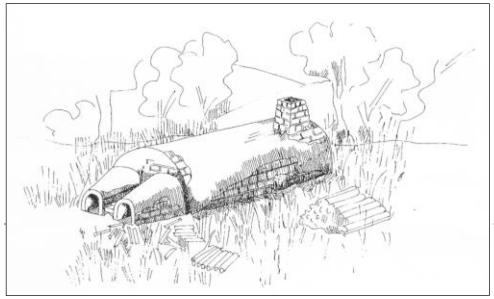
SCIENCE & PAST

MASTERING MATERIALS TO KNOW OUR HERITAGE

Zaragoza February 1-3 2017

Production technology and trade routes of ancient glass materials

Elisabetta Gliozzo

Glass making cycle

- **RAW MATERIALS SUPPLY AND PREPARATION**
- **PRIMARY /SECUNDARY WORKSHOPS**
- **TECHNOLOGY**
- **DISTRIBUTION AND USE**
- **POST DEPOSITIONAL PROCESSES**
- **CONSERVATION AND RESTORATION**

Glass research

- **Significant research objectives**
  - **Glass technology: vitrifying, fluxing, stabilising, colouring/decolouring agents**
  - **Glass provenance** → **REFERENCE GROUPS → ESSENTIAL**
- **Representative sampling**
  - **Typology, stratigraphy, chronology, conservation state…**
- **Appropriate methodology**
  - **Destructive/ non destructive, bulk/superficial, chemical/mineralogical/….**
- **Rigorous interpretation of the results**
- **Dissemination**

Research questions: glass technology

- **Vitrifying agents**

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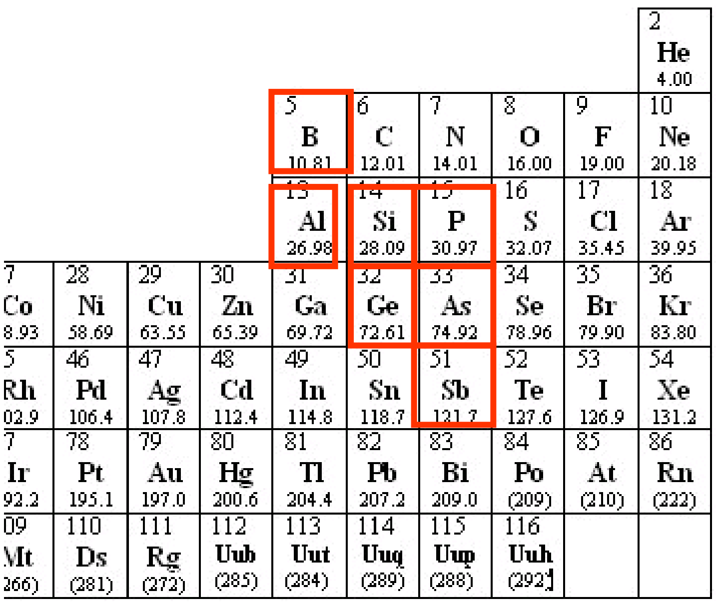
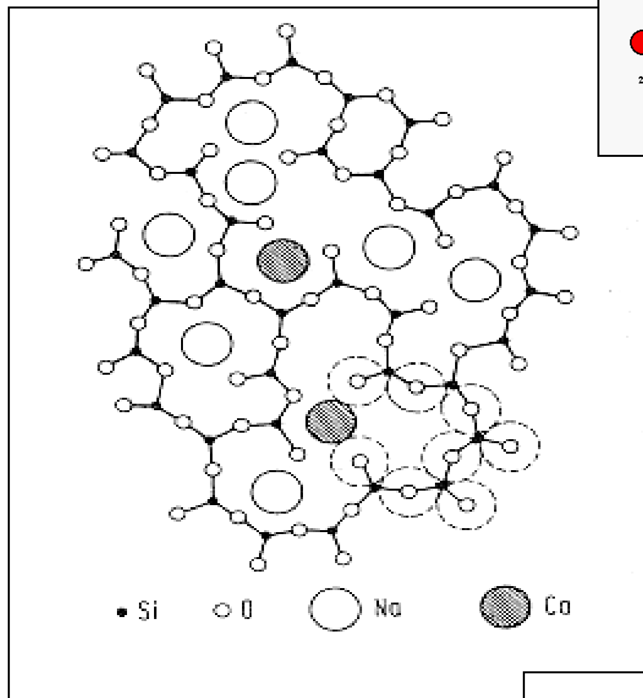
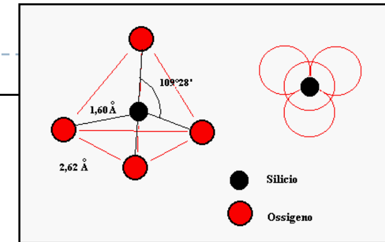
  network former

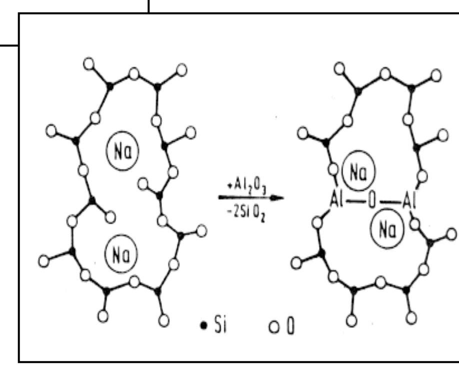
  (3- or 4-fold coordination)







Random distribution of $[SiO_4]$ tetrahedra chains



Al can substitute Si strengthening the network

Research questions: glass technology

- **Vitrifying agents**

↓

silica sources

Origin	*Reference**	*SiO_2*	*Al_2O_3*	*CaO*	*MgO*	*Na_2O*	*K_2O*	*Fe_2O_3*	*TiO_2*	*CoO*	*MnO*	*Sum*
Quartz pebbles												
Amarna	XXIVA.1298	99.83	0.05	0.05	0.01	0.05		0.01	[0.005]	[0.005]	[0.005]	100 0
Sand												
Amarna	AM44	87.36	2.79	5.50	0.55	0.55	0.53	1.76	0.76		0.04	99.8
Amarna	AM43	73.56	3.29	18.11	0.90	0.83	0.61	2.02	0.52		0.04	99.9
Belus River	XXIVA.673	87.75	3.3	6.18	0.34	0.9	1.06	0.47	[0.05]		[0.02]	100
Belus River	XXIVA.674	87.5	3.15	6.68	0.35	0.86	1.02	0.44	[0.03]		[0.02]	100
Belus River	XXIVA.675	83.75	2.62	10.85	0.61	0.74	0.97	0.46	[0.03]		[0.02]	100
Belus River	XXIVA.676	77.73	2.52	16.57	0.89	0.75	0.94	0.61	[0.05]		[0.03]	100
Karnak	Turner (1956, 281)	83.61	1.32	12.01	1.23			*				98.2
Fayoum	Turner (1956, 281)	95.22	1.86	1.85	0.09			*				99.0
Pyramids	Turner (1956, 281)	82.35	1.45	8.4	tr	0.19		*				92.4
Aswan	Turner (1956, 281)	93.78	3.59	0.67	tr	tr		*				98.0

Research questions: glass technology

- **Fluxing agents**

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natron and plant ash

Cut off values

< 1 wt% → quartz pebbles

1 – 1.5 wt% → intermediate

> 1.5 wt% → impure sand

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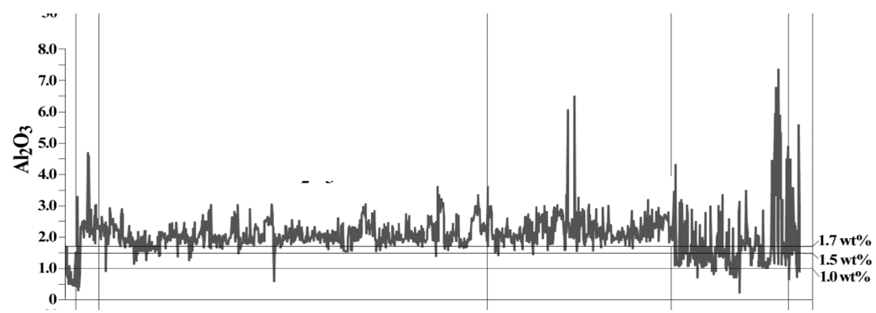
BULK CHEMISTRY

Al_2O_3

The Al_2O_3 content reflects the purity level of the silica source, unless it was introduced together with other components (i.e. fluxes or decolourants, like in cobalt blue glass). As a consequence, the amounts of Al_2O_3 are crucial for the identification of raw materials used as vitrifying agents. A level of about 1 wt% is generally considered as *the typical impurity level introduced with quartz or a relatively pure silica source* (Henderson et al. 2004), therefore, it is generally used as a cutoff value between crushed quartz and sand sources.



Research questions: glass technology

- **Fluxing agents**

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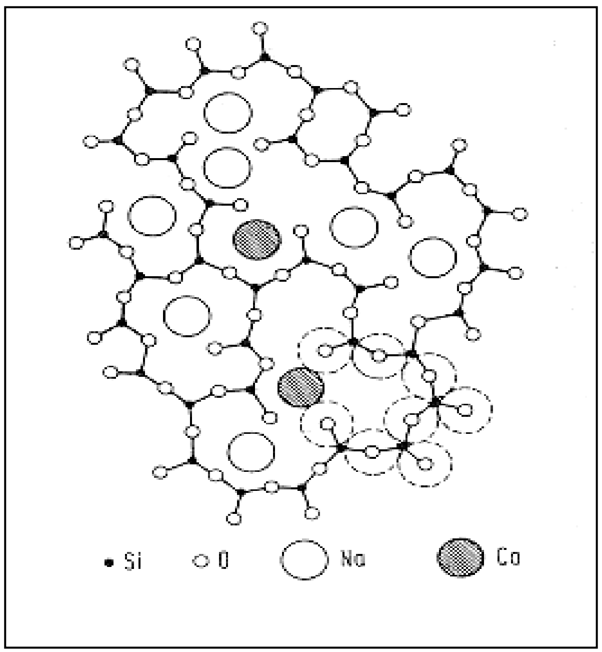
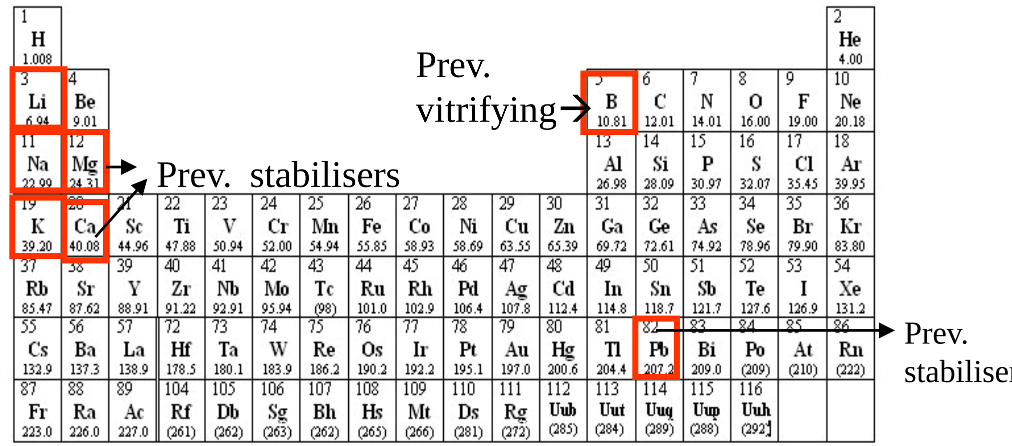
  network modifier

  (6- or 8-fold coordination)





SI-O =covalent → strong
Na-O=ionic → weak

Their function is to decrease the softening temperature, breaking some links among silica → silica melt at 1723°C !!!!

Research questions: glass technology

- **Fluxing agents**

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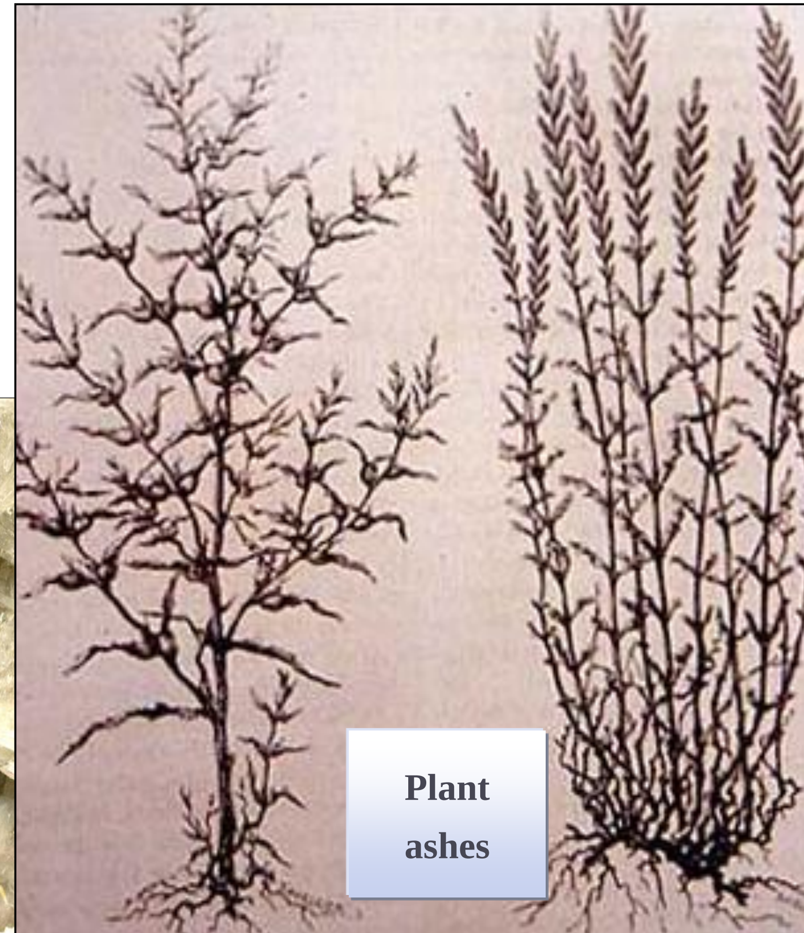
  network modifier



Research questions: glass technology

- **Fluxing agents**

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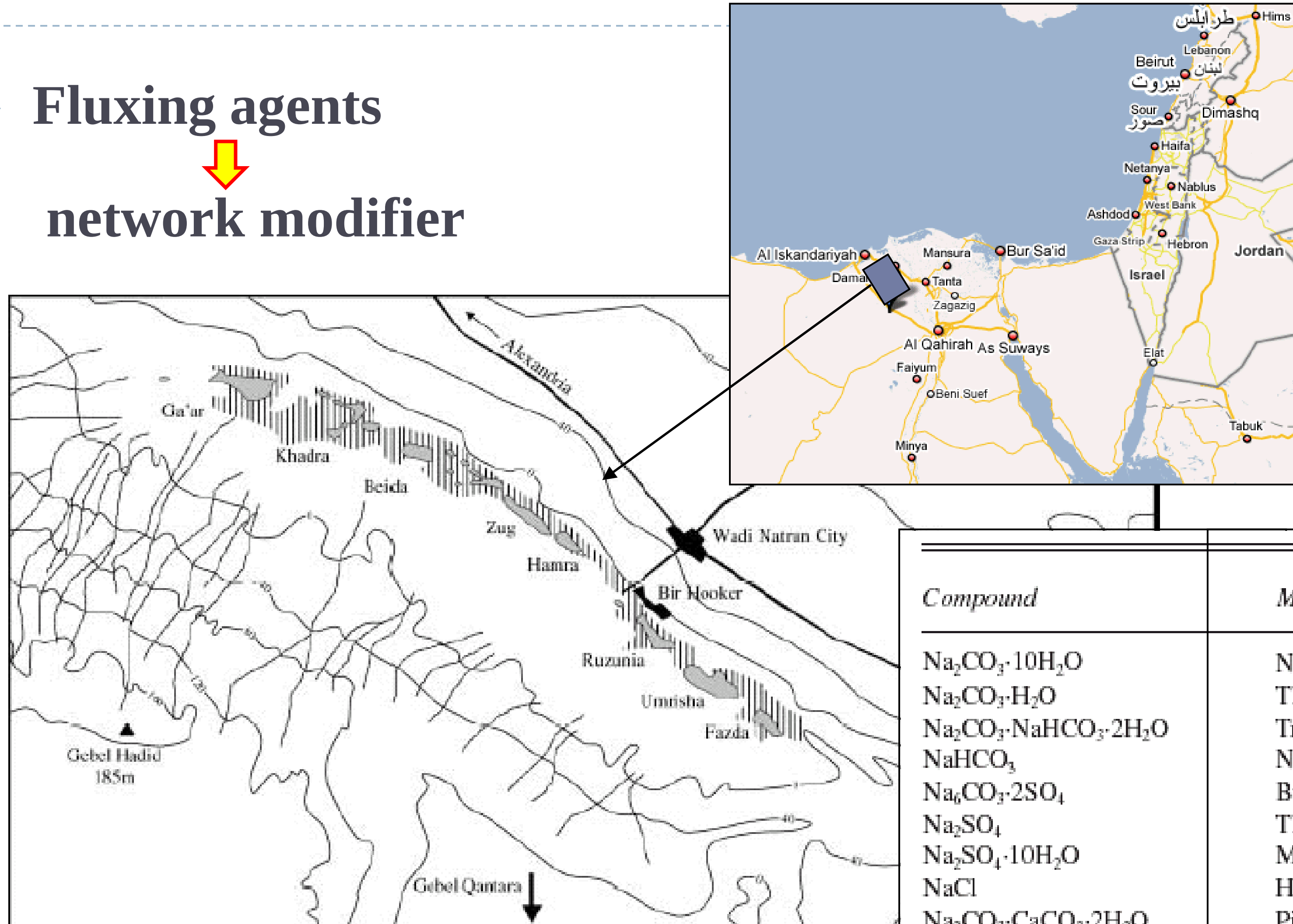
network modifier



