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Contribution of LA-ICP-MS analysis to lead glaze investigation: two case-studies in medieval and modern archaeology

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Introduction

Over the past fifteen years, electron backscatter diffraction (EBSD) coupled with energy dispersive X-ray spectrometry (EDS) have become routine analytical methods used on the scanning electron microscope (SEM) to explore archaeological issues pertaining to decorative techniques of ancient ceramics. However, SEM-EDS alone is not enough for a full characterization of the composition and microstructure of the ceramic decoration.

This poster illustrates two examples of a **combined SEM-EDS and LA-ICP-MS analysis of archaeological lead-rich glazed tablewares**. The aim is to provide further insights into the chemical fingerprint of ancient glazes. These results can help reconstruct **raw material choices** and **glaze recipes**, firing techniques of the ceramics, and **pigments used** for producing specific decorative styles in different socio-cultural contexts.

Materials and methods

- **62 samples of 14th-c. sgraffito tablewares** found during ASCSA excavations at Thebes & Corinth (Greece).
- **Provenance of the pottery** determined by thin section petrography at the Fitch Laboratory, BSA.

▼ Theban products ▼ Corinthian products ▼ Thessaloniki imports ▼ Anatolian imports ▼ Venetian imports



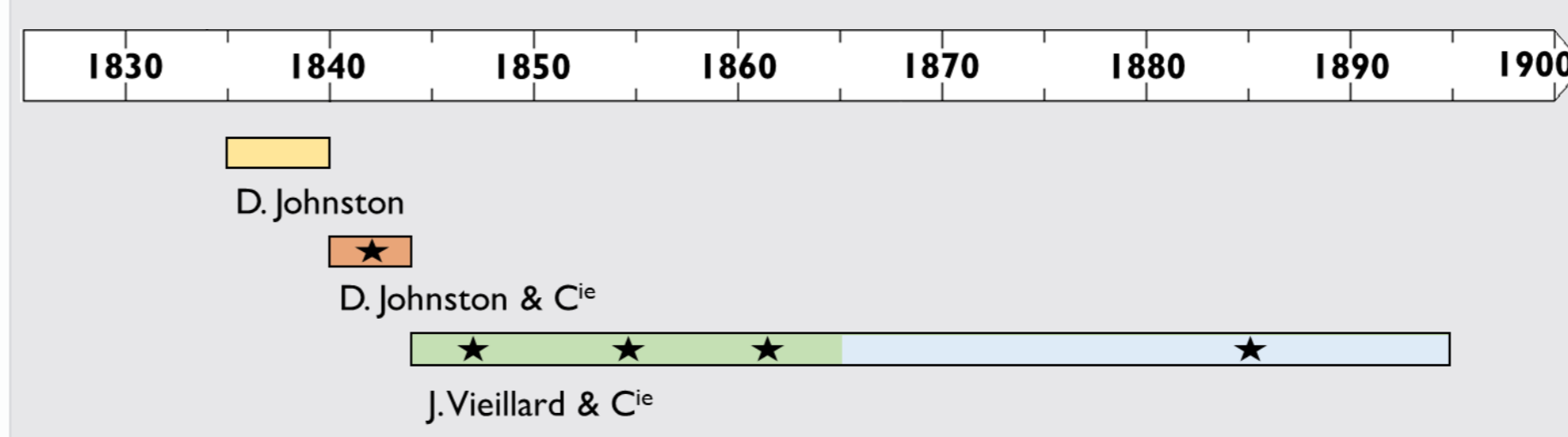
- **Diffusion of glaze recipes? Sources of lead? Use of pigments?**

- ✓ **SEM-EDS** → Microstructure + chemical composition of decorative materials (major and some minor constituents of the glazes: SiO₂, Na₂O, CaO, K₂O, Al₂O₃, MgO, PbO, Cl, P and Fe₂O₃). *Concentration range analyzed: 0.3 – 100%*
- ✓ **LA-ICP-MS** → **Major, minor, and trace** elemental composition of the glazes (coloring and opacifying agents and their associated impurities). In total, **57 elements between Li and U** were quantified [1]. *Concentration range analyzed: from a few ppm to several percents*

⇒ **TRACE ELEMENTS?**

⇒ **LIGHT ELEMENTS?**

- **80 samples of 19th-c. white earthenwares** from the Johnston-Vieillard manufactory in Bordeaux (France).

