Pigment Analysis of Wall Paintings and Ceramics from Greece and Cyprus. The Optimum Use of X-Ray Spectrometry on Specific Archaeological Issues

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This paper deals with archaeological issues which lend themselves to a simple but very effective treatment by means of x-ray spectroscopy. The common feature of all the samples presented here is that they can be reduced to a simple spectroscopic question concerning the presence or absence of certain chemical elements in the ancient pigments. Copyright © 2000 John Wiley & Sons, Ltd.

INTRODUCTION

The identification and quantification of the elements that compose objects with an archaeological interest provides a first strong indication for the origin of the raw materials and the technology applied in their production. In some cases (in metals or pottery materials) the concentration of the minor and trace elements might also address the question of age and provenance of the objects. The strong requirement by archaeologists and curators for the exclusive use of non-destructive analytical techniques during the examination of archaeological material makes x-ray analytical techniques a unique tool in the understanding of the cultural heritage.[1,2] The variety of the analytical techniques that have been developed over the last three decades, employing different excitation probes (ion or x-ray beams) and instrumentation, have successfully addressed the above questions in a very effective way. For example, the external proton induced x-ray emission (PIXE) technique with variable incident proton energy allows the determination of the elemental depth concentration profile of pigments and thus the arrangement of paint materials in definite layers.[3] In addition, when PIXE is combined with the Rutherford backscattering (RBS) technique, the characterization of the surface composition relative to the bulk, e.g. slip versus fabric in pottery materials, can be achieved.

However, x-ray techniques based on energy dispersion (PIXE, x-ray fluorescence) are suitable for determining only the elemental composition and not the chemical or geochemical form of the materials analysed. This certainly is a disadvantage, especially in pigment analysis. If archaeologists can provide some additional material so that x-ray diffraction (XRD) techniques may also be applied, the combination of the two methods is a powerful tool for the understanding of ancient pigment technology. If not, x-ray fluorescence alone may provide answers in cases where only well-defined questions have been posed, whose answer relies on the resolution of a given dichotomy. In the case of Bronze Age wall paintings from Knossos, Thera, Pylos, Tiryns and Mycenae, for instance,[4] the blue pigments identified were either the natural glaucophane, $Na_2(Mg,Fe)_3Al_2Si_8O_{22}(OH)_2$, from the amphibole group, or the synthetic Egyptian blue, $CaCuSi_4O_{10}$. The diagnostic elements in this case are Fe and Cu, respectively, and the question is whether glaucophane or Egyptian blue is spectroscopically translated to Fe or Cu.

A number of case studies dealing with similar questions which were undertaken by the authors during the last quarter of a century are presented chronologically, admitting simple qualitative but definite answers, and are discussed in terms of their archaeological relevance.

1976; BRONZE AGE WALL PAINTINGS: GLAUCOPHANE OR EGYPTIAN BLUE?

In the course of a broad research project dealing with systematic analyses of the inorganic pigments from the wall paintings discovered at Knossos, Thera, Pylos, Tiryns and Mycenae,[4–6] the blue pigments presented an intriguing chronological variation scheme in the case of Thera and Knossos (Fig. 1). The colour palette in the Bronze Age was mainly based on mineral pigments (i.e. goethite, limonite) and carbon for the red, yellow and black. The blue was either the well known Egyptian blue, the synthetic pigment produced in Egypt and imported to Greece as described in detail by Tite *et al.*,[7] or glaucophane, a hydrous sodium magnesium aluminium silicate mineral rich in iron from the amphibole group. Different shades and colour variations were obtained by mixing or overpainting the above basic colours.