Compound	*Mineral name*
$Na_2CO_3 \cdot 10H_2O$	Natron
$Na_2CO_3 \cdot H_2O$	Thermonatrite
$Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$	Trona
$NaHCO_3$	Nahcolite
$Na_6CO_3 \cdot 2SO_4$	Burkeite
Na_2SO_4	Thenardite
$Na_2SO_4 \cdot 10H_2O$	Mirabilite
$NaCl$	Halite
$Na_2CO_3 \cdot CaCO_3 \cdot 2H_2O$	Pirsonnite

Research questions: glass technology

- **Fluxing agents**

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  network modifier

Zug Lake

(Wadi Natrun, Sahara Desert, Egypt

Exploitation still active

Research questions: glass technology

- **Fluxing agents**

  ⇩

  network modifier

Origin	Reference*	SiO_2	Al_2O_3	CaO	MgO	Na_2O	K_2O	Fe_2O_3	TiO_2	MnO	Sum	Notes
Natron												
Egyptian tomb	XXIVB.655	0.5	0.10	0.30	0.38	50.5	0.55	0.14	0.005	0.0005	52.5	Plus CO_2 and SO_3
Egyptian tomb	XXIVB.657	2.0	0.61	0.39	0.42	42.7	0.48	0.40	0.20	0.005	47.2	Plus CO_2 and SO_3
Egyptian tomb	XXIVB.658	2.0	0.47	0.42	0.46	41.6	0.58	0.26	0.20	0.0005	46.0	Plus CO_2 and SO_3

→ Natron contains several impurities which enter the glass batch

→ Natron was initially used to embalm the dead

Research questions: glass technology

- **Fluxing agents**

  network modifier

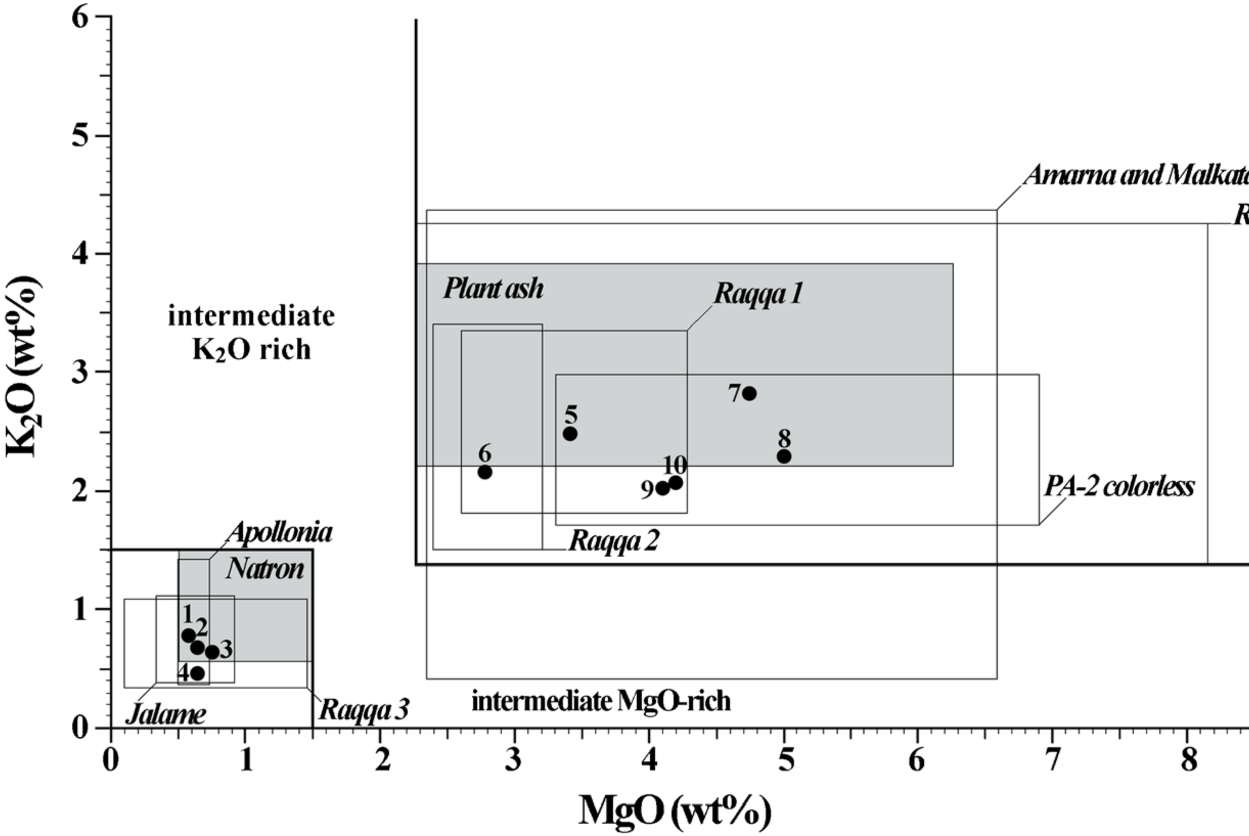
PLANT ASH

(POTASH)

Origin	*Reference**	*SiO_2*	*Al_2O_3*	*CaO*	*MgO*	*Na_2O*	*K_2O*	*Fe_2O_3*	*TiO_2*	*CoO*	*MnO*	*Sum*
Plant ash												
Turkey	XXIVC.650	Minor	5.90	12.20	6.25	14.2	3.98	3.79	0.80		0.02	47.1
Iran	XXIVC.1301		0.62	5.56	7.50	39.2	8.12	0.43	0.05		0.03	61.5
Iraq	XXIVC.1324	Minor	4.89	13.80	8.00	25.5	4.96	3.52	0.80		0.05	61.5
Syria	XXIVC.1380	0.5	0.72	9.54	6.04	31.3	5.23		0.05		0.01	53.4

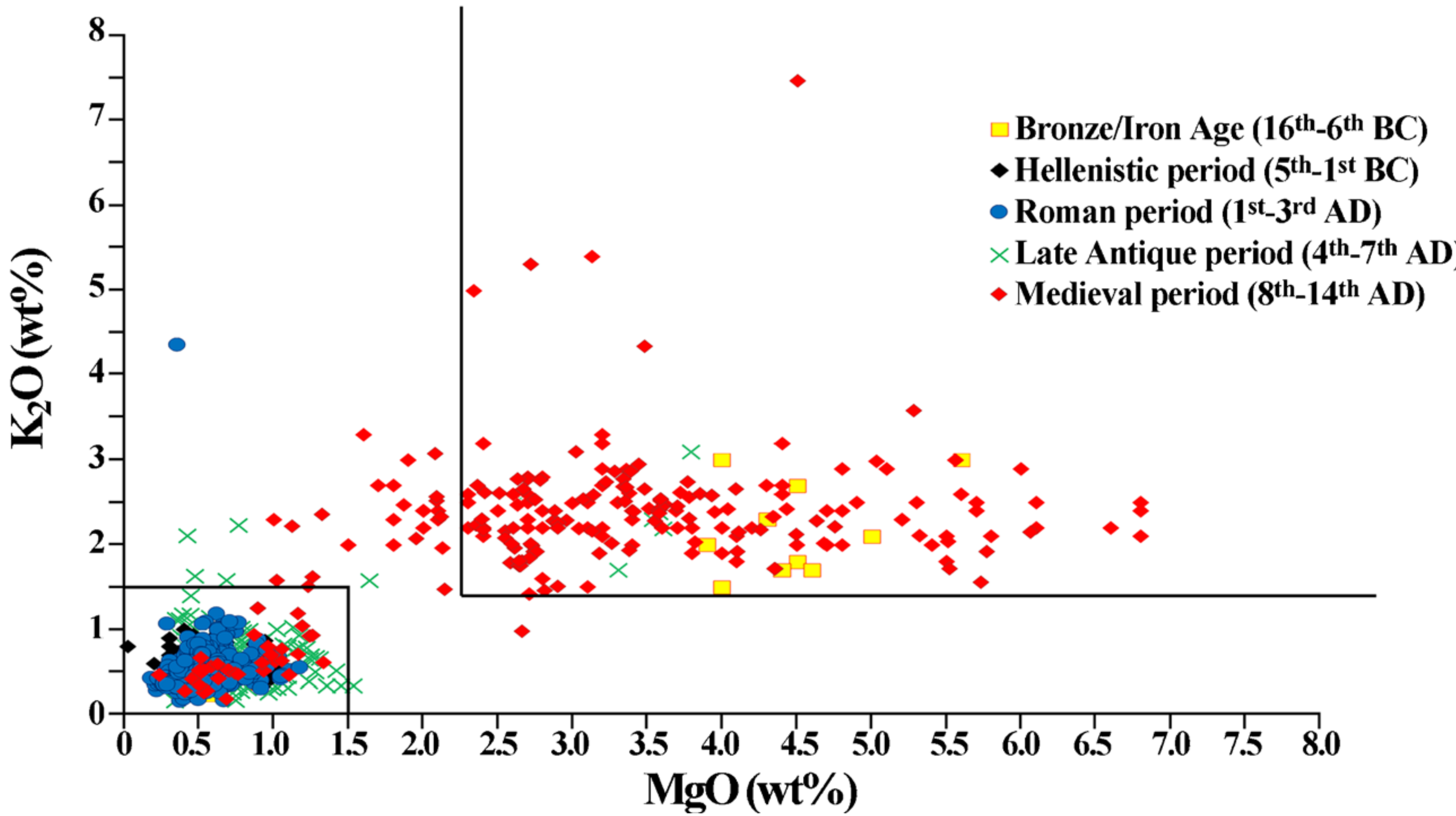
Research questions: glass technology

- **Fluxing agents**



Research questions: glass technology

- **Fluxing agents**



Research questions: glass technology

- **Stabilising agents**

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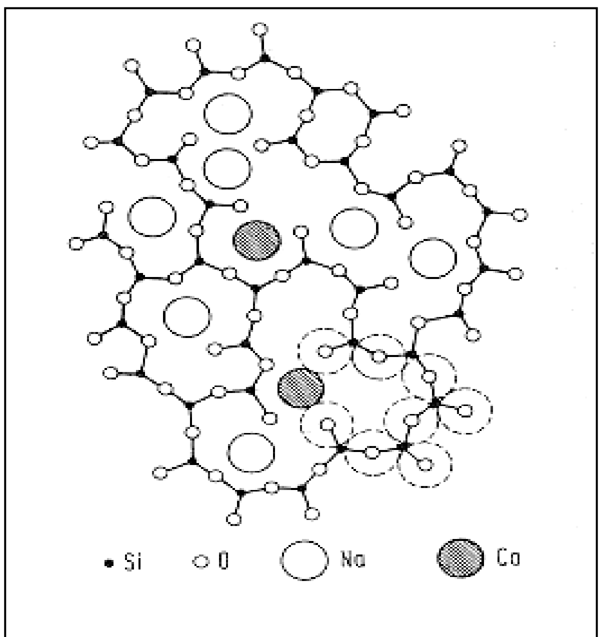
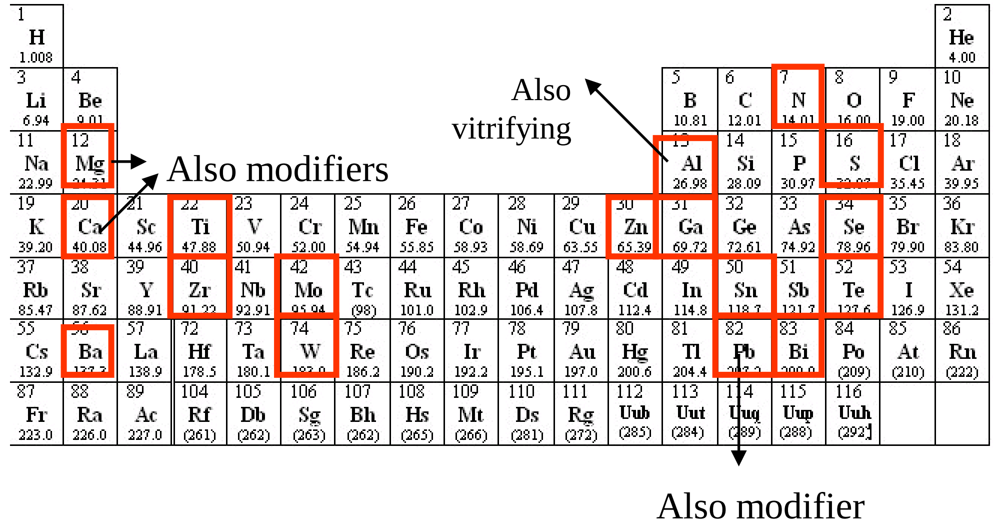
  network stabilisers

  (4-, 6- or 8-fold coord.)





A glass made of Si, Na and O only is unstable → e.g. dishwasher detergent
Their function is to stabilise the network, bridging spare oxygens with a stronger link than sodium.

Research questions: glass technology

- **Stabilising agents**

  network stabilisers

ARAGONITIC SHELLS

LIMESTONE

DOLOMITIC LIMESTONE

Research questions: glass technology

- **'Colouring' agents**
  - **Naturally included**
  - **Intentionally added**

Origin	Fe_2O_3
Quartz pebbles	
Amarna	0.01
Sand	
Amarna	1.76
Amarna	2.02
Belus River	0.47
Belus River	0.44
Belus River	0.46
Belus River	0.61
Karnak	*
Fayoum	*
Pyramids	*
Aswan	*

Fe

Fe^{2+} < 1%	**Light blue**
Fe^{2+} 2 - 5%	**Bluish green**
Fe^{2+} 8 - 10%	**Dark brown, blackish**
Fe^{2+}/Fe^{3+}	**Green hues**
$Fe^{2+}<Fe^{3+}$	**Greenish yellow**
Fe^{3+} very low	**Colourless**
Fe^{3+} 1 - 3%	**Light yellow**
Fe^{3+} 3 - 8 %	**Reddish brown**

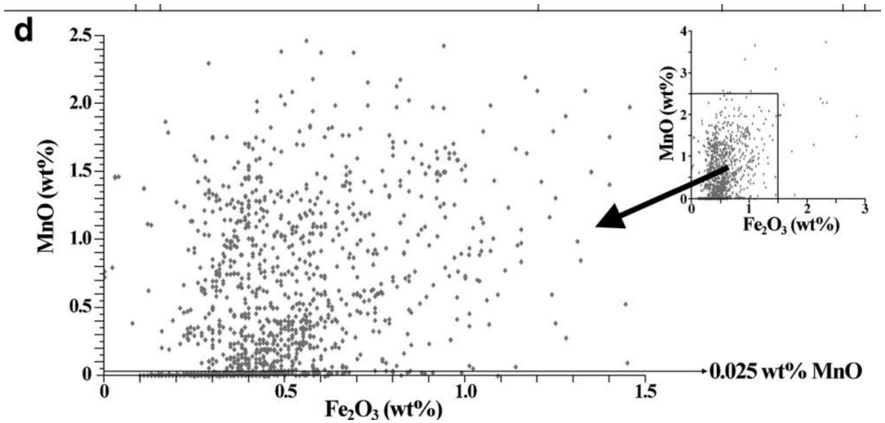
Origin	Fe_2O_3
Plant ash	
Turkey	3.79
Iran	0.43
Iraq	3.52
Syria	

Cutoff value?