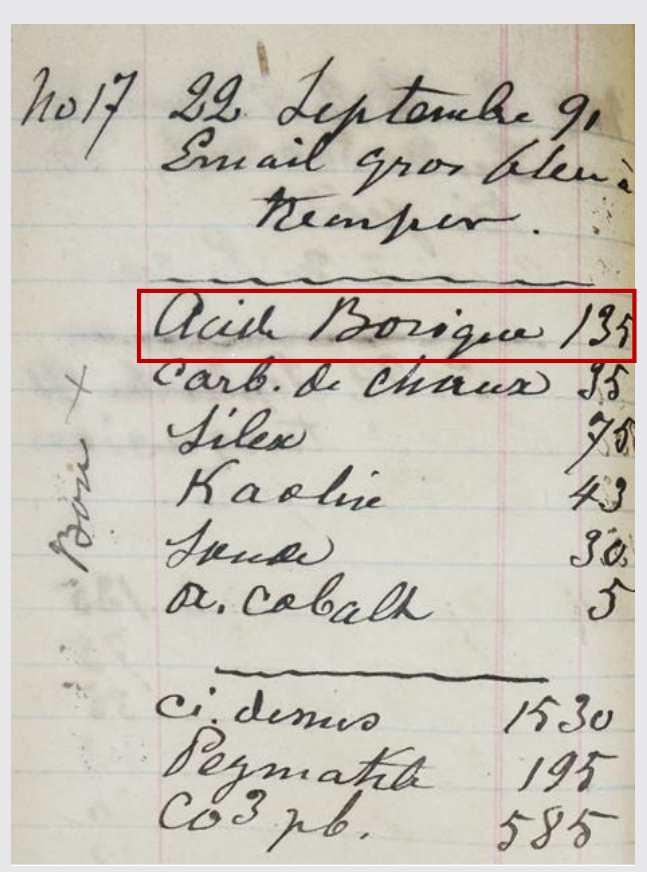


▲ Timeline of white earthenware production history in Bordeaux. Stars (*) symbolize the different periods which were concerned by archaeological sampling.

▼ Some examples representative of the printed sherds.



- **Evolution of glaze recipes?**



Results and discussion

SEM-EDS results

- **Fabrics** are non-calcareous (Venetian products, CaO < 1% wt) to low-calcareous (Anatolian & Greek products, CaO < 7% wt).
- **Slips** are of fine (Greece) to very fine textures (Venice, Anatolia) and mostly composed of Al₂O₃ + SiO₂ → kaolinites.
- Regional and local variations in **glaze** composition (in % wt):

	PbO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	Na ₂ O	K ₂ O	MgO	TiO ₂
Venetian product	43.6	44.7	3.53	3.83	1.56	0.68	0.90	0.52	0.12
Ligurian product	43.4	46.7	3.98	2.37	1.13	0.34	0.72	1.07	0.03
West Anatolian product	51.1	33.5	5.90	4.44	3.20	0.27	0.65	0.71	0.23
Nicaean product	46.5	36.9	6.02	4.60	3.27	0.43	0.77	0.98	0.25
Corinthian product	31.2	42.1	12.6	3.56	4.55	0.96	2.32	1.65	0.29
Chalkidan product	47.9	34.1	9.57	2.81	2.46	0.64	1.03	0.91	0.12
Thessaloniki product	45.6	37.6	8.48	2.51	2.91	0.59	0.86	0.74	0.05
West Cretan product	44.8	36.7	11.5	1.52	0.99	0.59	1.92	1.31	0.38
Theban product	45.7	36.9	8.47	2.66	1.86	0.77	2.50	0.93	0.07
Attica product	56.7	30.1	6.85	2.89	1.35	0.45	0.84	0.70	0.03

LEAD-SILICA MIXTURE?