The 50 samples of blue pigments selected were analysed by the x-ray fluorescence technique. A few milligrams of the pigment were placed on a thin Mylar sheet
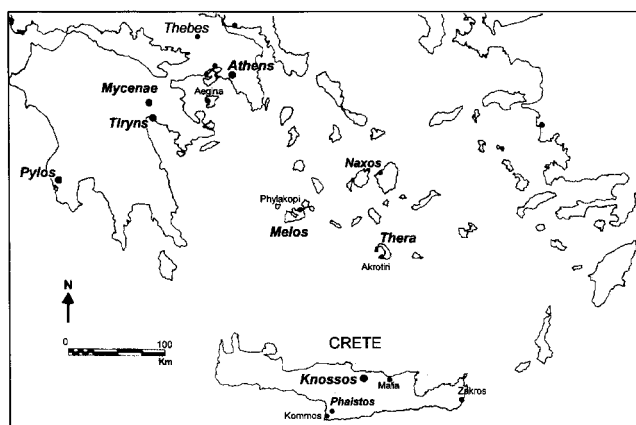
Figure 1. Map of Greece and Cyprus showing the places referred to in this paper.

and analysed. The elemental concentrations were estimated on a semiquantitative basis by normalizing all peak intensities to the strongest one.

According to the XRF data,[4] the samples were divided into three types. type A [Fig. 2(a)]: the dominant element is copper with significant Ca content. Pb, As, Sr, Sn as trace elements and Fe of the order of a few percent normalized to Cu were also detected. Type B [Fig. 2(b)]: the dominant element is iron with traces of Ti, Mn Rb, Cr, Ni, Y. The total absence of Cu is characteristic of this type. Type C: iron is the prominent element with varying amounts of copper.

The above analyses were complemented by x-ray diffraction and petrographic examination[4,8] that correlated type A with the presence of pure Egyptian blue, type B with glucophane and type C with a mixture of glaucophane with Egyptian blue. As shown in Table 1, Egyptian blue was used at all five sites. The samples from the palaces of Mycenae, Tiryns and Pylos (Mainland in Table 1) dated after 1400 BC and the samples from Knossos after 1500 BC show exclusive use of pure Egyptian blue (type A). For dates earlier than 1500 BC the Knossos pigments indicate use of the Egyptian blue as early as ca 3000 BC. The glaucophane was identified only in Middle and Late Bronze Age samples dated earlier than 1700 BC and not later than 1500 BC and in most Theran samples from the destruction level of Akrotiri due to the volcano eruption are dated before 1500 BC. In both Knossos and Thera, type C blue, i.e. mixtures of the two pigments, is associated with Late Minoan I period and the late part of Middle Bronze Age. Although glaucophane occurs as a mineral in both Thera and Crete, its presence has not been established in the geographic area from Knossos. The introduction of glaucophane in the colour palette of Minoan wall paintings was attributed to Theran artisans and in view of the extended relationship between the two settlements its presence in the wall paintings from Knossos was explained as an import from Thera. This claim is further supported by its abandonment after ~1500 BC or rather after the end of Late Minoan IA defined by the eruption of the volcano in Thera which destroyed the island. The discussion above is not affected by the absolute chronology of the Thera eruption. A recent analysis of well documented specimens from the wall paintings of the Xesti 3 (basically rooms 3 and 15, but also from the staircase of room 5), the House of the Benches and some other parts of the excavation area at Akrotiri (Sectors A, B and C),[9] verified the scheme of the parallel use of both pigments in Thera, included in Table 1. This last publication allowed a more precise identification of the mineral in the form of riebeckite $Na_2(Fe^{2+}, Mg, Fe^{3+})_3Si_8O_{22}(OH)_2$, which like glaucophane belongs to the group of amphiboles. Also the presence of exactly the same mineralogical phase in the 'glaucophane' blue pigments from Knossos pointed decisively to the Theran origin of the pigment.[8]