Research questions: glass technology

- **'De/Colouring' agents**
  - **Naturally included**
  - **Intentionally added**

Mn	**Mn^{2+}**	**Colourless**
	Mn^{3+} (high amounts)	**Violet**
	Mn^{4+}	**Violet**



<u>Cutoff value</u> → Fe_2O_3-MnO binary diagram demonstrates the reliability of **0.025 wt%** as the reference value . Considering the detection limits of several analytical techniques, this amount is rather low, however, it approximately corresponds to the <u>FeO/MnO ratio in the Earth's crust</u>. Actually, FeO and MnO contents in the Earth crust amount to 5.04 and 0.1 ppm respectively, with a FeO/MnO=50.4 (Rudnick and Gao, 2003), therefore, their ratio is equal to 0.020. Using values provided for the weathered crust (FeO=7.77, MnO=0.14; see Kamber et al. 2005), the ratio further decreases to a value of 0.018.

Research questions: glass technology

- ‘Colouring’ agents
  - **Naturally included**
  - **Intentionally added**

$Mn^{4+} + Fe^{2+} \rightarrow Mn^{2+} + Fe^{3+}$

Mn-bearing common minerals		
	Mineral formula	Mn content %
Hausmannite	Mn_3O_4	72.03
Braunite	$Mn^{2+}Mn^{3+}{}_6SiO_{12}$	63.60
Pyrolusite	$\mathbf{MnO_2}$	**63.19**
Ramsdellite	MnO_2	63.19
Alabandite	MnS	63.14
Manganite	MnO(OH)	62.47
Pyrochroite	$Mn(OH)_2$	61.76
Todorokite	$(Na,Ca,K)_2(Mn^{4+},Mn^{3+})_6O_{12}$•3-4.5$(H_2O)$	56.54
Tephroite	$Mn_2(SiO_4)$	54.41
Bixbyite	$Mn_{1.5}Fe_{0.5}O_3$	52.05
Birnessite	$(Na,Ca,K)_x(Mn^{4+},Mn^{3+})_2O_4\cdot 1.5(H_2O)$	50.94
Romanechite	$(Ba,H_2O)_2(Mn^{4+},Mn^{3+})_5O_{10}$	48.45
Rhodochroisite	$Mn(CO_3)$	47.79
Psilomelane (*)	$(Ba,H_2O)_2Mn_5O_{10}$	46.56
Hollandite	$Ba(Mn^{4+},Mn^{2+})_8O_{16}$	42.51
Rhodonite	$(Mn,Fe,Mg,Ca)SiO_3$	38.29

Research questions: glass technology

- **Decolouring agents and opacifying agents**
  - **Naturally included**
  - **Intentionally added**

Sb	{	**Sb^{2+}**	**Colourless**
		$Ca_2Sb_2O_7$, $CaSb_2O_6$	**White op.**
		$Pb_2Sb_2O_7$	**Yellow op.**

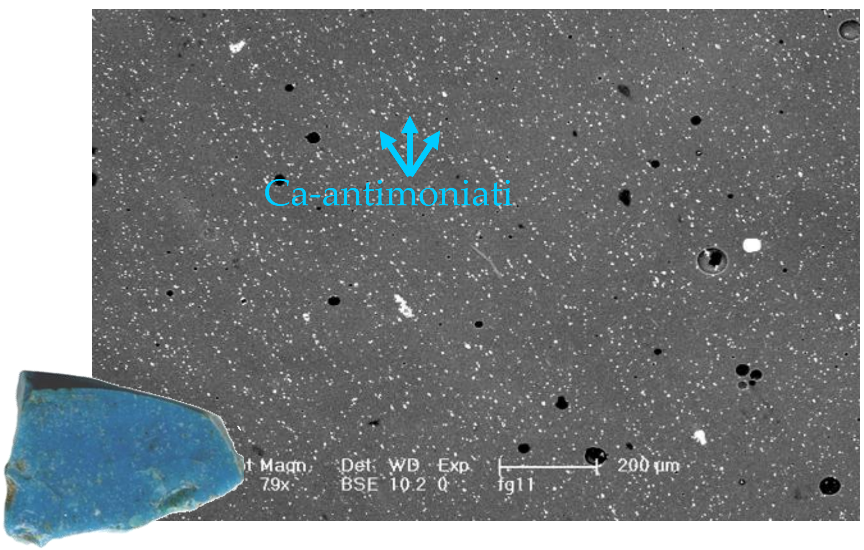
Cutoff value → The cutoff value for Sb could be reasonably fixed at **20 ppm**, based on studies available on sands composition (Degryse 2015). The latter provide an average antimony content of 1.4 ppm and a maximum content of 19.2 ppm. However, most analytical techniques used for glass analyses are not able to reach such degree of accuracy, therefore, the cutoff value has been here arbitrarily increased to **100 ppm**.

Research questions: glass technology

- **Decolouring agents and opacifying agents**
  - **Naturally included**
  - **Intentionally added**

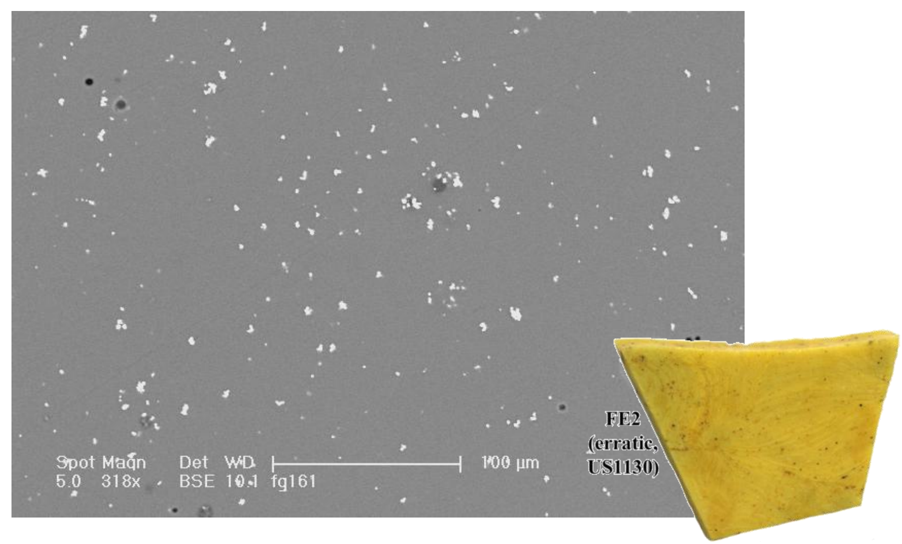
Sb	Sb^{2+}	**Colourless**
	$Ca_2Sb_2O_7$, $CaSb_2O_6$	**White op.**
	$Pb_2Sb_2O_7$	**Yellow op.**

Ca-antimonate in light blu tesserae



FS5 (panel 3)

Pb-antimonates in yellow tesserae

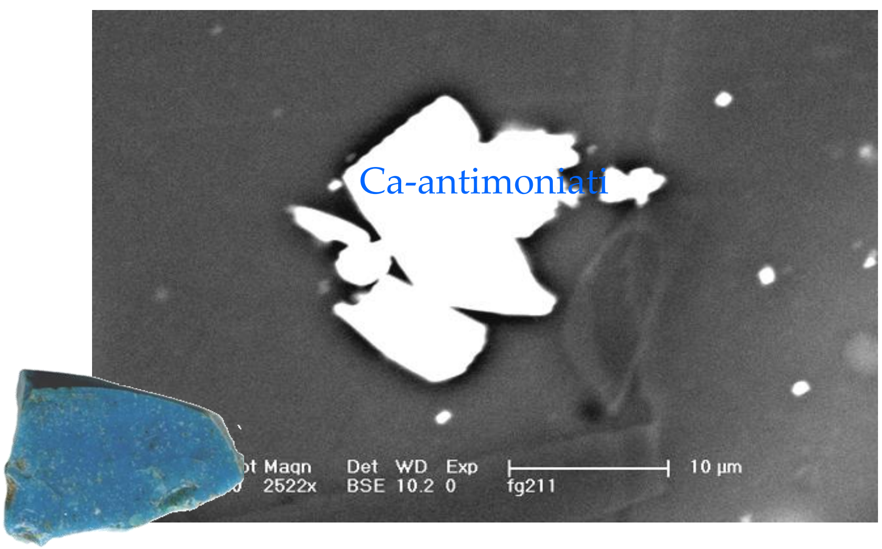


Research questions: glass technology

- **Decolouring agents and opacifying agents**
  - **Naturally included**
  - **Intentionally added**

Sb	{	**Sb^{2+}**	**Colourless**
		$Ca_2Sb_2O_7$, $CaSb_2O_6$	**White op.**
		$Pb_2Sb_2O_7$	**Yellow op.**

Ca-antimonate in light blu tesserae



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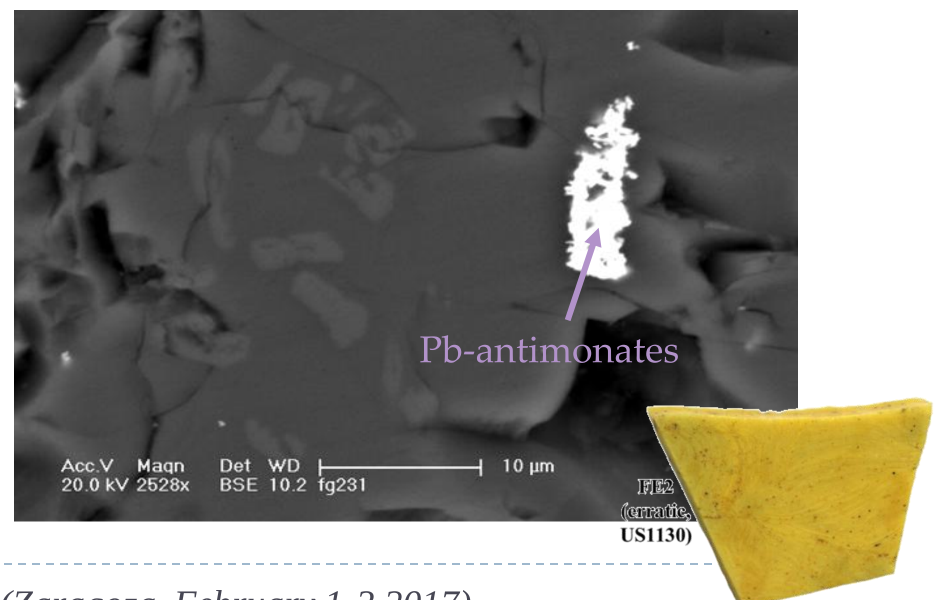
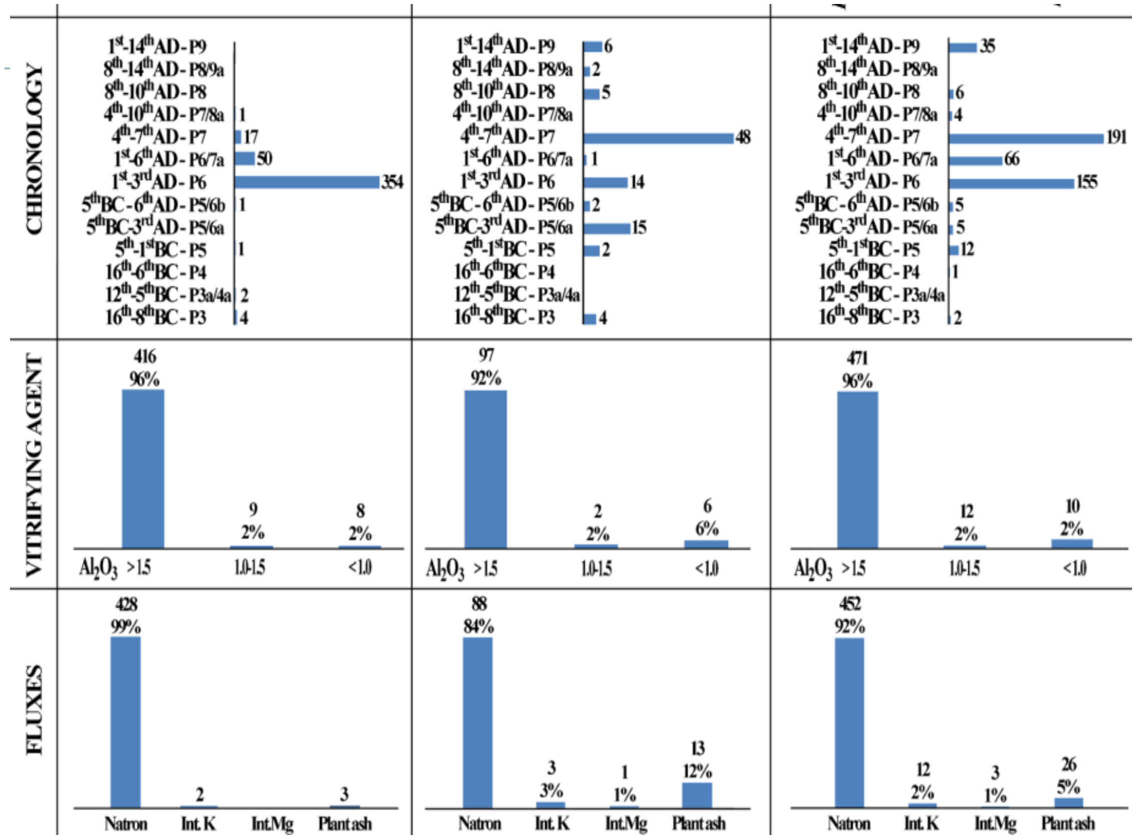


Research questions: glass technology

- **Decolouring agents and opacifying agents**
  - **Naturally included**
  - **Intentionally added**

Sb-bearing common minerals		
	Mineral formula	Sb content %
Paradocrasite	$Sb_2(Sb,As)_2$	91.92
Senarmontite	Sb_2O_3	88.39
Kieftite	$CoSb_3$	86.11
Valentinite	Sb_2O_3	83.53
Nisbite	$NiSb_2$	80.58
Cervantite	$Sb^{3+}Sb^{5+}O_4$	79.19
Stibiconite	$Sb^{3+}Sb^{5+}{}_2O_6(OH)$	76.37
Kermesite	Sb_2S_2O	75.24
Coquandite	$Sb_6O_8(SO_4)\bullet(H_2O)$	75.11
Stibnite	**Sb_2S_3**	**71.68**
Costibite	CoSbS	57.23
Berthierite	$FeSb_2S_4$	56.94
Aurostibite	$AuSb_2$	55.28
Chalcostibite	$CuSbS_2$	48.81
Romeite	$5CaO_3 \cdot Sb_2O_5$	44.54
Bindheimite	$Pb_2Sb_2O_6(O,OH)$	31.62

Research questions: glass technology

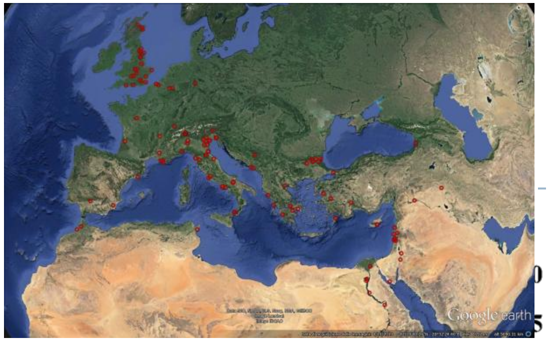


- **Mn-decoloured vs.**

  Sb-decoloured

Simplifying matters, the <u>**Egyptian coast**</u> was likely to produce **all Sb-decoloured glass** and **partly, Late Antique and Medieval Mn-decoloured glass**.
Conversely, the <u>**Levantine coast**</u> seems to have oriented its production toward **Mn-decoloured glass, from the Hellenistic to the Medieval period**.

