X-Ray Fluorescence Analysis of a Gold Ibex and other Artifacts from Akrotiri

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ABSTRACT

The in-situ X-ray fluorescence analysis (XRF) of ancient artifacts from the excavation area of Akrotiri, Greece was performed using novel instrumentation composed of a portable silicon PIN thermoelectrically cooled X-ray detector, a miniature X-ray source, and portable data acquisition devices. The main objective of the analyses was to explore the potential of the XRF technique to provide answers to a wide range of archaeometric questions. Of particular interest was the bulk composition of metal alloys, especially of gold, the characterization of bronze artifacts, identification of inorganic elements which are fingerprints of the minerals used in wall painting pigments, and identification of the painting materials used for the decoration of clay vase surfaces. The results of the in-situ XRF survey, primarily those of the bulk composition and welding technology of the gold ibex, are discussed and compared with existing archaeological literature.

Introduction

At the request and invitation of The Thera Foundation, a group from Amptek Inc. and Photoelectron Corp. journeyed to the island of Thera to analyze various artifacts found at the archaeological site of Akrotiri. Among the analysed artifacts were a unique gold ibex, a bronze dagger and blade, various pigments from the wall paintings of room 3 in Xeste 3, decorative pigments from faience rosettes, a bichrome jug, and other clay vases. Due to the specific characteristics of the instrumentation used, the analysis area was only a few square millimeters, allowing the compositional determination of the various welding locations of the gold ibex and of the rivets in the dagger.

The gold ibex was perhaps the most intriguing object analyzed in that it is the only artifact made of precious metals found at Akrotiri. All other precious objects were removed from the site by the inhabitants before the eruption that devastated the island and buried the settlement beneath meters of volcanic ash. Found during the construction of the pillars for the new shelter in December of 1999, the ibex was in perfect condition. Produced using the "lost wax" method,

Figure 1. The Gold Ibex Figurine with the Amptek XR100CR X-ray detector and the Photoelectron PRS400 X-ray tube.

the legs, neck, tail, and horns were welded after the inside core was removed. The artifact is also of note because it comes from an important public building, conventionally called the "building of the benches," which was in close proximity to the famous Xeste 3 building. The fact that the ibex was found *in-situ* makes its importance even greater, since this object is stylistically unique in the Aegean. Great debate has taken place concerning the origin and purpose of the ibex. It has been theorized that it could have been a gift from someone coming from the East or that it was a sacrificial object related to worship, having been found next to a pile of horns. Of particular interest was the difference in composition between the body of the ibex and the joints of the main body and the legs. A thorough quantitative analysis of the ibex has been completed.

In addition to the gold ibex, various other artifacts were analyzed including a bronze dagger and blade, a bichrome jug, a flower pot, a sauce boat, a pyxis, and wall paintings. At this point, only a qualitative analysis has been performed on these objects.

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Assembling and calibrating the XRF system

The XRF system used consisted of an Amptek, Inc., XR-100CR X-ray detector with power supply and amplifier, a Photoelectron, Corp., PRS400 transmission Au anode X-ray tube with power supply, and an Amptek MCA8000A card for data acquisition. The X-ray detector and tube were mounted on a bracket to create a fixed and reproducible geometry as is required to reduce the time and increase the accuracy of the quantitative analysis. The XRF set-up was calibrated by first measuring and then modeling the output spectrum of the tube. Pure iron, copper, gold, and silver samples were analyzed in the same geometry and appropriate calibration coefficients (sensitivities) were determined. These sensitivities, with the help of a fundamental parameter program, were used to convert the measured characteristic line intensities to corresponding elemental concentrations.
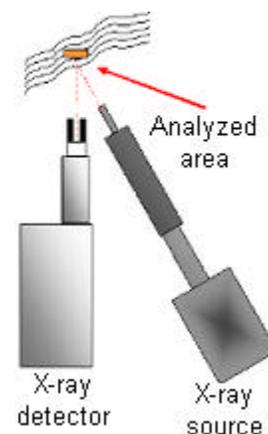
Figure 2. System geometry diagram.

The ibex analysis

Compositional results

Six spectra were taken of the gold ibex. The descriptions of the different locations are provided in Table 1 along with the compositional results. A comparison spectrum of the data of #1 and #4 is shown in Figure 3.