- Italian workshops

ADDITION OF CA-RICH CLAY?

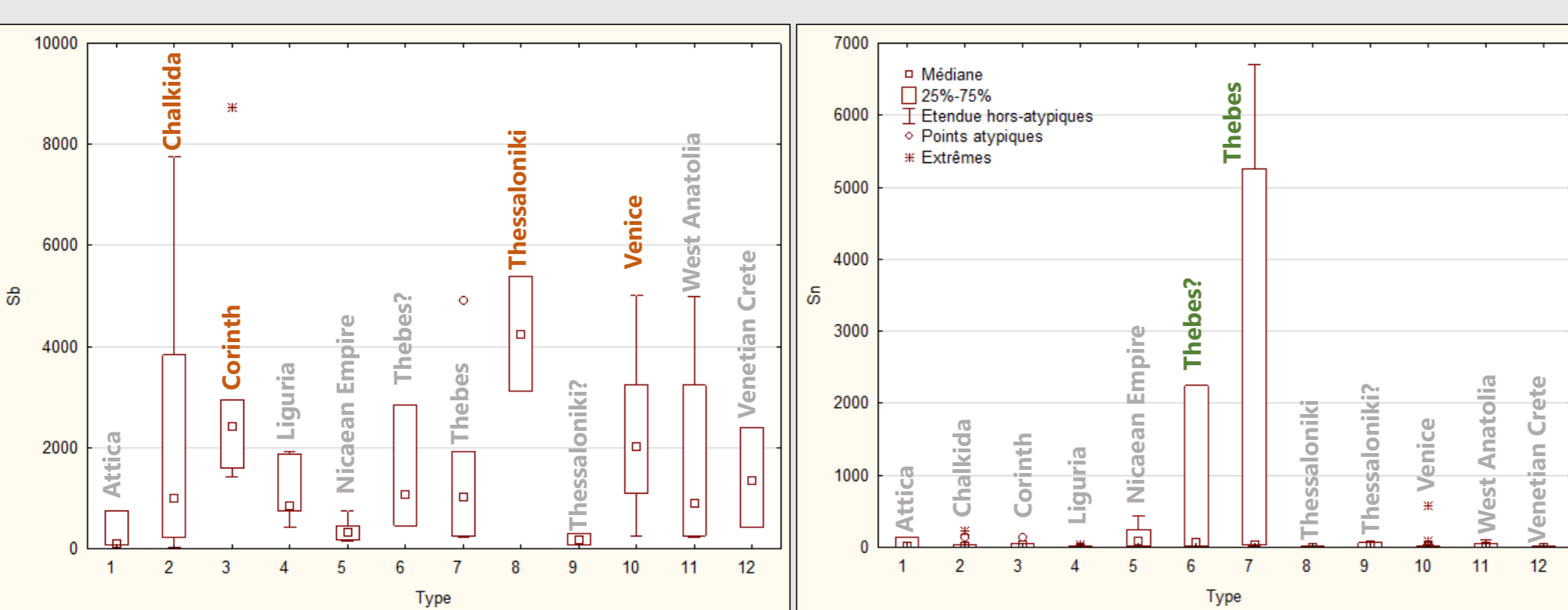
- Anatolian workshops
- Greek workshops of Byzantine tradition

▲ Chemical composition of the glazes measured by SEM-EDS, for one representative sample of each provenance (wt %, detection limit of 1σ).

DIGESTION OF SLIP BY LEAD COMPOUND? ADDITION OF CLAY? ADDITION OF CLAY (ILLITE)?