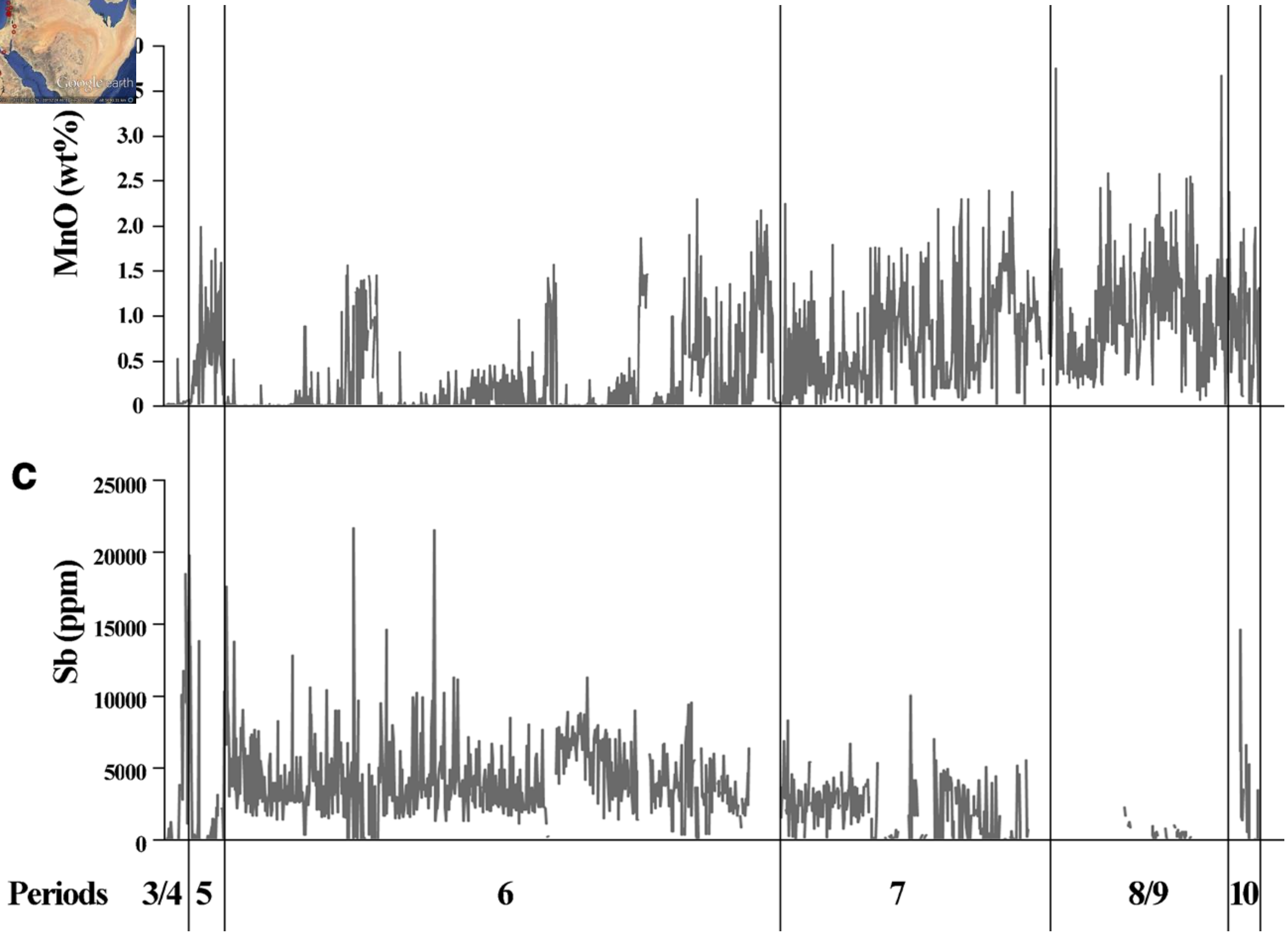
Research questions: glass technology



Mn-decoloured

vs.

Sb-decoloured



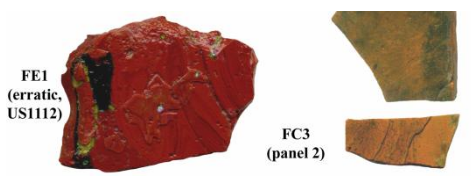
Research questions: glass technology

- ## Colouring agents

Co^{2+}	Blue with a purplish hues
Co^{3+}	Blue, purplish
Co^{2+}/Co^{3+}	Blue
Co>0.05 with Cu 0.02-1.3%	Blu intense
+ Cu/Fe/Mn	Black
Cu metallic	Ruby red
Cu^{+} (Cu_2O, cuprite)	Opaque red (*Hematinum*), orange
Cu^{2+}	Blue with greenish hues
Pb^{2+}	Yellow
Pb^{2+}/Pb^{3+}	Red

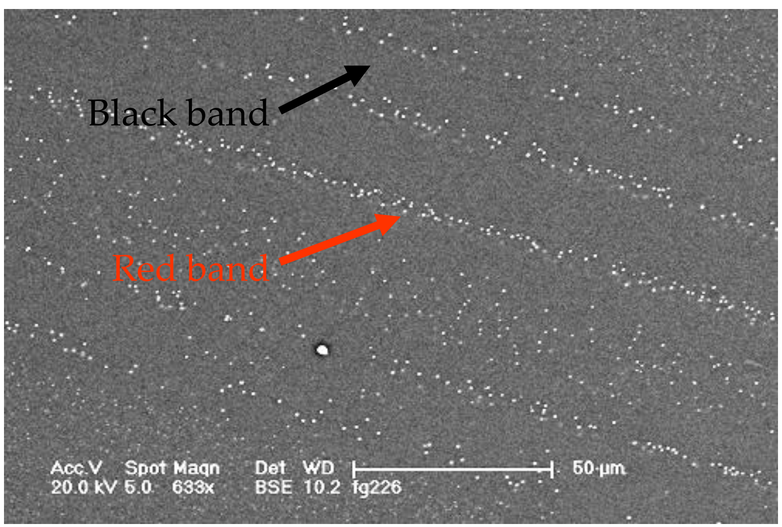
Research questions: glass technology

- **Colouring agents**

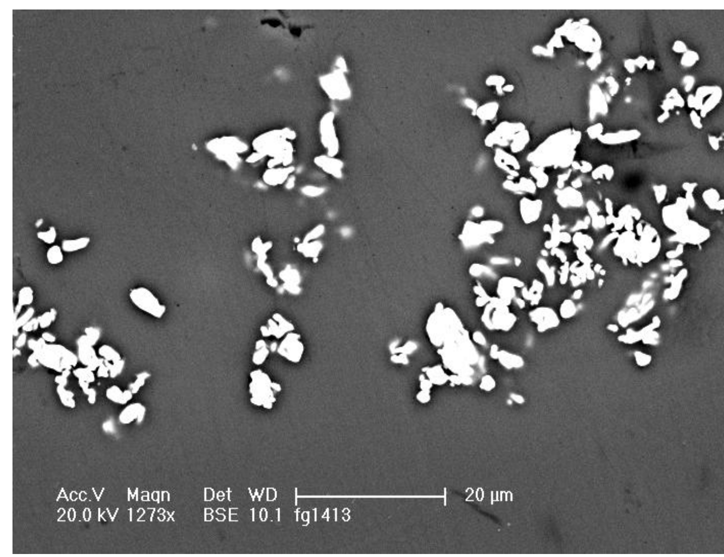


+ Cu/Fe/Mn	**Black**
Cu metallic	**Ruby red**
Cu^{+} (Cu_2O, cuprite)	**Opaque red (*Hematinum*), orange**
Cu^{2+}	**Blue with greenish hues**

Metallic Cu and Cu oxides in red tesserae



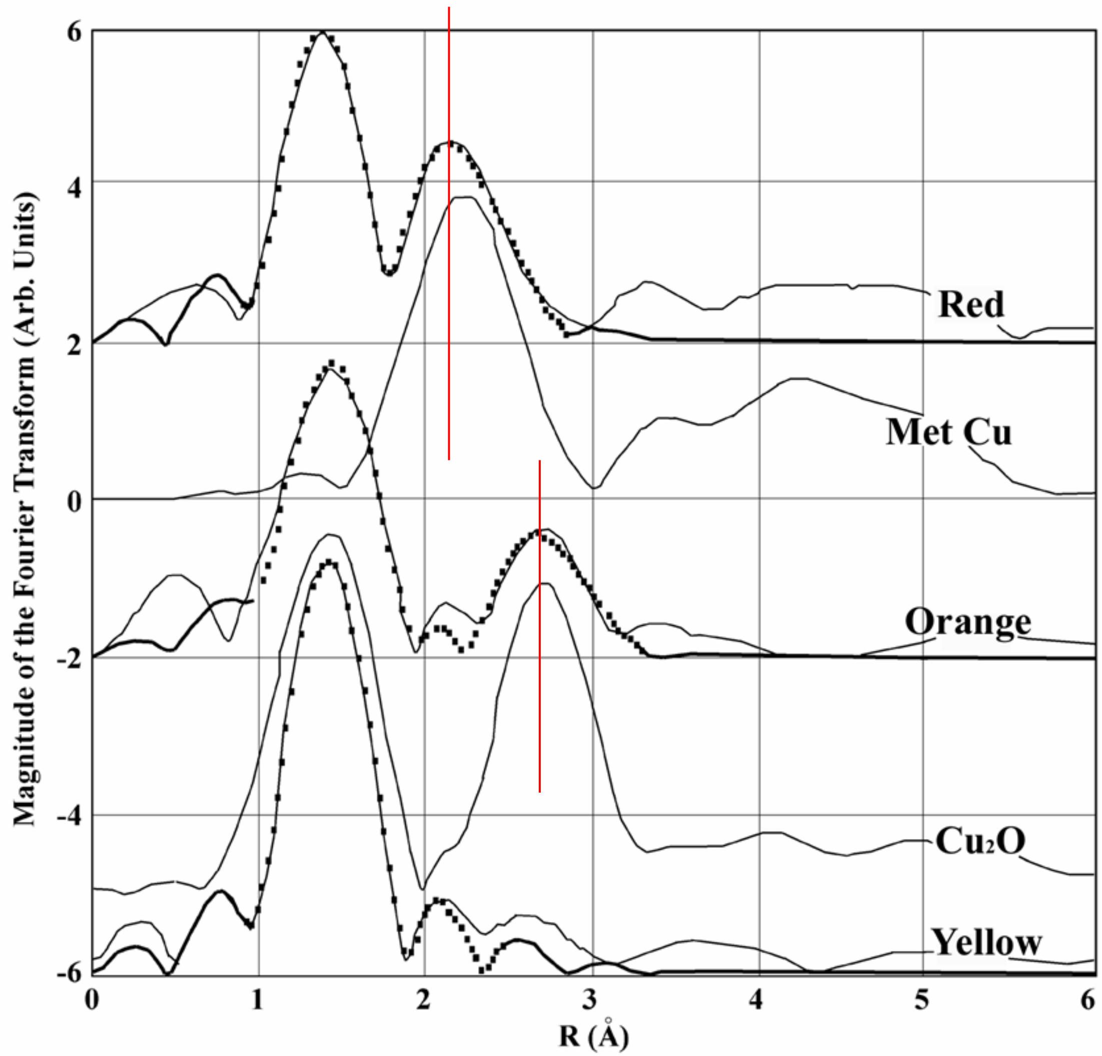
Cu oxides (cuprite) orange tesserae



Research questions: glass technology

- **Colouring agents**

X-ray absorption spectroscopy (XAS) Cu-K edge: red, orange, yellow *tesserae*

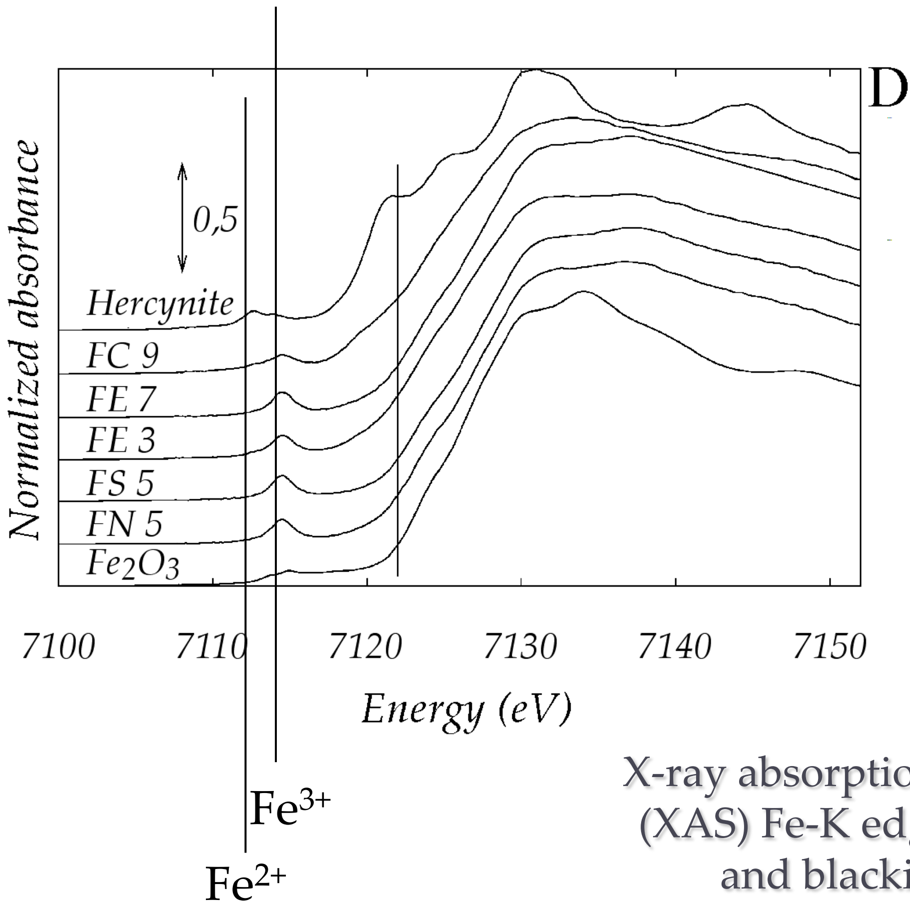


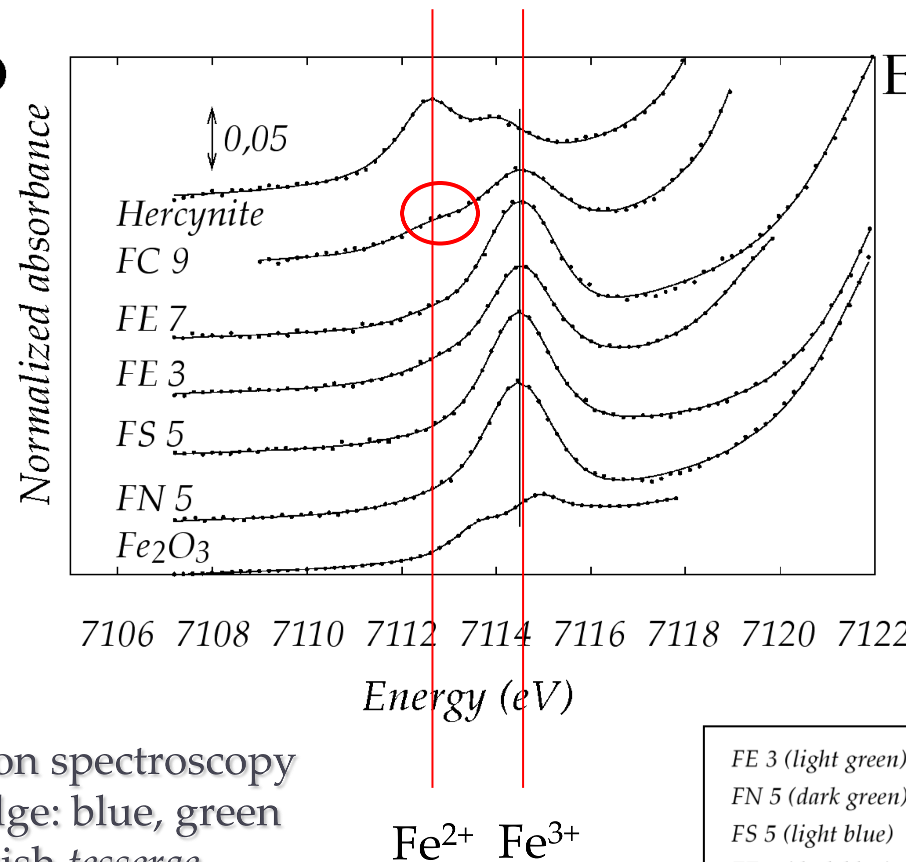
Research questions: glass technology

- **Colouring agents**

Hercynite → $Fe^{2+}Al_2O_4$

Hematite → $Fe^{3+}{}_2O_3$



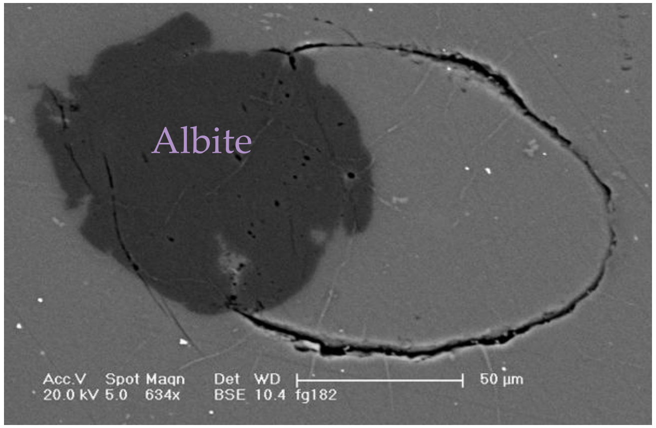


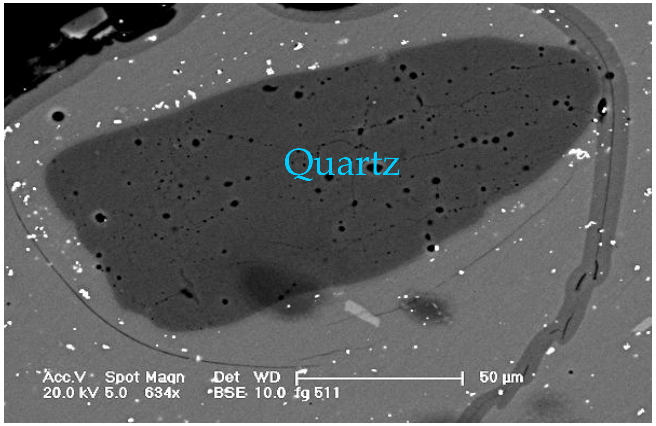
X-ray absorption spectroscopy (XAS) Fe-K edge: blue, green and blackish *tesserae*

