

PIXE contribution for a database of Phoenician pottery in Lebanon

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ABSTRACT

The study the ancient Phoenician cult place of Kharayeb, in the rural hinterland of Tyre, southern of Lebanon, dated to the Iron Age and Hellenistic periods is particularly helpful in evaluating the complexity and variability of the so called “Hellenism” and of “Greek cultural influences” in the Phoenician world. The PIXE analytical technique was used to characterize the elemental composition of several artefacts from this archaeological site, mainly figurines and some artisanal objects, with an attempt to analyze geological samples that could be potential clay sources in the area. Furthermore, the PIXE information about the composition of the studied objects helped to understand if the figurines were locally produced or imported from the coast and how was the process of production connected to the sanctuary. Hence, particle induced X-ray emission technique PIXE was used to determine the elemental composition of about 57 excavated fragments of figurines and pottery from Kharayeb site, as well as from two another archaeological sites, Jemjim and Tyre which is the prestigious city of antiquity, located on the eastern Mediterranean coast. Then, PIXE analyses with multivariate statistical methods were used to compare and to reveal characteristic groups. Finally, PIXE technique contributed to establish a first database of chemical composition of Phoenician pottery, which will broaden the existing database currently related only to archaeological pottery from coastal sites in Lebanon. Therefore, this work will probably be used for any future archaeological study on Phoenician pottery in the Phoenician colonies in the Mediterranean basin.

1. Introduction

The study of pottery is no longer limited to the morphological and functional aspects, but has been expanded to include examination of the production techniques, from the time when the clay is fired and fabricated by the potter. The many questions that the archaeologists are facing include: the determination of the provenance of the artefacts and location of production centers, or at least outlining the likely geographical areas of origin. Modern archaeometric techniques are sometimes able to respond to these problems and may also help to highlight differentiating factors of the artefacts at a technological level. The first use of ion beam analysis techniques IBA, in particular PIXE, to study archaeological artifacts dates back as early as these techniques were applied to characterize materials, such as obsidians, gemstones, ceramics, glass and more recently pigments [1]. Indeed, PIXE technique has already shown to be sensitive enough to characterize production workshops, at particular period, as well as to determine the provenance

of excavated potsherds, hence valuable insight into ancient trade connections can be determined. The use of PIXE technique with multivariate statistical methods attributed certain “carrot amphorae” found in southern France to Beirut production of the Roman period [2]. On the other hand, excavated ceramics from Beirut were attributed to North Syrian production from Amrit [3]. Other PIXE studies on Chinese ceramics and porcelain [4,5] were also very useful to characterize these artefacts. In this work, it is proposed to apply this technique to various excavated materials, some figurines and ceramics, from Kharayeb archaeological site (Fig. 1). This site is located in the hinterland of the vicinity of the prestigious city of antiquity Tyre, locally named Sour, and located at the eastern Mediterranean coast (85 km south of Beirut). The elemental composition provided by PIXE on the 12 most abundant elements, ranging from Mg to Zr, was used in a multivariate statistical program to identify and classify into groups the studied objects, with the objective to answer some of the questions raised by the archaeologists. It can provide information about the ancient technique of

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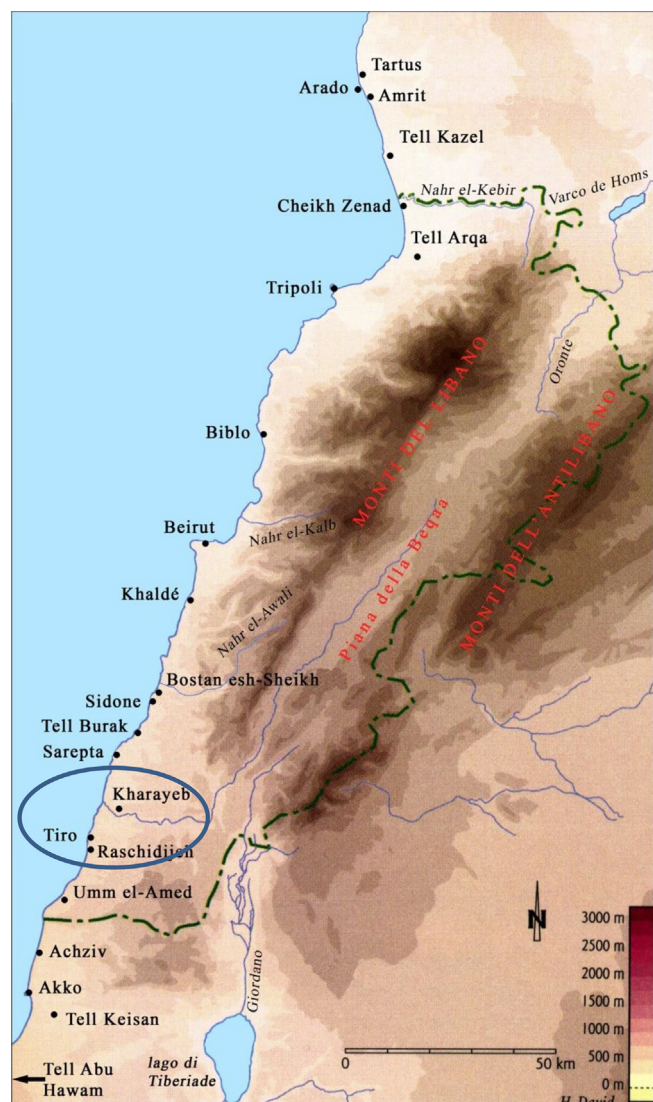