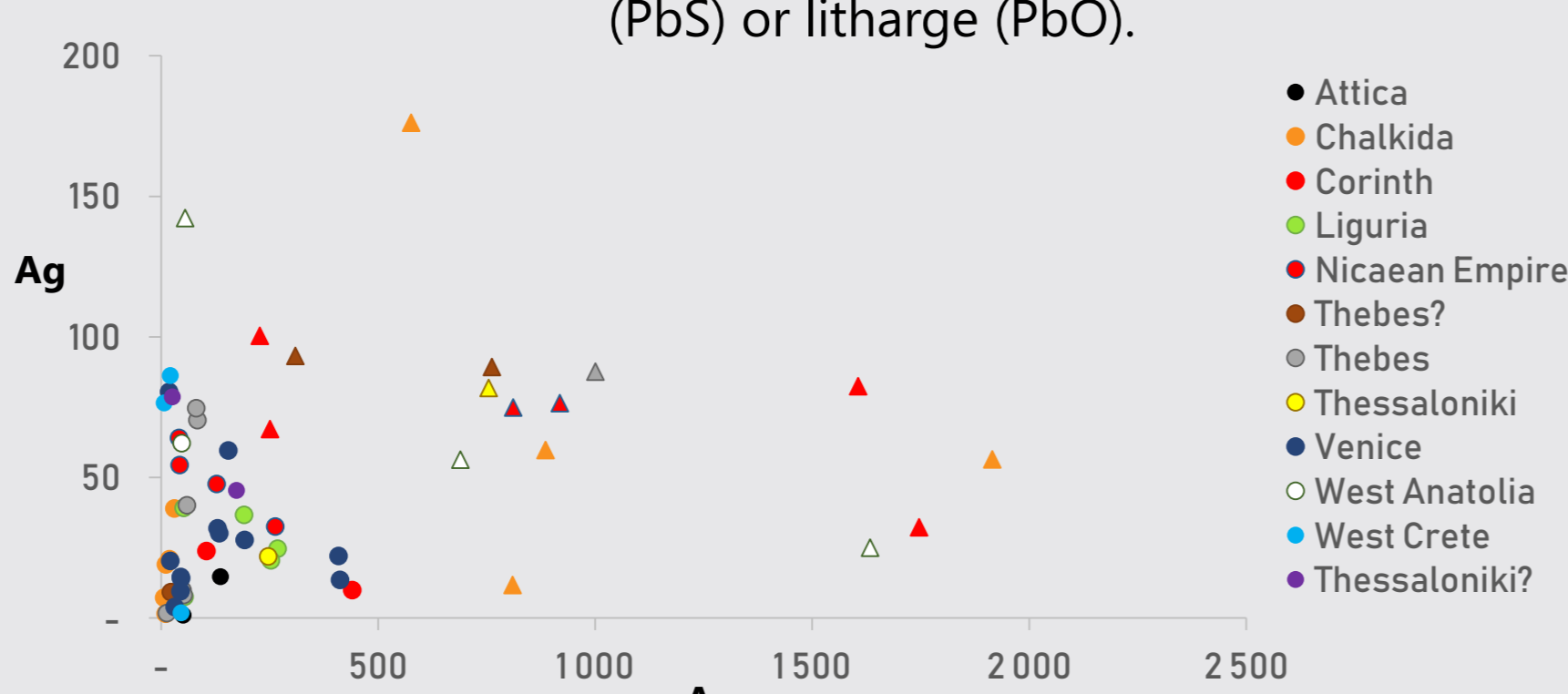
- Greek workshops
- Greek workshops

LA-ICP-MS results



Trace elements informing on the presence of opacifiers: Sn and Sb (in ppm).

- Products from Venetian territories (Chalkida in Euboea, Venice) and Greek workshops of Byzantine tradition (Chalkida, Corinth, Thessaloniki) display **antimonate-based opacifiers** (< 1% wt).
- Products from the Catalan-controlled city of Thebes in Boeotia contain **tin-based opacifiers** (< 1% wt).