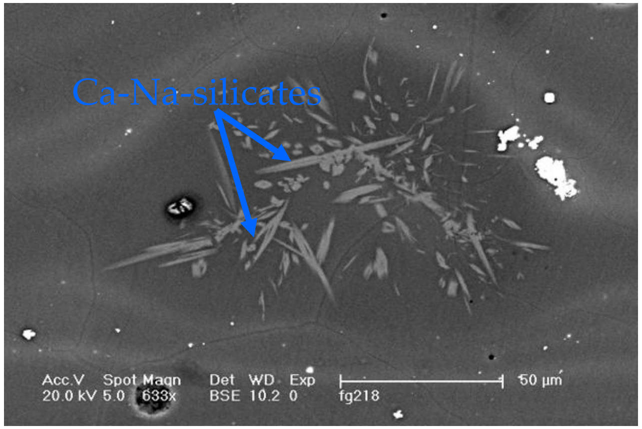
FE 3 (light green)
FN 5 (dark green)
FS 5 (light blue)
FE 7 (dark blue)
FC 9 (blackish)

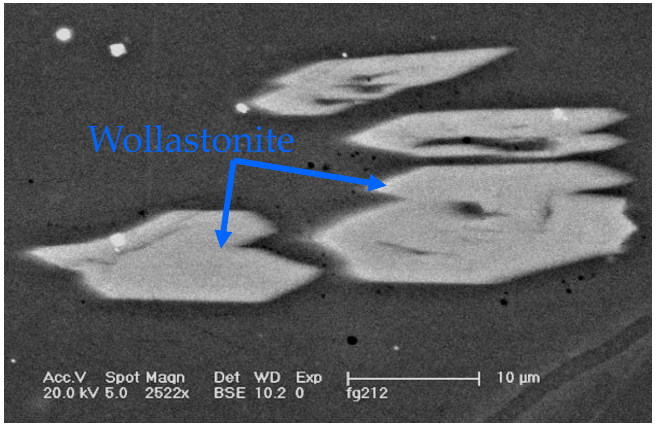
Research questions: glass technology

- **Relicts and newly formed phases**









Bulk chemical analyses

1. **X-ray fluorescence (XRF)**
2. **Inductively coupled plasma mass spectroscopy (ICP-MS)**
3. **Neutron activation (NA)**
4. **Scanning electron microscopy (SEM-EDS)**
5. **Electron microprobe analysis (EMPA)**
6. **Proton-Induced X-ray Emission Spectroscopy (PIXE)**
7. **Laser ablation ICP-MS (LA-ICP-MS)**
8. **Isotopic analyses**

SEM-EDS vs. EMPA

- SEM is a close relative of the electron microprobe (EMP) but is designed primarily for imaging rather than analysis. SEM-EDS does not have the accuracy and detectability of EMPA but has found wider use due to the SEM's lower cost and its data collection speed.

- EMPA is equipped with a range of spectrometers that enable quantitative chemical analysis (wavelength-dispersive spectrometry; WDS) at high sensitivity. Accuracy approaching ±1% (relative) is obtainable and detection limits down to tens of parts per million (by weight) can be attained.

- Both SEM-EDS and EMPA are unable to detect the lightest elements (H, He and Li); as a result, for example, the "water" in hydrous minerals cannot be analyzed.

- Both SEM and EMPA cannot distinguish between the different valence states (e.g. of Fe), so the ratio (e.g. ferric/ferrous) cannot be determined and must be evaluated by other techniques.

Analytical techniques

SEM-EDS vs. EMPA

Table 1. Major, minor, and trace element compositions of glasses (Brill, 1999) mass fraction $\times 10^2$

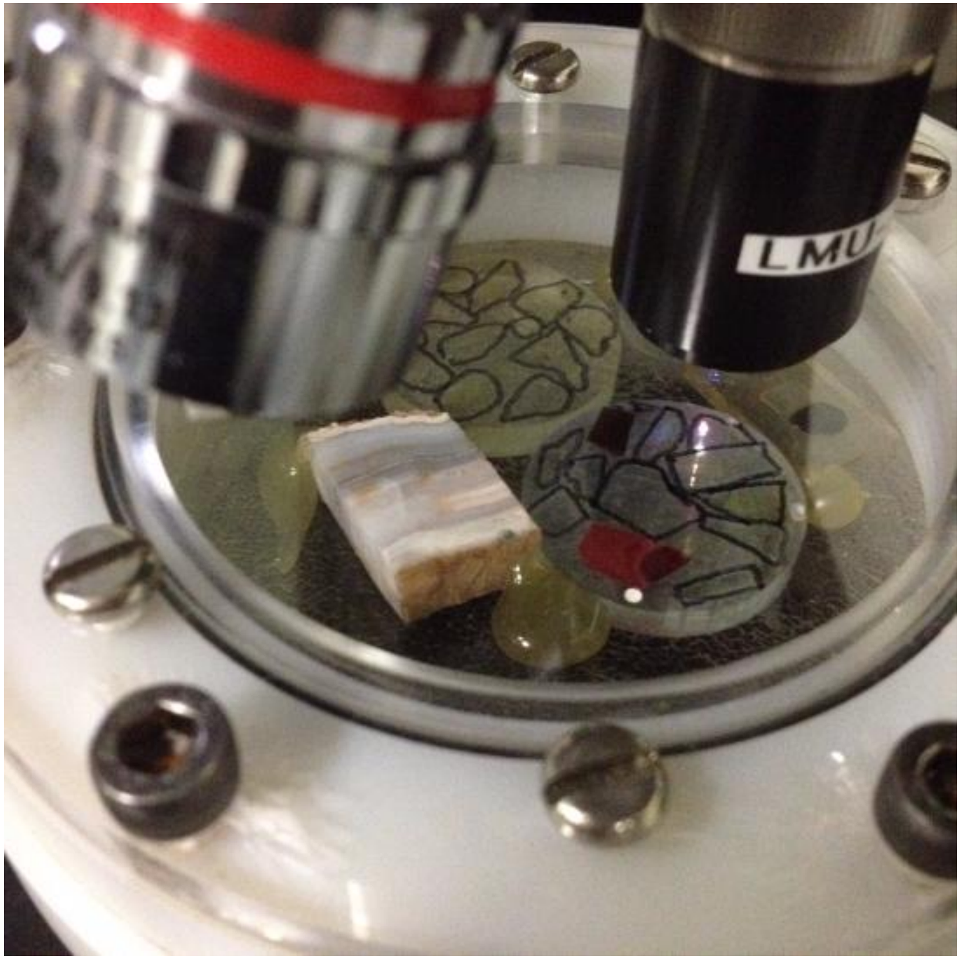
Corning USNM #	A 117218.004	B 117218.001	C 117218.002	D 117218.003
SiO_2	66.56[a]	61.55[a]	34.87[a]	55.24
Al_2O_3	1.00	4.36	0.87	5.30
Fe_2O_3	1.09	0.34	0.34	0.52
MgO	2.66	1.03	2.76	3.94
CaO	5.03	8.56	5.07	14.8
Na_2O	14.3	17.0	1.07	1.20
K_2O	2.87	1.00	2.84	11.3
MnO	1.00	0.25	0.82[a]	0.55
P_2O_5	0.13	0.82	0.14	3.93
TiO_2	0.79	0.089	0.79	0.38
Sb_2O_5	1.75	0.46	0.03	0.97
CuO	1.17	2.66	1.13	0.38
PbO	0.12	0.61	36.7	0.48
CoO	0.17	0.046	0.18	0.023
BaO	0.56	0.12	11.4	0.51
SnO_2	0.19	0.04	0.19	0.10
SrO	0.10	0.019	0.29	0.057
ZnO	0.044	0.19	0.052	0.10
Nominal compositions[b]				
B_2O_3	0.20	0.02	0.20	0.10
Li_2O	0.01	0.001	0.01	0.005
Cl	0.10	0.2	0.10	0.4
SO_3	0.10	0.5	0.10	0.3
Rb_2O	0.01	0.001	0.01	0.005
V_2O_5	0.006	0.03	0.006	0.015
Cr_2O_3	0.001	0.005	0.001	0.0025
NiO	0.02	0.10	0.02	0.05
ZrO_2	0.005	0.025	0.005	0.0125
Ag_2O	0.002	0.01	0.002	0.005
Bi_2O_3	0.001	0.005	0.001	0.0025
Total	99.94	99.87	99.95	100.59

[a] From Brill (unpublished data).
[b] Calculated from precursor mass fractions.

Vincenzi, E.P., Eggins, S., Logan, A., Wysoczanski, R. 2002. Microbeam Characterization of Corning Archeological Reference Glasses: New Additions to the Smithsonian Microbeam Standard Collection, Journal of Research (NIST JRES), 107, no. 6.

Analytical techniques

- **LA-ICP-MS**

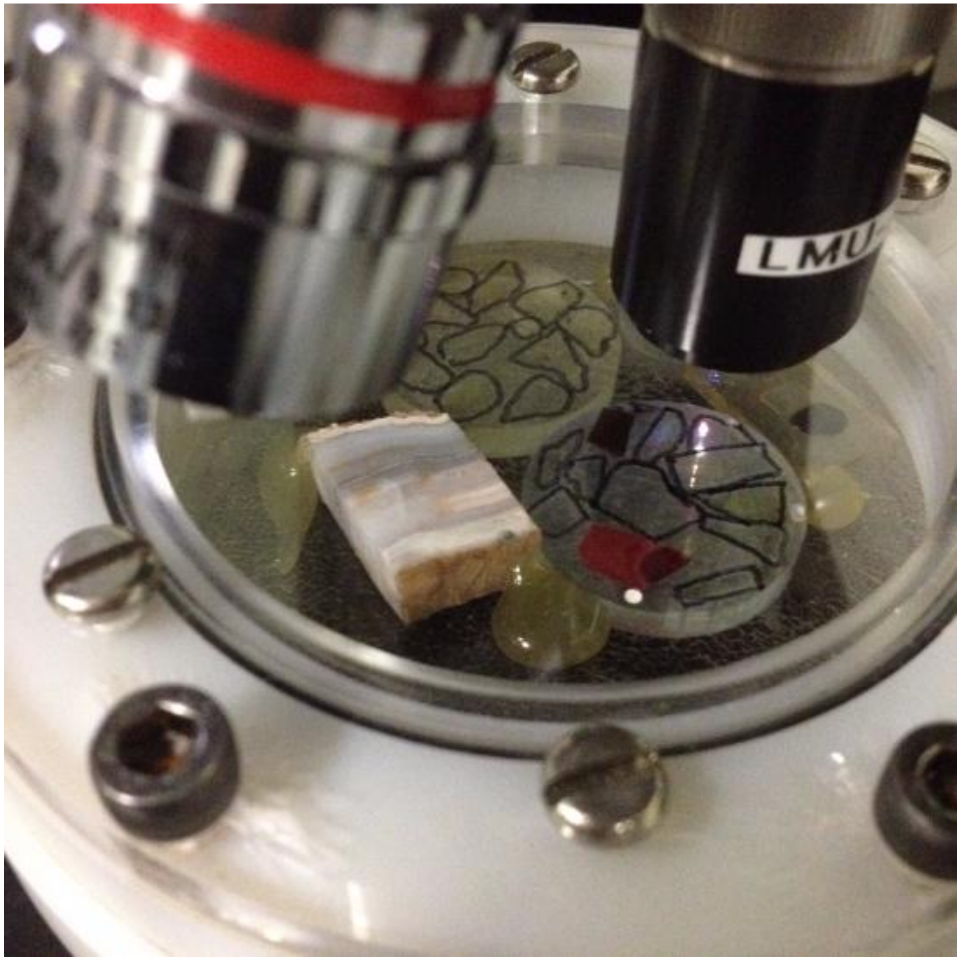


Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) is a direct sampling analytical technology that enables highly sensitive elemental analyses on solid samples

It removes (or ‘ablate’) material and transfer this to an ‘inductively coupled plasma’ (ICP) source, from which either ions for mass spectrometry or light for optical emission spectrometry can be produced.

Analytical techniques

- **LA-ICP-MS**



- **Sensitivity:** parts per billion (ppbw)
- **Depth Resolution:** approximately 1 µm
- **Typical Spot Size:** 10 – 100 µm
- **Very fast**
- **Limitation** (not for glass): Limited sample amount is consumed therefore it can be less representative of the bulk

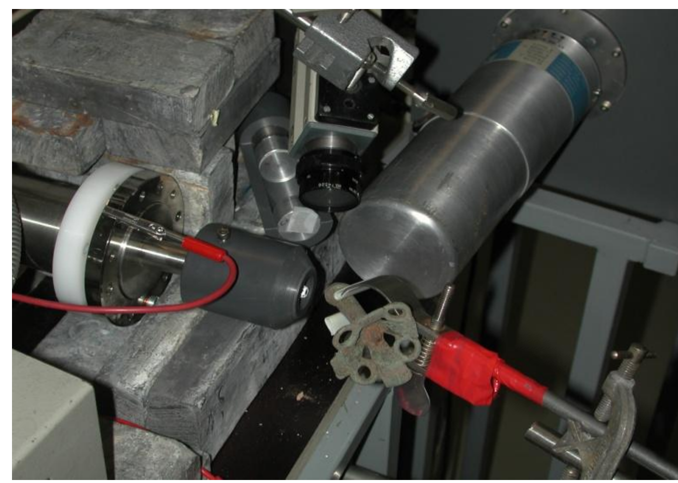
- **PIXE**

Characteristic X-rays are excited by bombardment with protons.

The X-ray **background is much lower than in EMPA** (a consequence of the higher mass of the proton compared with the electron), making **small peaks easier to detect**.

Detection limits are thus typically an order of magnitude lower (in the ppm range).

[http://assets.cambridge.org/052184/875X/excerpt/052184875X_excerpt.htm]



Analytical techniques

- **PIXE**

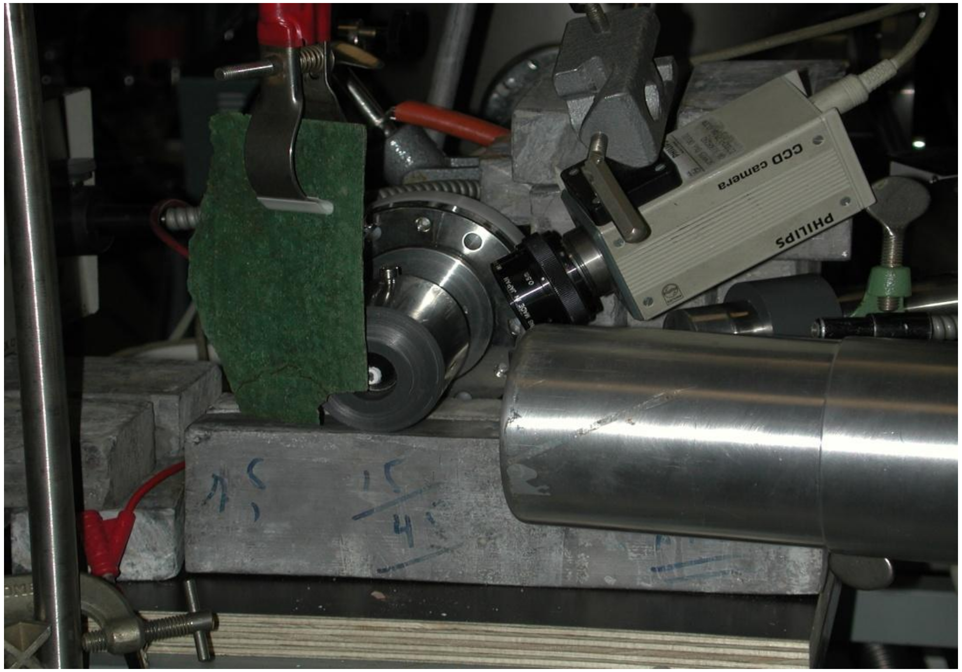
The equipment is quite costly and not very widely available

Analytical techniques

- **PIXE**

High-energy protons are difficult to focus in order to obtain high spatial resolution (**a beam diameter of 1 µm is attainable, but only with low current**), and they **penetrate much further** in solid materials.