Fig. 1. Map of the Lebanese Coast on Eastern Mediterranean sea, showing as encircled the studied archeological site of Kharayeb, linked to Phoenician period, with its neighboring site of Tyre, the famous city of antiquities.

pottery production, sources of used clay and link to workshops of coastal sites could be obtained. Therefore, some clues could be revealed about the life of ancient society, the movement of artisans, the spread of know-how and people from the coast to the hinterland.

2. Archaeological context

The study the ancient Phoenician cult place of Kharayeb, in the rural hinterland of Tyre, southern of Lebanon, dated to the Persian and Hellenistic periods is particularly helpful in evaluating the complexity and variability of the so called “Hellenism” and of “Greek cultural influences” in the Phoenician world [6,7]. Earlier excavations focused on a rectangular building, so-called *favissa* (a deposit near the temple). This cult place was intensely frequented between the seventh and the first cent. B.C. and so many objects were collected. In this context, it is crucial to understand if the figurines were locally produced or imported from the coast and how was the process of production connected to the sanctuary. Besides, it will be very helpful to obtain information about the technique of production of ancient pottery workshops of this area. The comparison between materials of different periods can give us information also about change in the productions (manufacturing technology and cooking temperatures) during the transition from the

ancient system of production, typical of the Iron Age, to the new system of the Hellenistic period (with the introduction of the double mould technique). Therefore, the PIXE method was applied to 57 excavated fragments of figurines and pottery: 32 from Kharayeb (named from LB582 till LB614), 13 nearby site Jemjim (LB627 till LB639) and 12 from the coastal archaeological site of Tyre (LB615 till LB626). Beside figurines, ceramic objects of different periods are among the studied samples (Fig. 2). Selection of the samples to analyze has been done on the base of specific criteria, not exclusively of quantitative character. Therefore, the database will be formed using different attributes: the mineral and chemical aspect of the clay and “cultural” elements like the chronology and the function of the objects.

3. Experimental

3.1. Sample preparation

After surface removal, the samples were heated for one hour at 950 °C to eliminate the organic elements and the humidity. Afterward, the fragments were grinded into small grain sizes, far smaller than the beam size (~2–3 mm), and hence a better homogeneity of the samples is achieved. The resulting powder was pressed and transformed to pellets (~1 mm thick and ~1 cm of surface area). To ensure conductivity and to prevent charge build-up, samples were covered by a very thin carbon layer (< 10 µg/cm²).

3.2. Set-up and PIXE protocol

The elemental composition of the archeological ceramics was determined by using proton beam of 3 MeV and 13 µC of integrated charge on the samples placed in a conventional in-vacuum PIXE chamber of the 1.7 MV tandem Pelletron accelerator [8] of the Lebanese Atomic Energy Commission. However, instead of the Si(Li) detector, the target chamber houses now an AMPTEK silicon drift detector SDD with 30 mm² (collimated to 17 mm²) of active area, 8 µm Be window, 0.5 mm Si crystal and a resolution of 130 eV at 5.9 keV. If needed, a PIPS particle detector is present to collect simultaneous spectra in RBS mode of the analyzed samples. The PC-controlled multi-sample wheel can allow moving the sample in small steps around the beam center which enables to analyze a larger surface of the sample. Since one X-ray detector is used, two-run measurements, using respectively 1 MeV and 3 MeV protons, should be used in order to determine both major and trace elements [2]. However, the use of a pinhole aluminum filter (also called funny filter), of 250 µm of thickness and used as X-ray absorber, could allow a good simultaneous detection of both lighter (10 < Z < 27) and heavier elements (Z > 26) in the same spectrum [9]. Thus, a time consuming is avoided, in particular when having a large number of samples. While it is reasonably straightforward to characterize a normal foil as X-ray absorber, this is not the case for a funny filter [10,11]. In fact, its main characteristic parameter, which is the fractional pinhole size or the ratio between the whole area and the surface of the detector, was determined experimentally and found to be equal to 0.21%. This essential determination was realized by analyzing a set of thin film standards (Micromatter® reference materials).