#	X-Ray Tube Voltage	Gold % (Au)	Silver % (Ag)	Copper % (Cu)	Iron % (Fe)	Description
1	40	84.2	15.0	0.49	0.32	Main body
2	30	82.5	15.0	2.25	0.30	Stain/weld under the neck
3	40	84.4	14.7	0.51	0.38	Near weld of rear left leg
4	40	82.4	14.5	2.80	0.38	Weld at the tail
5	30	84.7	14.4	0.55	0.37	Right horn
6	40	83.4	15.7	0.66	0.29	Bottom red spot
Ave.	--	83.6	14.88	0.55 no weld 2.53 weld	0.34	Average of the 6 runs

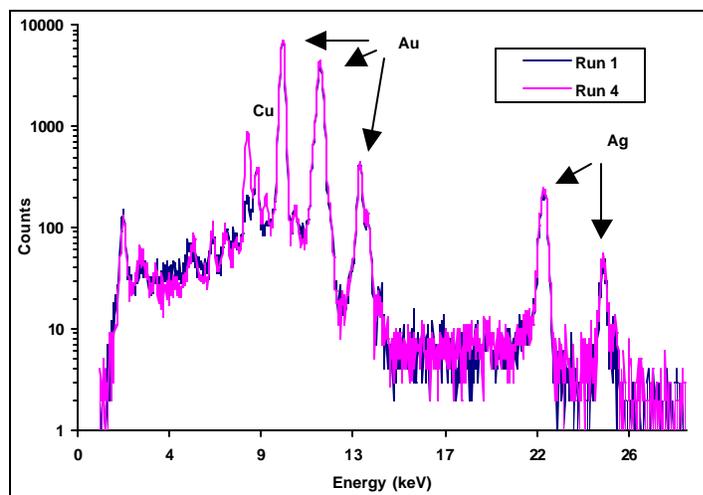Table 1. Compositional differences and descriptions of the various positions.

Figure 3. Comparison of #1 and #4. The difference in concentration of the copper peak at 8 keV indicates that the artists used more copper at the welds.

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Welding process

Many welding processes have been reported in literature (G. Demortier 1989); forging by rapid fusion of discrete parts in contact, brazing with an alloy with higher Cu content and lower melting point than the basic alloy (as is the case for a more complex ternary Au-Ag-Cu alloy compared to a binary Au-Ag alloy), welding in a reducing atmosphere with copper mineral salts involving a process known as solid-state diffusion bonding, and brazing with an alloy containing cadmium. Since an increased Cu concentration was measured at the welding areas and no statistically significant difference in the Ag/Au concentration ratio was observed, the welding was most likely done using a copper mineral (chrysocolla or malachite) and the solid-state diffusion bonding process. This welding procedure begins by heating, but not melting, the high purity gold alloy in the presence of a copper powder. This forms an Au-Cu alloy with a melting point considerably lower than the gold itself, which fills the gap between the two components (R. Tylecote 1987).

Native or alloyed gold?

The Chalcolithic (5th millennium BC) cemetery discovered near Varna in Bulgaria constitutes a landmark in the history of ancient metallurgy. Its abundant gold artifacts have been acknowledged as the earliest evidence of gold working in the world. Of the analyzed artifacts a few show a high percentage in silver content (20-25% for a small figurine and 39-50% for some beads). Since intentional alloying was unlikely, the silver content implies the use of gold from a primary (not alluvial) source. The silver content of the majority of the analyzed items ranges between 7 and 17% (A. Hartmann 1978). An average 6% silver content has been found in samples from the placer deposits of the St. Mandilios river near Nigrita in Macedonia (K. Michailidis, M. Vavelidis 1987), and 14-17% in natural gold grains from Thassos (R. Tylecote 1987). Recent analysis of the chemical composition of 27 (of a total of 50) Neolithic gold pendants of a confiscated hoard, has shown that a majority had Ag concentrations less than 10%, centered at about 5% (Y. Maniatis et al. 2000). The pendants have been dated according to their typology and method of manufacture by K. Dimakopoulou (1998) to the late Neolithic or Chalcolithic period (roughly the same period as the Varna cemetery). These finds tend to confirm that the gold sources in the Balkans were exploited in prehistoric times, thus changing the old view that this was not the case.

According to literature sources, the initial silver content in native gold can range from less than 1% up to 50% or more (J. Ogden 1982), but usually ranges between 5 and 30% (J. Ogden 1982, R. Tylecote 1987, P. Craddock *et al.* 1997). Copper can generally be detected in native gold up to levels of 2.5%. Typically, it is present in quantities less than 1% (P. Craddock et al. 1997). Data obtained from gold grains/nuggets, as well as from objects made possibly by native ore, indicate that Cu values rarely exceed 1%. All of the ibex spectra from the non-weld locations average 0.55%. This supports the argument that the artifact was made from native gold. Since iron is a trace element that is expected in native gold in concentrations less than 0.5% (G. Demortier 1989), the measured Fe content of 0.34% supports further the fact that the gold alloy used for the ibex was native.