Protons of energy 1–4 MeV, which give efficient X-ray excitation, can penetrate the full 30-µm thickness of a petrological thin section and it follows that the spatial resolution with respect to *depth* is relatively poor.



Research questions: glass provenance

PRIMARY WORKSHOPS

Tyre, Lebanon

Raw glass chunk analysed by Freestone 2002

Beth She‘an, Israel

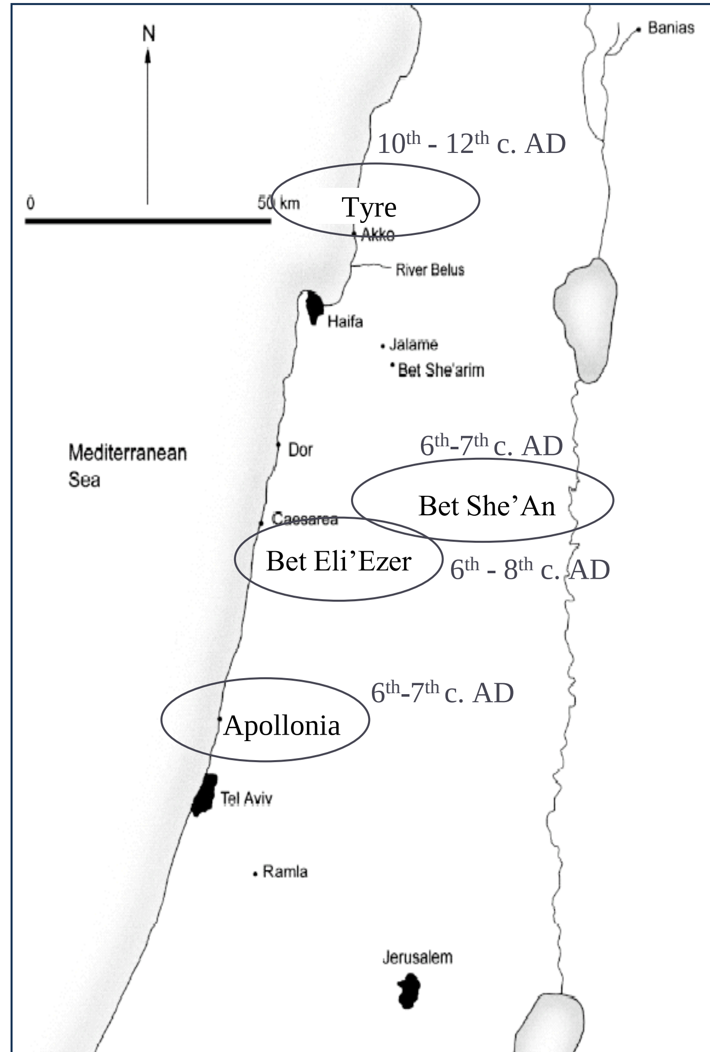
Raw glass chunk analysed by Freestone *et al.* 2003

Bet Eli’Ezer, Israel

Raw glass chunk analysed by Freestone *et al.* 2000, 2003

Apollonia, Israel

Raw glass chunk analysed byGorin-Rosen 2000; Freestone *et al.* 2000



Research questions: glass provenance

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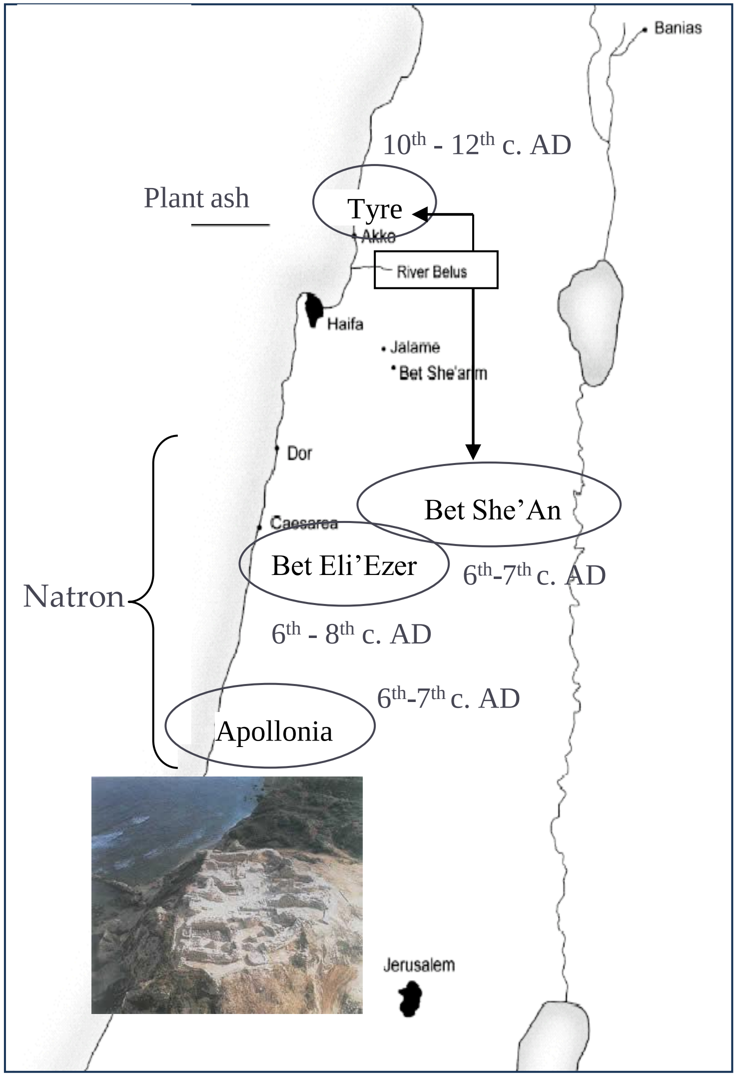


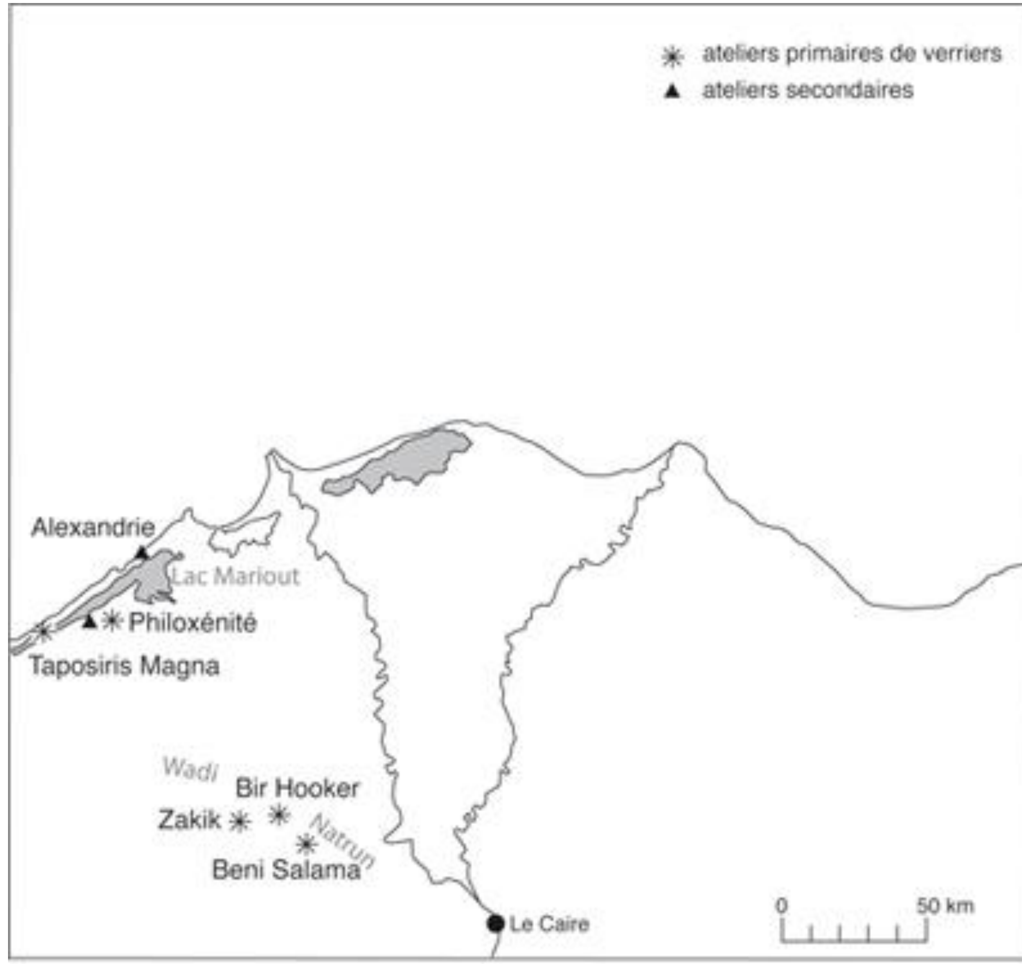
Research questions: glass provenance

PRIMARY WORKSHOPS

EGYPT

Primary glassworkshop in Beni Salama, Wadi Natrun. © M.-D. Nenna

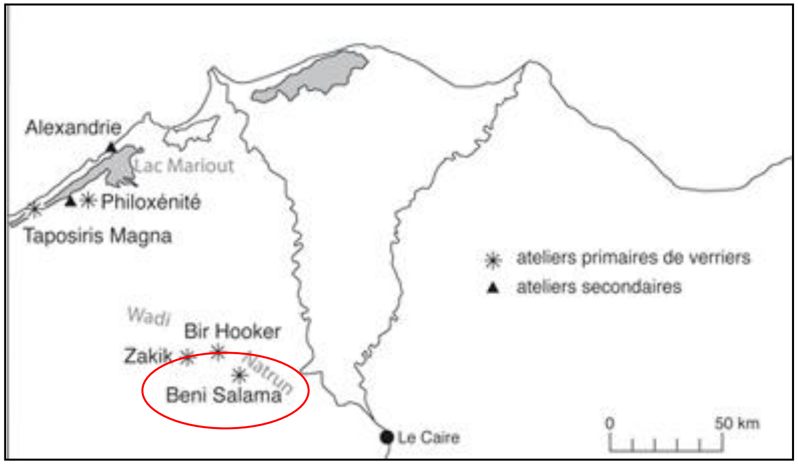
www.diplomatie.gouv.fr/en/



Emplacement du Wadi Natrun et des sites de l'opération

Research questions: glass provenance

PRIMARY WORKSHOPS



Primary glassworkshop in Beni Salama, Wadi Natrun. © M.-D. Nenna

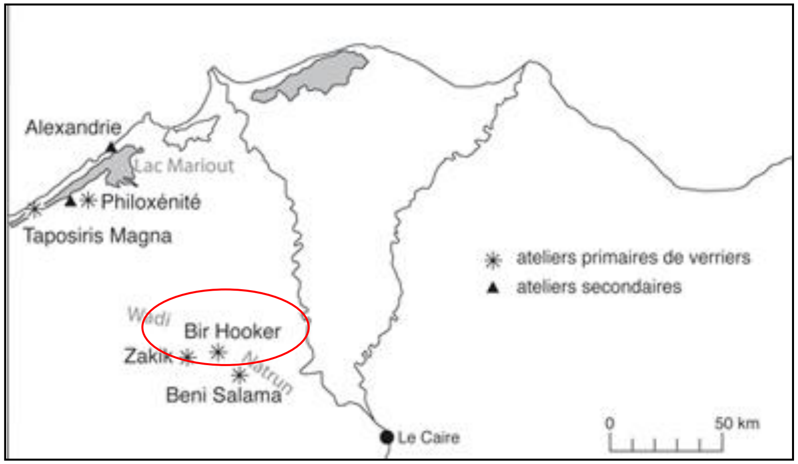
The Beni Salama site, located 14 km east of the Wadi Natrun village, includes a series of hills formed by the accumulation of successive generations of basin furnaces, used for glass fusion.

At the surface, bricks have been identified - covered with light-coloured and translucent glass when they come from the furnace vaults and an opaque vitreous material when they come from the basin walls and bottom - mixed in with layers of ash, as well as infinitesimal glass fragments.

Methodical geophysical prospecting carried out on 2003 ha shown that they date from the middle of the Middle Empire until the 7th century after JC.

Research questions: glass provenance

PRIMARY WORKSHOPS

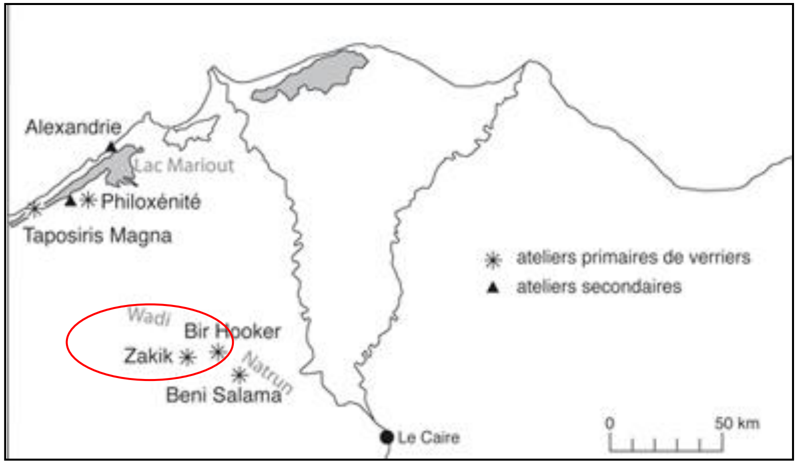


A second site south of the lakes, **Bir Hooker**, was identified in 2002. It is located just south of the modern-day village of Wadi Natrun on the road leading to the monasteries, bordering a fossil dune currently mined as a quarry.

The geophysical prospecting (2004) has indicated the presence of magnetic anomalies similar to those in Beni Salama and regular underlying occupation (village?). The ceramological prospecting has made it possible to date the occupation between the 3^{rd} century BC and the 2^{nd} century AD.

Research questions: glass provenance

PRIMARY WORKSHOPS



The third site, again south of the lakes, is located 10 km northwest of the village Wadi Natrun, in the locality **Zakik**.

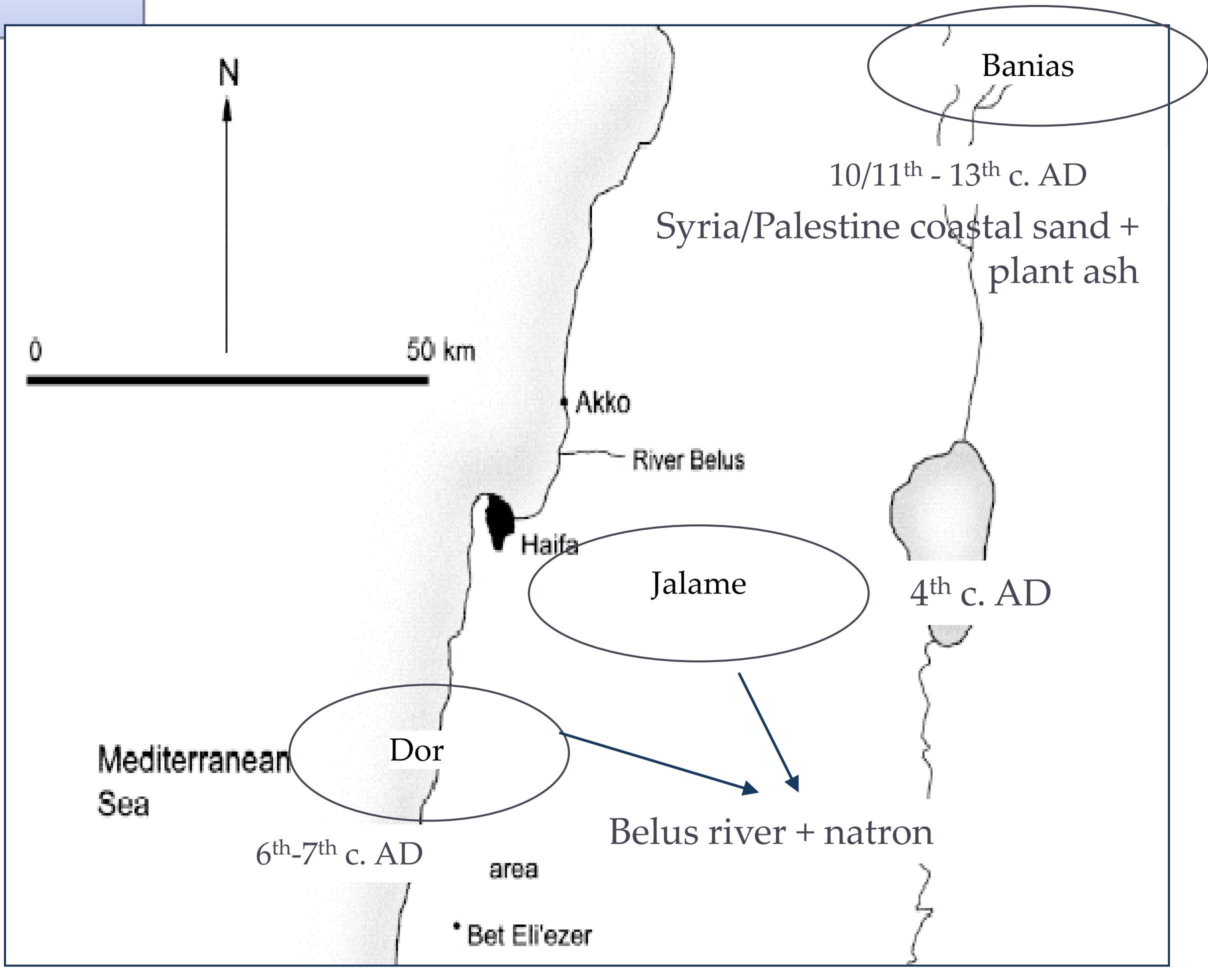
The site contains some of the same type of waste as in Beni Salama and Bir Hooker, but the geophysical prospecting carried out in 2002 yielded but little information, as a village involved in natron mining had settled on the rubbish mounds at the start of the 19th century.)