Another interesting result of the work by Filippakis et al.[4] was the identification of Egyptian blue in Knossos
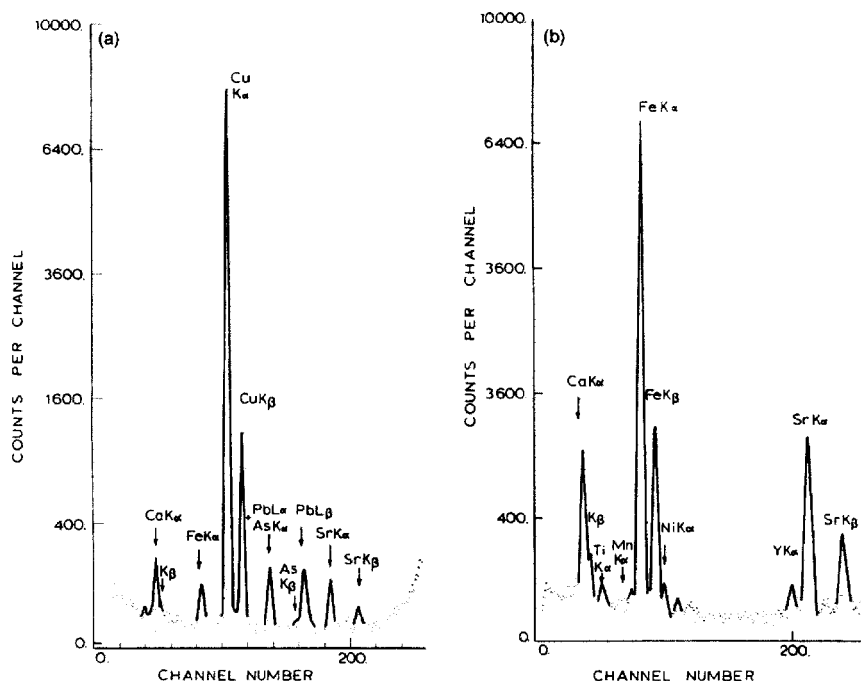

Figure 2. Typical XRF spectra of blue pigments based on (a) Egyptian and (b) glaucophane blue.

Table 1. Overview of the blue pigment distribution as a function of provenance and chronology (● = Egyptian blue (presence of Cu); □ = amphiboles (glaucophane, presence of Fe); ▲ = mixture of both (presence of both Cu and Fe))

Calendar year BC	Knossos (Ref. 4)		Thera (Ref. 4,8)		Mainland (Ref. 4,8)	
	Historical scale	Pigment type	Historical scale	Pigment type	Historical scale	Pigment type
1300	Late Minoan LM III 1,2	● =1	Late Cycladic		Late Helladic III	● =18
1400	Late Minoan LM II	● = 3			Late Helladic I,II	
1500	Late Minoan LM I A,B		Low age ▲			
1600	Middle Minoan MM III A,B	□ = 4 / ▲ = 5	Volcano eruption / High age ▼	● = 6 / □ = 18 / ▲ = 7		
1700					Middle Helladic	
1800	Middle Minoan MM II A,B	● =1	Middle Cycladic			
1900	Middle Minoan MM I A,B					
2000		● = 4	Early Cycladic III	● =1	Early Helladic	
2100	Early Minoan EM III					

as early as the 3rd millenium BC that coincides with the first appearance of the pigment in Egypt during the 4th Dynasty. This observation which contradicts earlier assertions by Sir Arthur Evans[10] led the authors to raise interesting archaeological questions introducing the idea of a simultaneous local production of the synthetic blue pigment in early Minon Crete, which still remain to be addressed.

1989; LATE BRONZE AGE WALL PAINTINGS FROM THERA: EARTHEN OR MARINE PURPLE?

Contrary to the previous study, the question to be answered here concerns a single sample of a purple material found in 1969 in Akrotiri, Thera. The material was sampled for comparison with the pigments of Theran wall paintings within the framework of a larger pigment analysis study as a follow-up of the work described above. The visual examination of the material was compatible with a ferruginous nature (i.e. ochre). However, the non-destructive XRF analysis of about 50 mg of this very light and powdered material (Fig. 3) revealed a calcitic matrix (Ca 34%) with a low Fe content (1.5%) combined with very high Br concentration (5300 ppm). Traces of Mn (2300 ppm), Cu (600 ppm) and Zn (600 ppm) were also detected. In general, bromine offers a very powerful discriminating criterion between marine and terrestrial environments. Br occurs in the hydrosphere as soluble bromide salts. Its concentration in seawater is 65–70 ppm whereas in the earth's crust and streams are only 4.0 and 0.02 ppm, respectively. This is further accentuated between the marine and terrestrial biosphere (seaweed, sponges, shells, plants, etc.) owing to the formation of organic bromine compounds. The use of bromine and its compounds as a tracer of the contact between seawater and sea-salt with ceramic and lithic artifacts is the subject of an on-going research project.[11]