The different PIXE spectra were processed with the GUPIXWIN package (Windows version of the Guelph PIXE software package) [12].

4. Results and discussion

Using 250 µm thick aluminum pinhole filter, it was possible to determine more than 20 elements in one spectrum (i) Na, Mg, Al, Si, S, P, Ca, K, Ti, Mn and Fe as major and minor elements, and (ii) V, Cr, Ni, Cu, Zn, Ga, As, Rb, Sr, Y, Zr, Nb, Ba and Pb as trace elements. Prior to the measurements, some reference powder materials, such as the basalt geological standard BEN [13], were analyzed as thick targets. The pinhole filter offered good detection sensitivity for the elements that



Fig. 2. Some of the figurine samples, dated to the Persian and Hellenistic periods, which were characterized by PIXE. They were found among huge number of artefact objects in excavations of the Kharayeb site.

Table 1

Elemental composition of some of the studied samples, with the reference geo-standard the basalt BEN (the certified values are shown between brackets), obtained with 3 MeV protons and Al “pinhole filter”. It shows also two selected geological samples (S1 and S2) from the surrounding area that could be probably one of the clay sources. The concentrations of oxide forms of the major elements, as well as their corresponding limit of detection (LOD), are shown as wt%, while those of the trace elements are in ppm.

	BEN	LB582	LB583	LB584	LB615	LB616	LB638	LB627	S1	S2	LOD**
MgO	11.01 (13.55)*	1.19	1.69	1.59	1.57	1.56	1.97	1.59	0.29	1.14	0.174
Al ₂ O ₃	11.78 (10.39)*	7.89	12.24	11.48	15.37	15.3	13.62	13.24	3.54	6.54	0.125
SiO ₂	39.38 (39.41)*	24.82	34.15	32.35	43.59	45.55	49.87	51.07	8.61	21.55	0.171
K ₂ O	1.40 (1.43)*	0.85	1.86	1.85	2.38	2.33	1.85	2.21	0.2	0.59	0.018
CaO	14.29 (14.31)*	57.67	41.7	44.69	27.59	27.29	24.99	23.82	84.81	64.69	0.046
TiO ₂	2.72 (2.69)*	0.81	0.81	0.77	0.97	0.88	0.87	0.78	0.25	0.67	0.027
Fe ₂ O ₃	13.19 (13.25)*	5.46	5.61	5.23	6.53	6.11	4.99	5.15	1.71	3.94	0.029
Ni	230 (275)*	58	69	73	62	65	51	55	42	45	14
Cu	62 (74)*	60	433	466	84	26	40	32	53	43	7
Zn	123 (123)*	91	213	353	149	138	135	101	72	60	5
Rb	54 (48)*	36	91	86	104	95	87	72	7	44	3
Sr	1574 (1413)*	931	1111	1181	507	579	525	593	1323	490	5
Zr	288 (273)*	115	110	125	171	165	101	310	44	149	30

* Certified working values based on dried powder after heating.

** Average limit of detection.

will be used in the cluster analysis (Table 1). However, its use contributed to the deterioration of the detection limit for Na (0.5% in average for the whole analysed samples) and hence a consequent quantification for such low content was less accurate. Nevertheless, this Na determination was not needed for the purpose of cluster analysis, since the Na determination was just used to complete the elemental composition to 100%. In fact, for such samples, the sum of major elements under oxide forms could approximate 100% when humidity and organic elements are eliminated during sample preparation. Thus, any possible inaccuracy in the determination of the beam charge and the solid angle, that are mandatory for the quantification, could be avoided.

Because the samples could not be differentiated based on the concentration of a single element, a hierarchical cluster analysis was performed, using a multivariate statistical software code, to group together

objects having comparable elemental compositions. The statistical analysis method, using STATISTICA software code, was applied to the GUPIX data matrix, containing the sample identification and the concentration of the most abundant chemical elements determined by PIXE analysis: MgO, Al₂O₃, SiO₂, K₂O, CaO, TiO₂, Fe₂O₃ as major elements and Ni, Cu, Zn, Rb, Zr and Sr as trace ones (Table 1). The data was standardized before clustering [14], to make all compositional elements contribute equally to the discrimination process. Indeed, cluster analysis was applied to standardized data, using Euclidean distance as the distance measure and unweighted pair-group centroid as the linkage rule [15].