Research questions: glass provenance

SECUNDARY WORKSHOPS

Research questions: glass provenance

SECUNDARY WORKSHOPS



Banias, Israel

Raw glass chunk analysed by Freestone *et al*. 2000, 2003

Dor, Israel

Raw glass chunk analysed by Freestone *et al*. 2000

Jalame, Israel

Cullets and vessels analysed by Brill 1988

Research questions: glass provenance

SECUNDARY WORKSHOPS

Carthage, Tunisia

4th-6th, 10th-12th

HIMT Raw glass chunk analysed by Freestone 1994

Sand of unknown origin + natron

Museum Collection

? 6th-7th c. AD

Egypt I Glass weights analysed by Gratuze and Barrandon 1990

Sand of unknown origin (middle Egypt) + natron

Museum Collection

8th-9th c. AD

Egypt II Glass weights analysed by Gratuze and Barrandon 1990

Sand of unknown origin (middle Egypt) + natron

Tel el Ashmunein

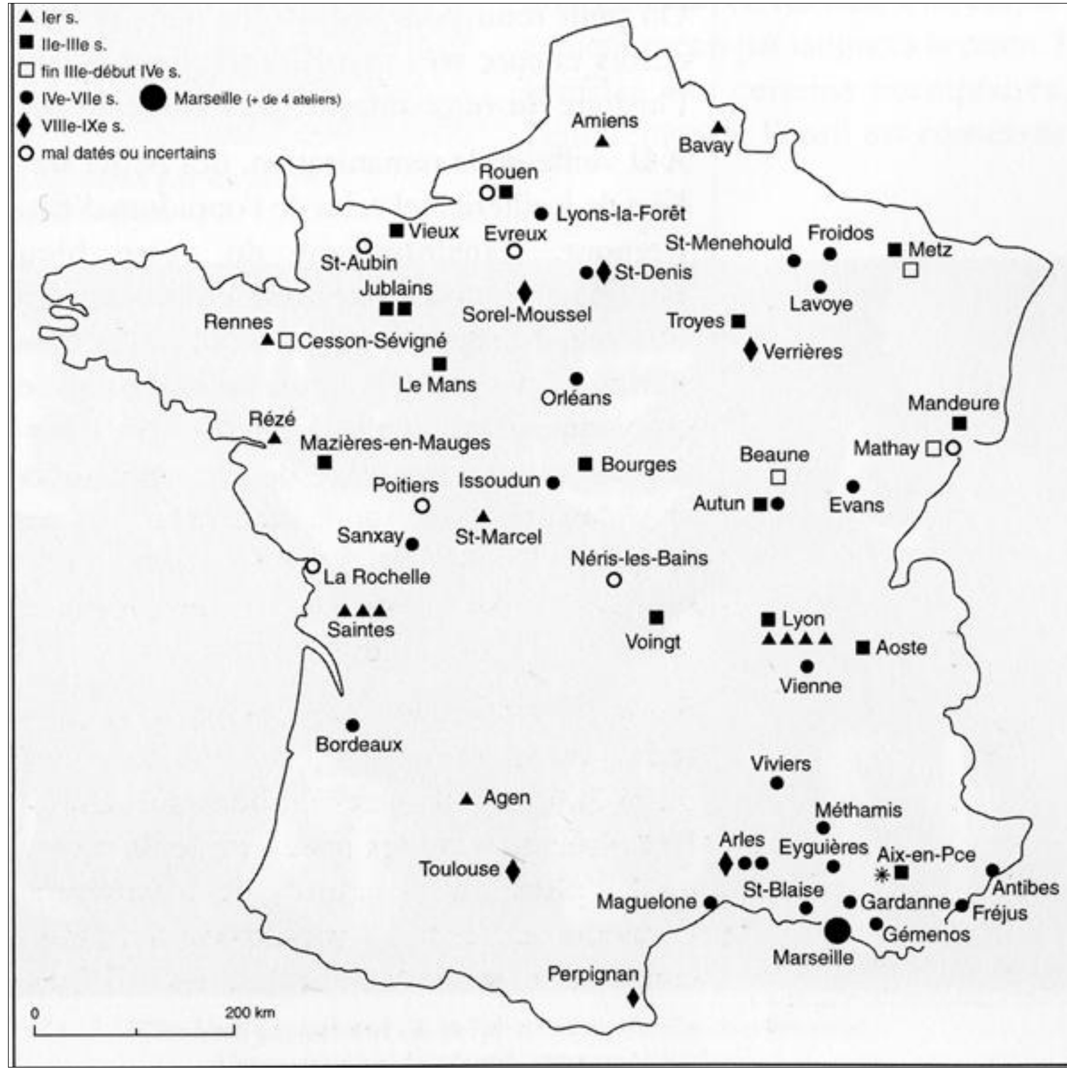
8th-9th c. AD

Egypt II Vessels and waste analysed by Bimson and Freestone 1985, Freestone *et al.*2003

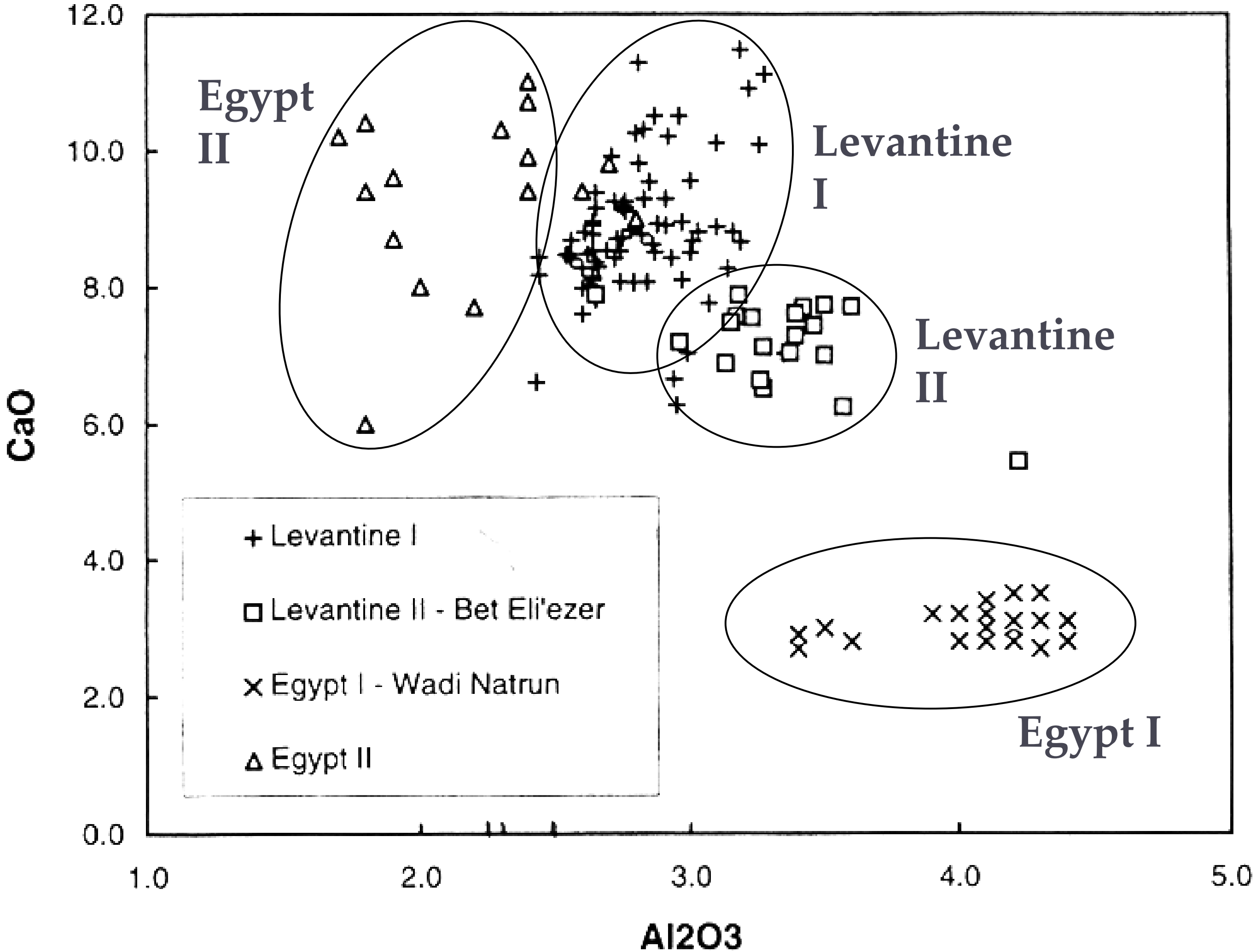
Sand of unknown origin (middle Egypt) + natron