In the case of the purple Theran material, the high Br concentration strongly indicates a Br-enrichment mechanism which naturally led to the possible presence of an organic dye. More specifically it pointed to the precious 'royal' or 'Tyrian' purple, based on 6,6-dibromoindigotin, $C_{16}H_8N_2O_2Br_2$, derived from
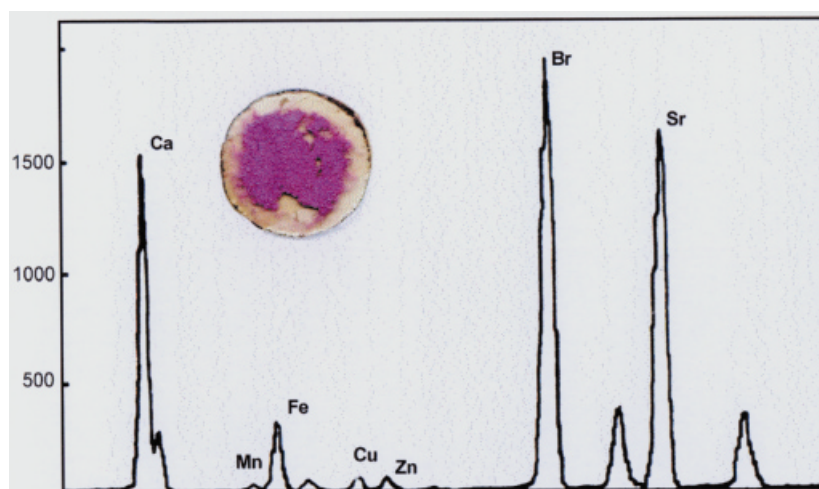
Figure 3. XRF spectrum of the purple material from Akrotiri, Thera (inset photograph), showing high Br concentration.

murex shells (*Murex brandaris* and *trunculus*) and related species (*Purpura haemastoma*), which was identified by Friendländer in the beginning of the century.[12]

The organic nature of the dye was confirmed by dissolving a small quantity in HCl and treating the solution with $CHCl_3$ and observing the purple colouring in the phase of the solvent. A stoichiometric calculation of Br content in the molecule of 6,6-dibromoindigotin leads to 1.5% (w/w) for the dye compound contained in the sample.

XRD analysis of the bulk material indicated the abundant presence of aragonite and calcite. The presence of aragonite, which is the characteristic phase of $CaCO_3$, in sea-shells combined with the high Br concentration led to the conclusion that the material in question originated from crushed and pulverized live molluscs possibly followed by sieving, thus leading to a concentrated dye. The original study[13] suggests a cosmetic use of the material although its use as a wall painting pigment cannot be excluded, especially in view of a recent identification of the material in Minoan wall- paintings from the Minoan Palace at Malia,[14] Crete (Fig. 1). Subsequent analysis of pigments from Theran wall paintings[9] based on the use of analytical scanning electron microscopy–electron probe microanalysis (SEM–EPMA) would not have been able to detect Br. We therefore believe that all future analyses of wall paintings, Theran or Minoan, should include XRF-based Br detection. This becomes particularly relevant following the advent of portable XRF systems.

Tyrian purple in a calcitic matrix, referred to as 'purpurissum,'[15] had been also identified in most of the purple pigments contained in the ceramic bowls found in Pompeii.[16] It is widely known that Tyrian purple was amongst the most expensive of antiquity's goods, reserved for kings, emperors and the upper classes of society. It is also known that Phoenicians dominated the trade of the precious dye in the Mediterranean basin during the historic period. It therefore becomes clear that the evidence of its use in Crete and the Aegean, prior to its introduction by Phoenicians, is obviously important for the prehistory of the Aegean.[17,18]

1994–96; CYPRIOT TERRACOTTA FIGURINES: CINNABAR OR OCHRE-BASED RED?