Consequently, one can see the formation of a dendrogram (Fig. 3) with a big group having most samples from the three sets (41 samples among 57) and ranging from LB637 till LB587. Unlike the other studies

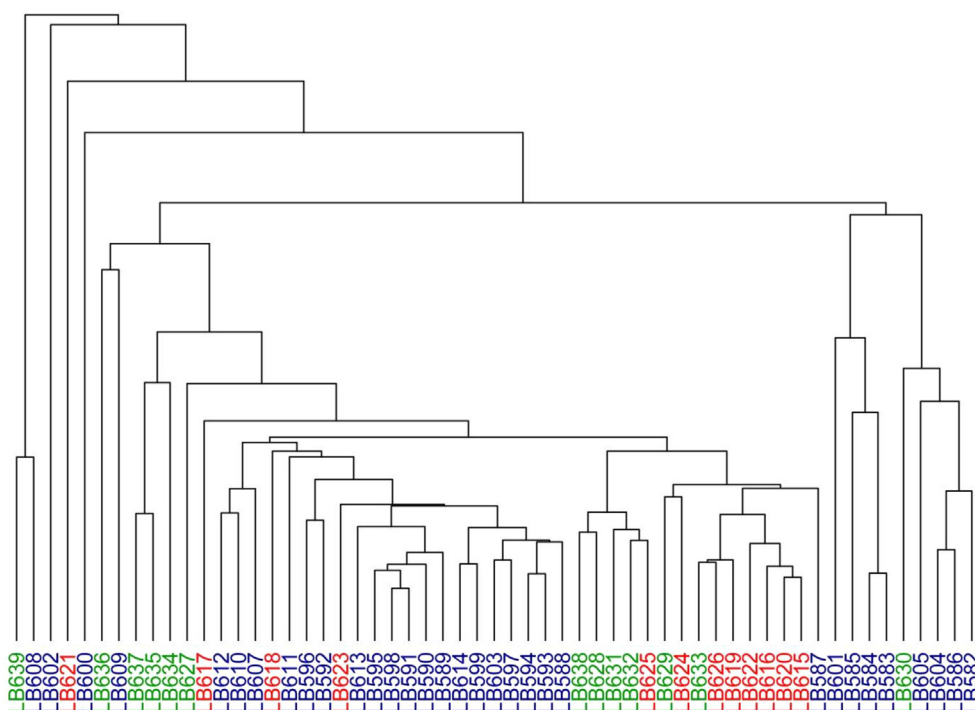


Fig. 3. Hierarchical cluster analysis based on the standardized concentrations of 13 chemical elements, of about 57 samples, including mainly figurines and other pottery from Kharayeb (blue), and compared with ceramics from Tyre (red) and Jemjim (green) sites. One can see a main group containing 41 samples with sub-groups. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 2

Average of the elemental concentration m and standard deviations σ for the main characteristic group containing 41 samples from the 3 sites. The concentration is wt% for the oxides and in ppm for trace elements.

	m	σ	min	max
MgO	1.57	0.37	0.68	3.05
Al ₂ O ₃	14.4	1.42	11.5	16.8
SiO ₂	43.9	5.55	34.3	58.1
K ₂ O	1.97	0.43	0.95	2.61
CaO	29.3	5.99	17.2	41.7
TiO ₂	0.92	0.09	0.74	1.13
Fe ₂ O ₃	6.39	0.61	4.99	8.19
Ni	75	16	42	127
Cu	43	23	19	135
Zn	154	59	74	487
Rb	89	17	43	117
Sr	650	135	460	1152
Zr	174	47	101	310

undertaken till now, the main specificity of this group is its unusual high content of calcium (Table 2). In general, the CaO concentration, of the whole analyzed samples, showed high values that ranged between 17.2% and 57.7% (as wt%), with the exception of the two samples of ceramic fragments, LB608 from Kharayeb and LB639 from the nearby Jemjim site. These two samples have around 3% only of CaO and are grouped together at the extreme left of the dendrogram (Fig. 3). The main characteristic of the specified group are presented in Table 2.