Research questions: glass provenance

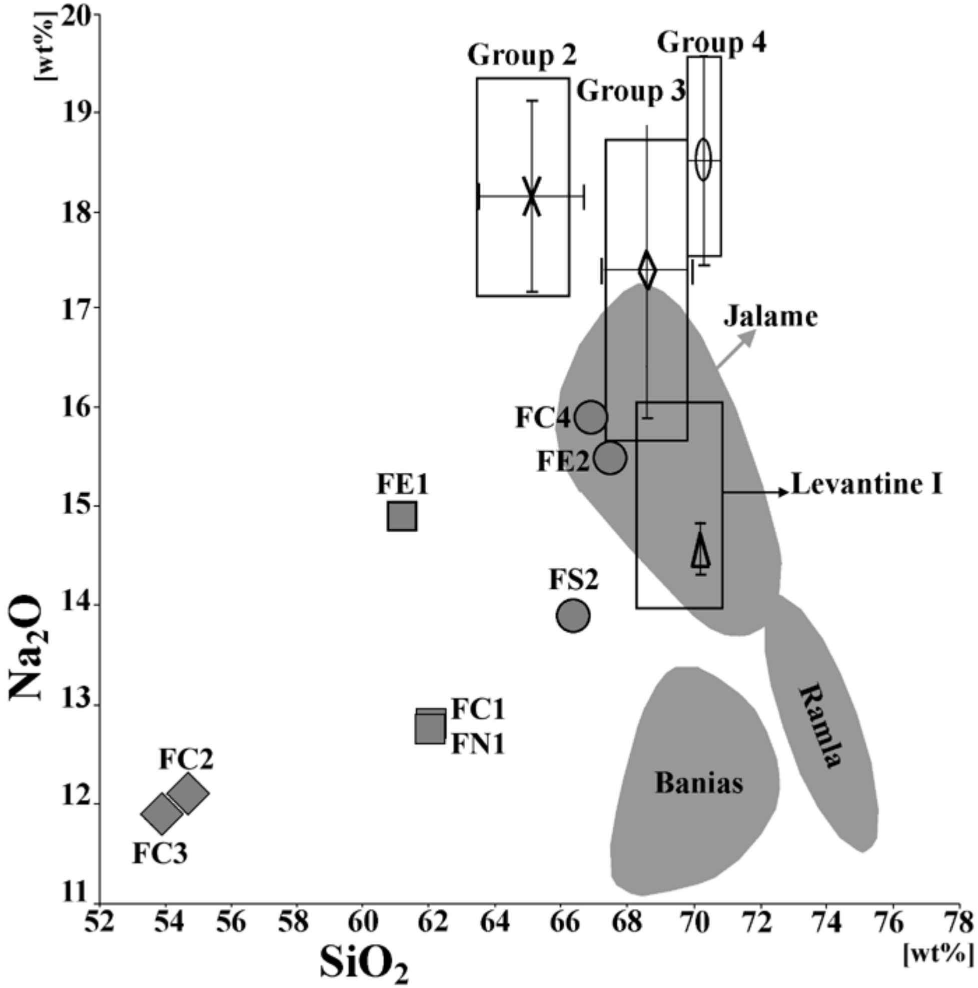
SECUNDARY WORKSHOPS



Research questions: glass provenance

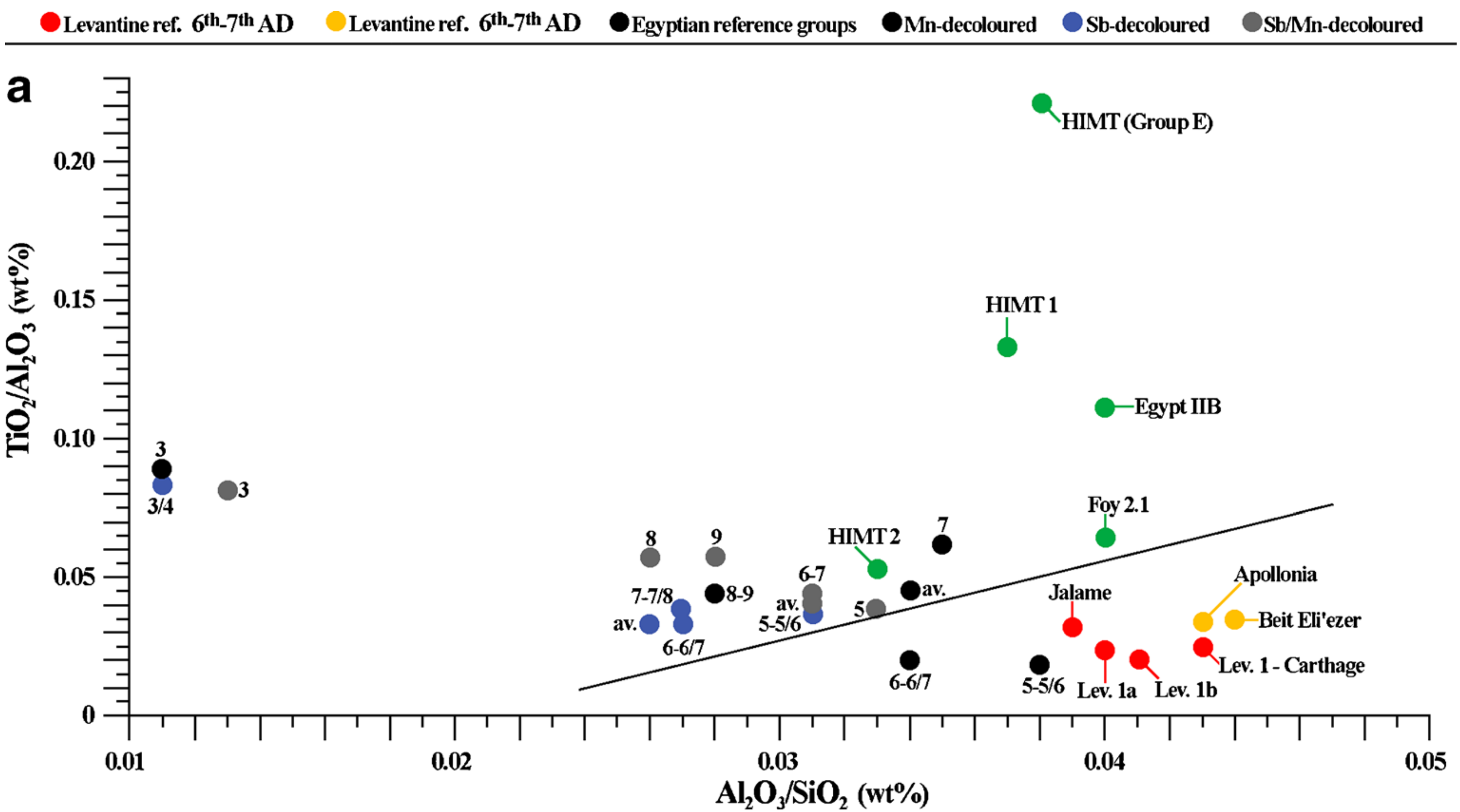


Research questions: glass provenance



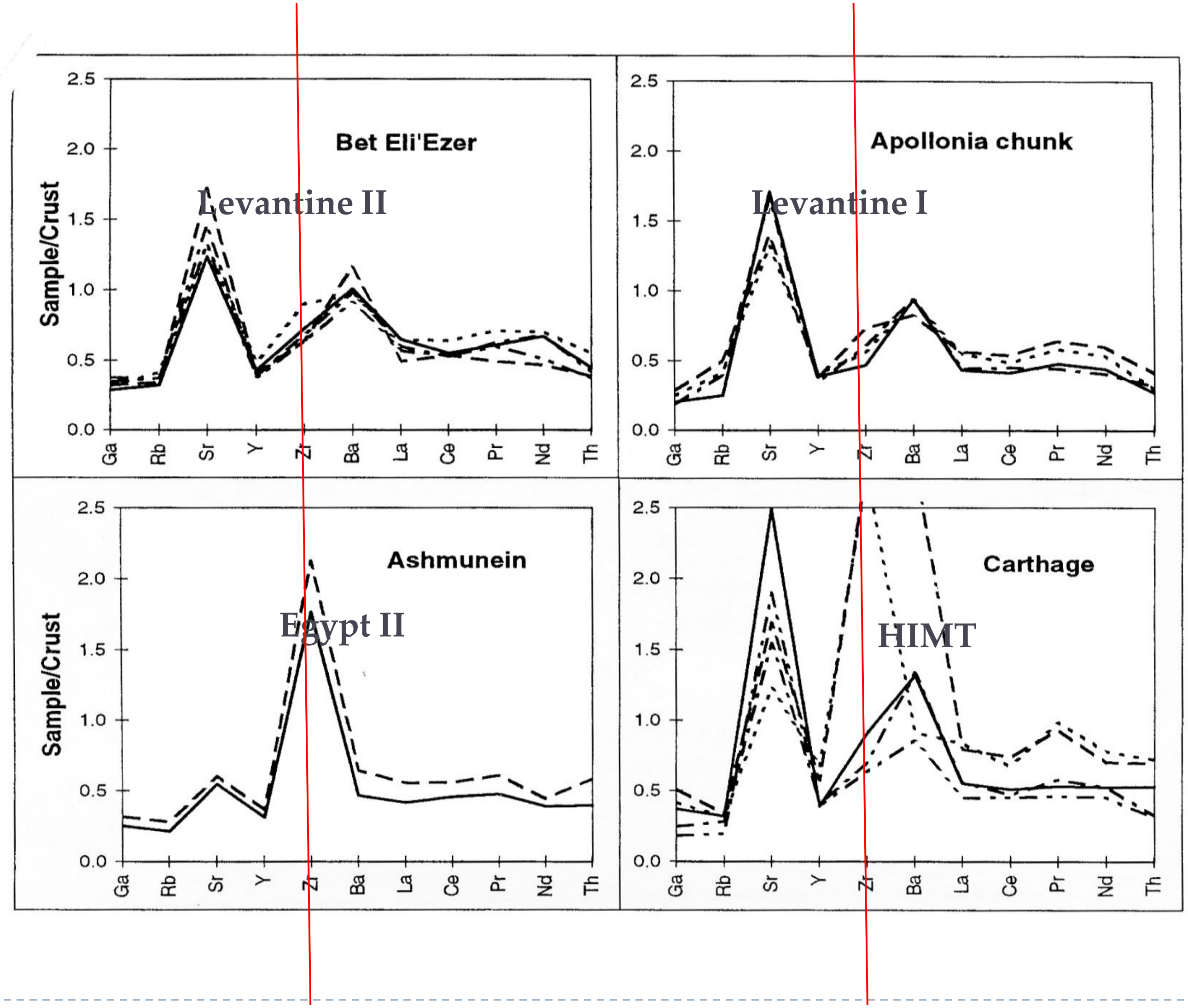
- Group 2 samples (4th-5th century AD) found in the Western Mediterranean area and Egypt
- Group 3 most of the Roman and early medieval glasses (made until the ninth century) found in the West and probably made with Belus sands
- Group 4 including glasses (2nd-3rd century AD) found in the West and characterized by the use of antimony as decolourant (Foy *et al.* 2003, Picon and Vichy 2003)

Research questions: glass provenance

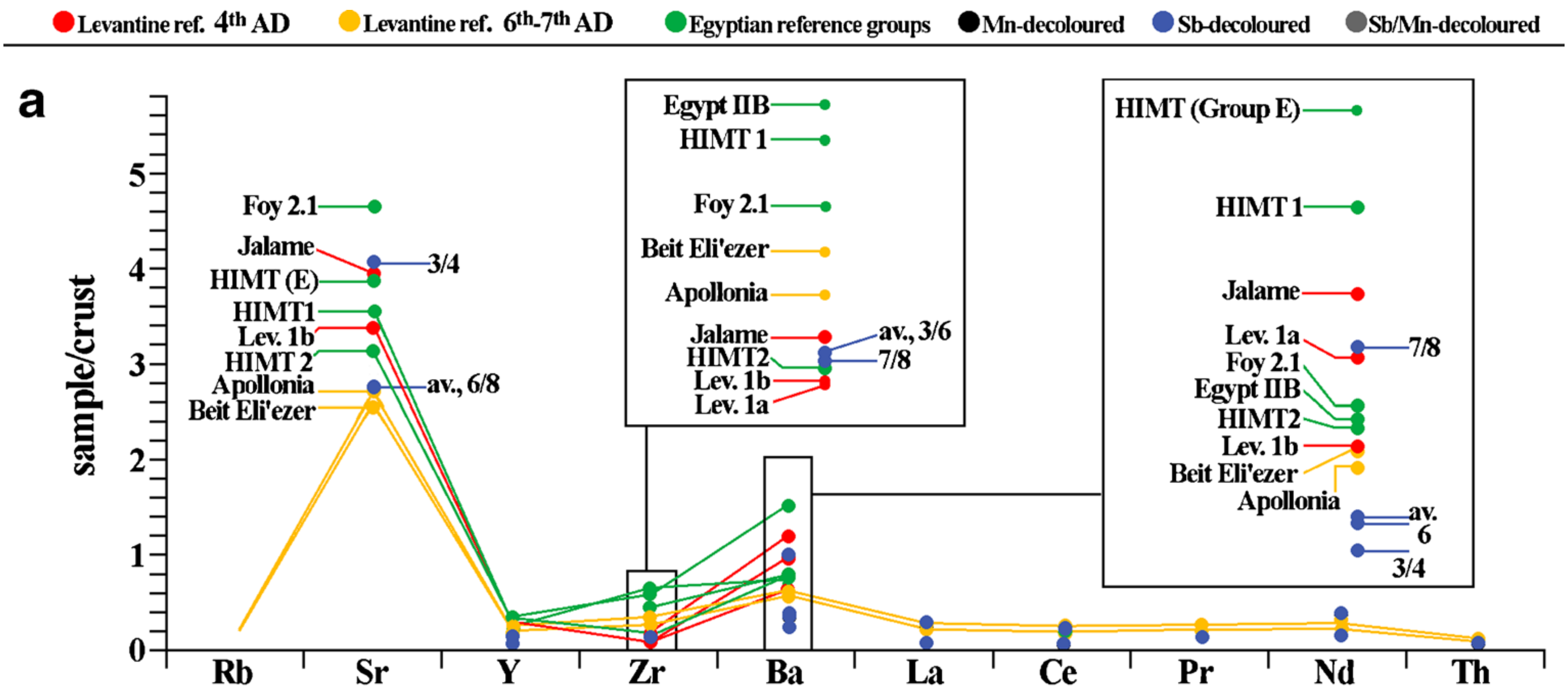


Al_2O_3/SiO_2 - TiO_2/Al_2O_3 binary diagram, after Schibille et al. 2016

Research questions: glass provenance



Research questions: glass provenance



Research questions: glass provenance

ISOTOPES : A example regarding $^{87}Sr/^{86}Sr$ ratios

The application of strontium isotopes to the interpretation of ancient glass depends on the assumption that the bulk of the strontium of many glasses is incorporated with lime-bearing constituents in the glass (e.g. shell, limestone, plant ash).

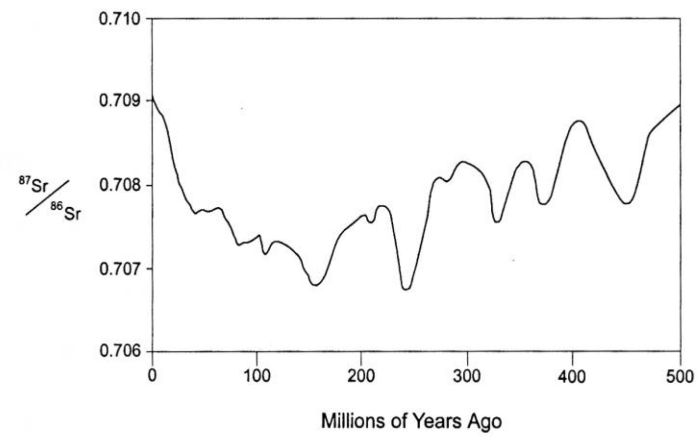


Figure 1 *Variation in the strontium isotope composition of seawater versus time, based on Burke* et al. *(1982) (drawing by A. Simpson).*

Freestone *et al.* 2003

$CaCO_3$ derives from Holocene beach **shell** → the $^{87}Sr/^{86}Sr$ ratio should reflect that of modern seawater.

$CaCO_3$ derives from **limestone** → the $^{87}Sr/^{86}Sr$ ratio should reflect that of seawater at the time the limestone was deposited

$CaCO_3$ derives from **plant ash** → the $^{87}Sr/^{86}Sr$ ratio should reflect the bioavailable strontium from the soils on which the plant grew.

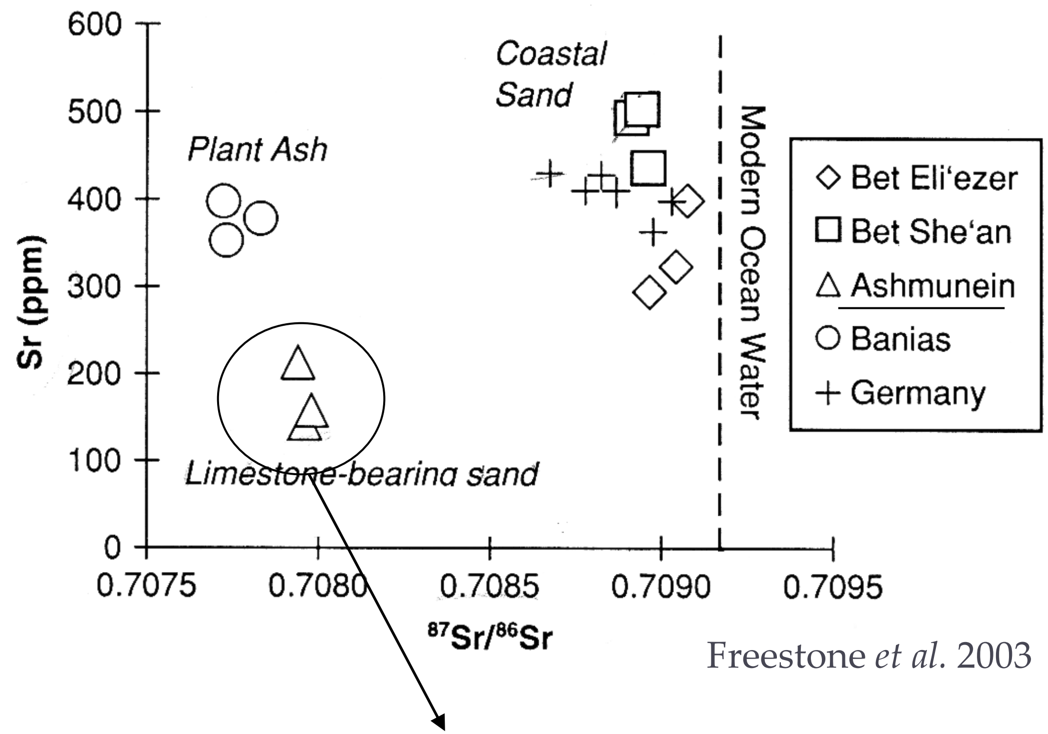
Research questions: glass provenance

ISOTOPES : $^{87}Sr/^{86}Sr$ ratios

LIMITS OF THE METHOD

Tendency of the $^{87}Sr/^{86}Sr$ ratio in the limestone to change as the limestone undergoes diagenesis (cation exchange with groundwater and clay minerals).

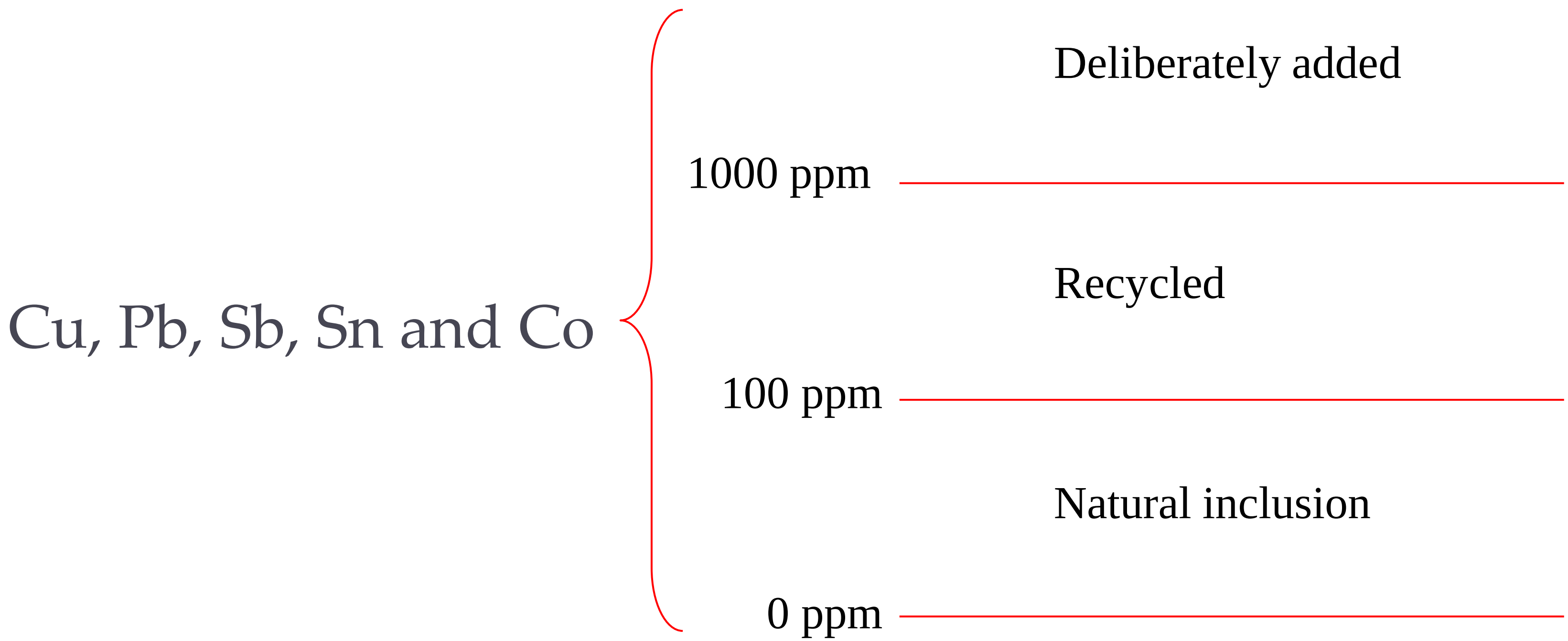
Strontium isotopes in the investigation of early glass production



Freestone *et al*. 2003

Outcrops of Oligocene limestone, occurring north of the region of Ashmunein, around the latitude of modern Cairo

RECYCLING INDICATORS



Research questions: glass technology

RECYCLING

- **Mn-decoloured**
- **Sb-decoloured**
- **Mn/Sb-decoloured**