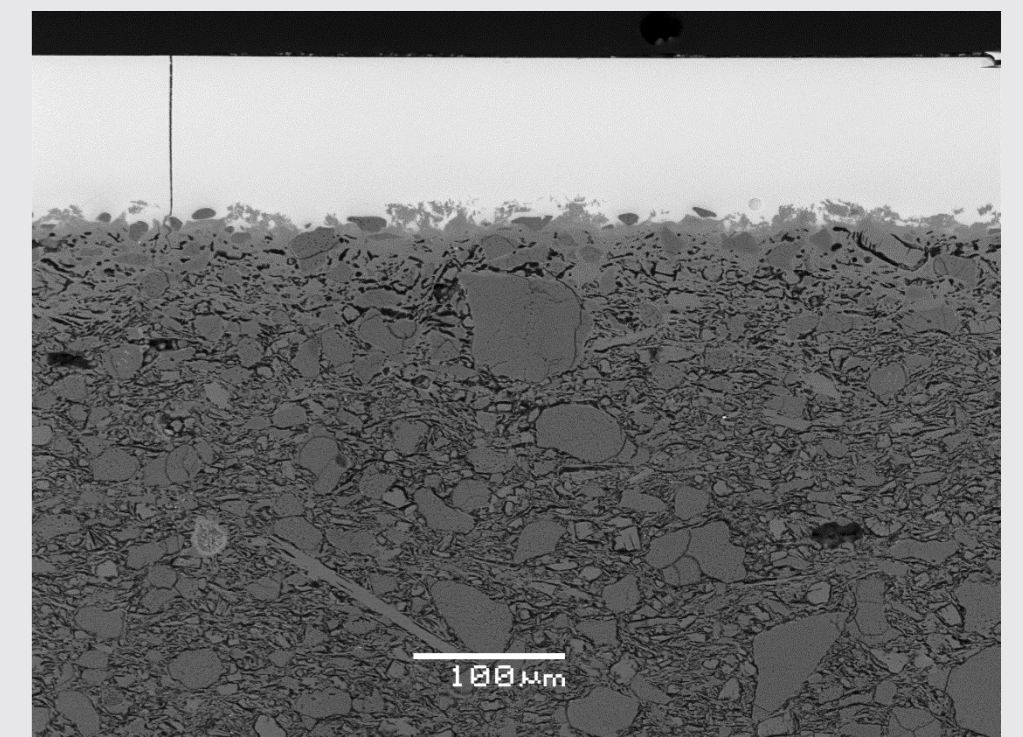


Trace elements that may inform on the processing of lead: As / Ag (in ppm)

- Several products from workshops of Byzantine tradition contain traces of As (>250 ppm) or Ag (>50 ppm): Chalkida, Corinth, Thessaloniki, Anatolia (▲).
- Most products from Latin territories have negligible As and Ag contents: Catalan Thebes, Frankish Attica, Venice, Venetian Crete (●).
- This might indicate different processing of lead source in the form of galena (PbS) or litharge (PbO).

SEM-EDS results

- **SEM** images show homogeneous and transparent glazes, various thickness (between 40 and 100 μm).
- **EDS** indicates that glazes mainly contain SiO₂, Al₂O₃ and PbO and others fluxes in different proportion (depending to the chronological period) → change of recipes?



▲ Example of representative glaze

EDS detected Boron within glazes

Presence OK ✓ but what about B₂O₃ concentrations?

