformed into base-10 logarithmic values.
- A variance-covariance matrix PCA employing algorithms in the STATISTICA 8 Software was used.

PCA biplots





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Conclusions

- The samples from Argolid show different technological characteristics providing new insights into the technology of glass during the Mycenean period.
- The application of a wide range of techniques made the identification of raw materials possible.
- The study of specific major and minor elements revealed interesting correlations between samples and revealed possible different glassmaking traditions.
- The majority of samples from Palaia Epidavros show very consistent chemical characteristics indicating the same manufacturing center. These samples most likely have an Egyptian origin and were imported to Greece as glass ingots. This is corroborated by their chemical traits such as their potash content, their silica and soda levels and the chemical fingerprint related to the coloring agent of the cobalt- containing samples.

Conclusions

- Samples from Mycenae present very interesting technological patterns. They share common flux characteristics with Egyptian samples, but the excess of alumina they exhibit makes the interpretation more complicated. The excess of alumina ~~it~~ can be a marker of a high alumina sand.

- The application of PCA analysis revealed the existence of 2 small subgroups having interesting chemical characteristics providing new insights about the technology of the Mycenean glass.

- Further investigation is carried on with the incorporation of more data from Peloponnese in order to have an overall idea about the glassmaking during the so important Mycenean era.

- Finally, more techniques such as isotopic (TIMS) and trace element (LA-ICPMS) analyses should be applied to give more useful and secure information about the provenance of the samples- their destructive character, though, renders them not always applicable.

THANK YOU FOR YOUR ATTENTION

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