The study of six Cypriot–Archaic polychrome terracotta figurines (750–475 BC) of the Louvre Collection[19] by using the proton induced x-ray emission (PIXE) non-destructive technique of the AGLAE accelerator facility[20] of the Laboratoire de Recherches des Musées de France revealed the presence of cinnabar (mercury sulphide, HgS) in the red pigment of one figurine representing a horse-rider (Fig. 4, left). Interestingly, the blue-green pigment on the same figurine was identified as a zinc-based material, which was initially related to the natural zinc carbonate (smisthonite). These observations provided a contrast with the most frequent use of ochre for the red and green earth (celadonite) for the green, detected in the rest of the figurines which have been analysed. The latter two minerals (i.e. iron hydroxides and green earth) are abundant in Cyprus, whereas cinnabar and smisthonite are not known to be present in the island. A plausible explanation was that the use of such pigments, probably imported from Anatolia or even Spain, characterizes the production of a distinct ceramic workshop. The consolidation and interpretation of this suggestive evidence could only be achieved through a large-scale systematic study, which was undertaken during a wider project referring to the diachronic investigation of ceramic decoration techniques in ancient Cyprus.

As a follow-up of the above study, all figurines of the Nicosia Museum collection on which the red paint was still preserved (43 pieces in total) were analysed *in situ* using a portable XRF system. The system was built at the Institute of Nuclear Physics, NCSR Demokritos and consisted of a [109]Cd source, a Peltier-cooled Si(PIN) detector and portable data acquisition and analysis systems.

A typical example of these terracotta figurines that represent singers and musicians, riders and horses, chariots, animals and birds is given in Fig. 5. As shown in a typical x-ray spectrum in Fig. 6(a), the red pigment is an iron-rich material obviously derived by the use of ochre without signs of mercury in their XRF spectra. In view of these results it was then safe to conclude that the presence of mercury sulphide (i.e. cinnabar) in the single

Figure 4. Cypriot terracotta figurines representing a complex of a horse and a rider (Cypriot-Archaic I, ca 750–600 BC), Musée du Louvre. The one on the left (No. AM 235, height 12.3 cm) revealed the unusual presence of cinnabar for the red and a zinc-based material for the green (photograph provided by D. Bagualt).

Figure 5. Cyproarchaic terracotta figurines (750–475 BC) from the collection of the Nicosia Museum analysed *in situ* with a portable XRF system.

figurine in the Louvre Museum must be attributed to post-excavation retouching having taken place in the period 1870–80 when the above terracotta collection was bought by the Louvre Museum. The date coincides with the first introduction of synthetic cinnabar, commonly known as vermilion. As for the blue–green Zn-based pigment, given the restriction of performing exclusively non-destructive analyses, PIXE results alone could not allow the drawing

of any reliable conclusion on the nature of this pigment. We note, however, the introduction of a synthetic blue–green pigment known as Rinmann's green which was based on ZnO with varying CoO content[21] by the end of 19th century.

The collection of 43 figurines was examined in less than 2 h. This illustrates the power of new technology in a case where the archaeological question is very specific.
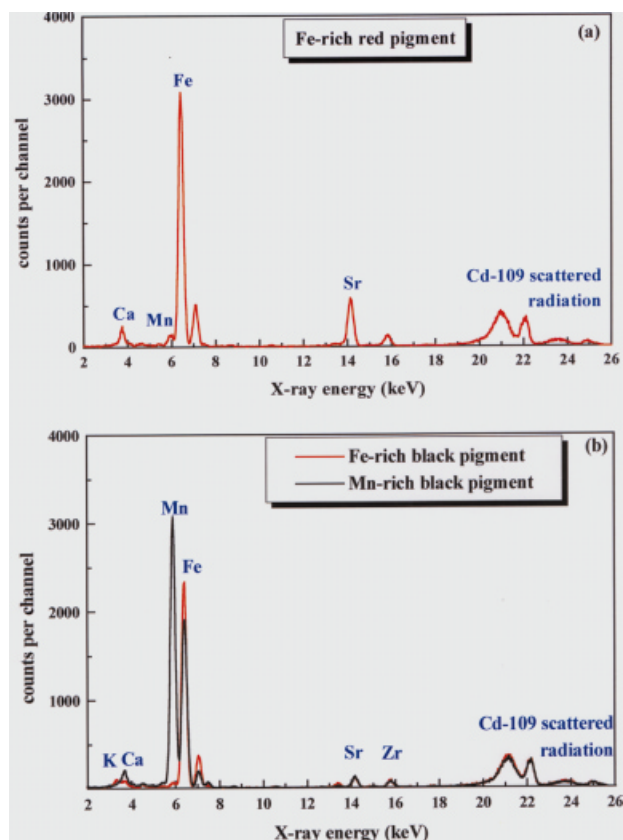
Figure 6. Typical XRF spectra of (a) Fe-rich red pigments and (b) Fe-rich and Mn-rich black pigments on Cypriot ceramics from the Nicosia Museum. The spectra were obtained *in situ* at the Nicosia Museum with a portable XRF system consisting of a Peltier-cooled x-ray detector (XR-100T, 240 eV resolution at Mn Kα and a ^{109}Cd radioactive x-ray source (20 mCi).