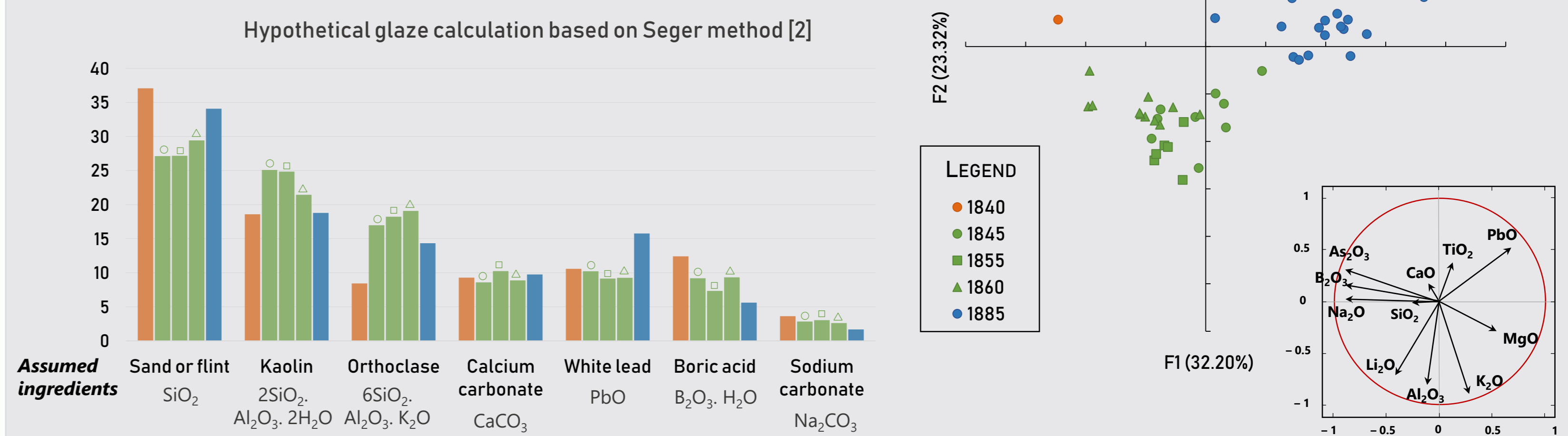
	SiO ₂	Al ₂ O ₃	PbO	K ₂ O	Na ₂ O	CaO	B ₂ O ₃
○ 1840 - DJ & C ^{ie}	61.3	12.8	15.3	1.53	2.91	5.37	++ (13.3)
○ 1845 - JV & C ^{ie}	58.6	15.9	14.0	3.29	2.19	4.80	+ (10.7)
○ 1855 - JV & C ^{ie}	59.1	15.5	12.6	3.35	2.35	5.93	+ (8.50)
△ 1860 - JV & C ^{ie}	60.9	14.5	13.2	3.58	2.00	4.95	+ (11.5)
○ 1885 - JV & C ^{ie}	58.8	12.1	19.0	2.66	1.22	5.13	n.d.

▲ Chemical composition of the glazes measured by SEM-EDS for different chronological periods (average of samples of the same period expressed in wt %, detection limit of 2σ). ++ and + indicates that B₂O₃ was detected with a detection limit of 2σ and 1σ respectively; n.d. means that, in most cases, B₂O₃ has not been detected.

LA-ICP-MS results

- **Quantitative indications on glaze recipes:**

- Distribution of the glazes composition in **three different production groups** that are chronological homogeneous.
- Evolution of ingredients proportion.



- **PbO** more used in last fabrication period (1885) while, **B₂O₃** represent a significant part of glaze recipes in 1840.

▲ PCA score/loading plot obtained with the LA-ICP-MS data of some detected elements on glazes.

Conclusion and perspectives

- ✓ SEM-EDS results indicate a regional diversity in glaze preparation recipes in the 14th-c. Mediterranean.
- ✓ LA-ICP-MS analyses allowed us to detect the presence of opacifiers and to suggest the possibility of a different treatment of the lead source (in the form of galena, or litharge?) to prepare the glazes.
- ✓ Raman analyses are underway to characterize the crystalline composition of the opacifiers and identify the use of pigments.

- ✓ Determination of glaze chemical composition that evolves with chronological periods (proportion and nature of fluxes, quantity of kaolin, SiO₂ and calcium carbonate).

↳ Evolution and adaptation of the body compositions through time ?

↳ Use LA-ICP-MS results to quantify Laser Induced Breakdown Spectroscopy (LIBS) spectra and to analyse non-destructively glazed white earthenware.

References

[1] Gratuze, B. *Glass characterization using laser ablation-inductively coupled plasma-mass spectrometry methods*. In *Recent Advances in Laser Ablation ICP-MS for Archaeology*, Series: Natural Science in Archaeology; Dussubieux, L., Goltko, M., Gratuze, B., Eds.; Springer: Berlin/Heidelberg, 2016; pp. 179–196.

[2] Rhodes, D. *Terres et glaçures : Les techniques de l'émaillage*. Dessain et Tolra: Paris, 1976; pp. 87–95