However, some sub-groups can be revealed within this main group, where it is worthy to notice some observations. Indeed, the statistical analysis confirms the idea that the figurine dated to the 8th and 5th century BCE were produced in workshops using different sources of clay than those used by the artisans of Hellenistic period. The group of Hellenistic period, in fact, is strictly connected with the group of samples from Tyre. It is known that the mould techniques used for the production of the figurines were originally introduced in the area from the large production centers of Hellenistic periods such as Alexandria in Egypt. It is probable that artisans working in relation with the religious structures dedicated to the cult of Egyptian gods were present in Tyre where the existence of a cult of Serapis (inscription dated to the 3th

century BCE) is known. The similarity of the clay from Tyre (even if used for pottery of the Iron Age Period) with that of the Hellenistic production of the figurine from Kharayeb suggests that figurines were produced in some big workshops of Tyre and then simply sell in some shop near the cult place. The production of figurines in the Iron Age and Persian period seems different and connected to other places than Kharayeb, maybe imported from other parts of the country.

These first results, and the related interpretations, are only the first step and give a roadmap for a long course of research. Further investigations should consider comparison of the obtained data with coroplastic materials of Hellenistic period from Tyre. In fact, currently the local potters use clay from different parts of the region Furthermore, a geological approach should be undertaken in order to understand the characteristic of the used clays. A first set of geological samples was collected and analyzed but need further interpretation from a geologist point of view. Indeed, in an attempt to find probable sources of clay, analysis of some geological samples from the surrounding area showed a high content of calcium oxide ranging from 57% to 85% (Table 1). In addition, thin section analysis was performed on selected samples where three main types of inclusions were found in silt and sand size and include quartz, carbonates and hematite. The presence of these inclusions possibly indicates the use of the easily accessible Early and Middle Eocene nummulitic limestone and marls found on the southern Lebanese coast and especially in the area of Tyre [16].

5. Conclusion

In this study, PIXE analytical technique was used to characterize the elemental composition of figurines and other excavated pottery, having Phoenician characters, from the hinter archeological site of Kharayeb in southern Lebanon. The application of statistical analysis on the determined PIXE results showed a compositional similarity between the samples of the Hellenistic period with the samples from Tyre, the coastal site. In fact, Tyre is a historical site, known for its long time prosperity as an important center of ceramics production and maritime trade for several centuries (IV B.C. till XIII A.D.). This suggests that most of the figurine samples from Kharayeb are produced in Tyre and the other samples could be imported from other areas in the country.

However, the main characteristic of most of the samples is the unusual high Ca content which characterizes the geological area surrounding the 3 archeological sites (Tyre, Jemjim and Kharayeb). Finally, the available database on excavated pottery from coastal sites in Lebanon and corresponding to different periods (mainly Roman and Byzantine) is consolidated with Phoenician artefacts.

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References

- [1] L. Beck, Nucl. Inst. Meth. B 332 (2014) 439.
- [2] M. Roumié, S.Y. Waksman, B. Nsouli, S. Lemaitre, P. Reynolds, Nucl. Inst. Meth. B 215 (2004) 196.
- [3] M. Roumié, P. Reynolds, C. Atallah, E. Bakraji, K. Zahraman, B. Nsouli, Nucl. Inst. Meth. B 249 (2006) 612.
- [4] H.S. Cheng, Z.Q. Zhang, J. Song, M.H. Gao, D. Zhu, J.W. Lin, S.L. Feng, Nucl. Inst. Meth. B 249 (2006) 601.
- [5] H.S. Cheng, Z.Q. Zhang, B. Zhang, F.J. Yang, Nucl. Inst. Meth. B 219–220 (2004) 16.
- [6] M. Chehab, Syria 32 (1955) 327.
- [7] I. Oggiano, et al., BAAL 16 (2016) 193.
- [8] M. Roumié, B. Nsouli, K. Zahraman, A. Reslan, Nucl. Inst. and Meth. B 219–220 (2004) 389.
- [9] M. Roumié, B. Nsouli, C. Atalla, S.Y. Waksman, Nucl. Inst. and Meth. B 227 (2005) 584.
- [10] J.F. Harrison, R.A. Eldred, Adv. X-ray Anal. 17 (1973) 560.
- [11] Z. Nejedly, J.L. Campbell, S. Gama, Nucl. Instr. and Meth. B 219–220 (2004) 136.
- [12] J.L. Campbell, N.I. Boyd, N. Grassi, P. Bonnick, J.A. Maxwell, Nucl. Inst. and Meth. B 268 (2010) 3.
- [13] Geostandard Newsl., 13 (Special issue) 1989.
- [14] H.C. Romesburg, Cluster Analysis for Researchers, Lifetime Learning Publications, Belmont, 1984.
- [15] B.S. Everitt, Cluster Analysis, Hastled Press, New York, 1993.
- [16] C. Walley, Lebanese Sci. Bull. 10 (1) (1997) 81.