A recent analysis of similar terracotta figurines from the Cesnola Collection of the Metropolitan Museum of Fine Arts in New York by the SEM–EPMA technique verified the presence of iron-based red pigment in all figurines examined. The analysis was undertaken in the course of the conservation procedure,[22] as part of the reinstallation of the Metropolitan Museum of the Cypriot galleries scheduled for the spring of 2000. The 230 Cypriot–Archaic figurines of the Cesnola collection constitute one of the most significant collections of these objects and this will be their first exhibition since 1873, when they were brought to New York from Cyprus.

1996; CERAMIC DECORATION TECHNIQUES IN CYPRUS: Fe- OR Mn-BASED BLACK?

Ceramic artifacts provide excellent material against which cultural interactions can be studied since they contain multi-dimensional information with respect to the shape, the style of decoration (incised, painted, plastic), the fabric, the raw materials used, the manufacturing techniques, etc. It is now widely recognized that the investigation of ancient ceramic technology, which was usually based on the analysis of the ceramic body in the past, can be complemented through the analysis of the pigments used for the surface decoration.

The ceramics in the Cyprus Museum in Nicosia provide a complete and comprehensive archaeological collection

for the study, which spans more than 40 centuries from Neolithic to Hellenistic times (5000–325 BC). Owing to the nature and wealth of the material, the first step of the project consisted of an *in situ* survey using non-destructive XRF analysis and examination under a stereoscope, in conjuction with digital recording of visual information (digital camera, 3-D image recording system).[23]

The XRF analysis of 75 ceramic artifacts revealed a very clear chronological pattern in the nature of the ubiquitous black or dark colour [Fig. 6(b)]. Essentially all dark decorations in Cypriot pottery from the Neolithic to the Middle Bronze Age (5000–1625 BC) are based on the use of iron-rich materials. As is well known, iron-rich clays (Fe_2O_3 ∼9–18%) with low CaO (<3%) and relatively high K_2O content (∼3.5–6%) produce dark-coloured pigments when fired in a reducing atmosphere and for this reason the technique is mostly known as 'the iron reduction technique.' From the end of the Late Bronze Age onwards (1050–325 BC), the dark colours were achieved through the use of Mn ores (umbrae). These materials with varying Mn_3O_4 (2.5–15%) and Fe_2O_3 (20–65%) contents produce black or brown easily with firing without any special requirements in kiln atmosphere. Figure 7 summarize the XRF results and shows clearly that the transition between the two dark-colour techniques occurs during the Late Bronze Age (1625–1050 BC) on the so-called White Slip Pottery (WSI and WSII shreds in Fig. 7).

The alternative use of Mn-rich and Fe-based black indicates the use of both different raw materials and firing processes, which consequently point to different technological traditions.[24–26] The latter, seen in the context of the different ethnic origins of the various potters in Cyprus (native Cypriots, Cretans, Mycenaeans, Syro-Palestinians, Phoenicians) during several periods was initially attributed[27] either to the introduction of new production techniques or the resistance of local tradition to external influence. Recent detailed analyses on a well documented sequence of this characteristic Cypriot pottery[28] revealed that the change from Fe-black, in WSI, to Mn-black, in WSII monochrome ware was introduced through the bichrome WSI wares in order to facilitate the simultaneous production of red and black on the same object. Whereas the ancient craftsmen were able to produce black and red, separately, using iron-based pigments, when called upon to produce a bichrome effect they found it more convenient to use Mn for the black. This is understandable if we consider the difficulties of the fine tuning between firing atmosphere and temperature required to produce a bichrome effect based on Fe only.[29] It can then be argued that given the availability of all required raw materials in Cyprus, the subsequent adoption of a more convenient technique for the production of dark monochrome wares [see proto White Painted I (pWPI) and White Painted I (WPI) samples in Fig. 7] and its subsequent spread over the whole island was not surprising.

CONCLUSIONS

It is clear that the use of x-ray-based analytical techniques provide archaeologists with extremely important clues and information about our ancestors' technology, commercial and cultural contacts. In return, physicists who employ
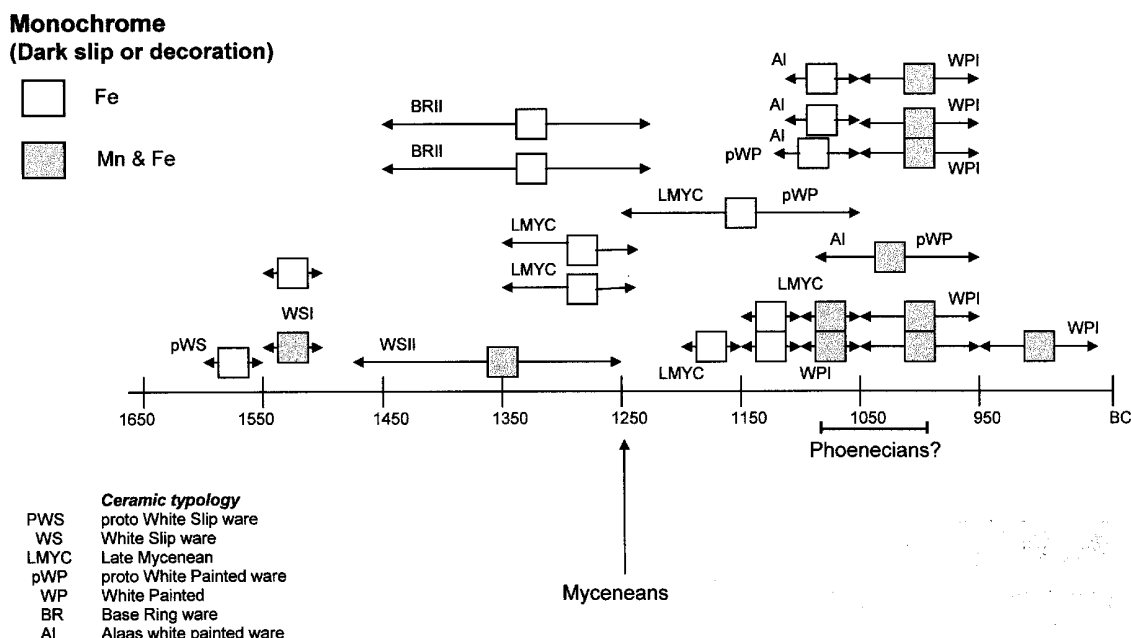
Figure 7. Chronological distribution of Fe- and Mn-based pigments produced by non-destructive *in situ* XRF analysis of 75 Cypriot ceramic artifacts from the collection of the Nicosia Museum. The time-scale focuses on Late Bronze Age objects bearing monochrome dark decoration.

these techniques do share with them the excitement of these discoveries and the joy of a significant participation in the process of understanding our history. Today, all European Union research-funding agencies give significant priority to the understanding and conservation of cultural heritage. We are confident that in this framework, x-ray-based analytical techniques developed so far and the significant expertise accumulated will prove relevant to these projects.

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