In Table 2, data from literature concerning the composition of ancient gold alloys are presented. For an appropriate comparison with the ibex data the criterion that a Cu content less than 1.5% implies native provenance of the gold was adopted. Therefore, in Table 2 only those data obtained from Y. Maniatis *et al.* (2000) and A. Hartmann (1982) that satisfy this criterion were included and averaged. These data correspond in the first case to 23 of a total 27 alloys, and 40 of 61 for the Mycenaean archaeological site. The average Ag concentration of 14.9% of the ibex figurine from Akrotiri is a value which brings it chemically close to the gold artifacts from the Aegean and Balkan regions in general. This is of particular importance since typologically the gold ibex does not seem to have parallels in the Aegean. However, an in depth study of other relevant published data may help for a correct assessment of possible provenance sites. Finding Pt and other PGEs (Platinum Group Elements) like Ir, Os and Ru with complementary techniques may help substantially in this determination.

Site	Period	Source	Number	Ag (%)	Cu (%)
Varna	Neolithic	Hartman, 1978	125	11.0 ± 2.6	0.50 ± 0.37
Confiscated Hoard	Neolithic	Maniatis et al., 2000	23	6.61 ± 2.66	0.36 ± 0.32
Mycenae	Mycenaean	Hartman, 1982	40	16.0 ± 7.5	0.51 ± 0.34
Ibex	Thera	--	--	14.9	0.55

Table 2. Summarizing the Ag and Cu content of artifacts from various sites.

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The bronze dagger and blade

Two bronze objects were also analyzed, a dagger and a blade. However, there are certain complications with analyzing ancient bronzes. Surface analysis of corroded objects is inherently unreliable since different elements can be enriched or depleted by the corrosion process and the degree and direction of such compositional changes depend on many variables. XRF analysis can be used to identify the nature of the alloy, for example, if it is tin bronze or leaded tin bronze.

Even though a full quantitative analysis is not possible, looking at the relative concentrations can reveal important information. Table 3 shows the results of the semi-quantitative analysis of the bronze dagger and blade. The ratios with respect to Cu show an increase in the amount of Sn for the blade. Since Sn was used to add strength, it is logical that the blade had increased amounts as compared to the dagger which would not need to withstand as much force. The dagger rivets were made of silver. Various corrosion products of silver were found, mostly silver salts (AgCl and AgBr). The bromine originates, most probably, from the sea-water.
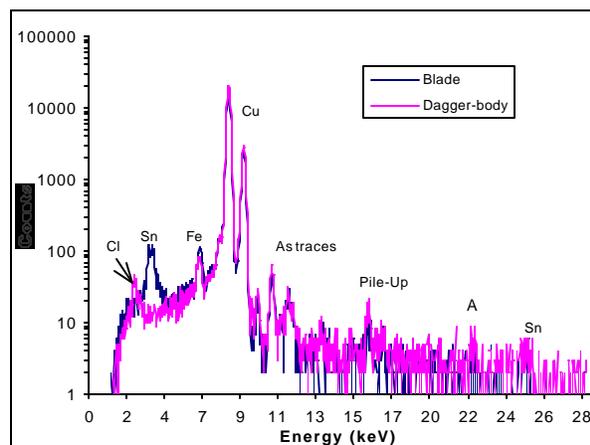

Figure 4. Comparison of the dagger (Mus. No. 8597) and blade (Mus. No. 6219) spectra.

	Relative Concentration (%)	
Element	Dagger	Blade
As/Cu	0.82	0.26
Fe/Cu	0.13	0.36
Sn/Cu	0.32	4.8

Table 3. Semi-quantitative analysis of the dagger and blade.

Wall paintings

Among the most incredible archaeological finds at Akrotiri are the wall paintings. The blue Theran pigments were classified first by S. Philipakis *et al.* (1976), and the red, pink, yellow, orange and brown pigments by S. Profi *et al.* (1977). A more complete approach was conducted by V. Perdikatsis (1998) and more recently by V. Perdikatsis *et al.* (2000) based on XRD, SEM-EDAX, and optical microscopy examination. The aim of XRF measurements of pigments on Theran wall paintings was to identify fingerprint elements for specific mineral pigments and to assess the applicability and capability of the XRF technique.

The XRF analysis of the white background at three different locations of the Xeste 3, Room 3 wall paintings (Table 4) showed high Ca and minor Fe content indicating the presence of calcite with minor contributions of amphiboles. All three spectra (Figure 5) are in excellent agreement and show great uniformity of the white plaster background. Two blue pigment locations were examined, the youngest boy head (Figure 6) and the belt of the "Lady with the Belt" (Chr. Doumas, 1992 137, fig. 100) in Xeste 3, Room 3. In both cases, the high Ca, Cu, and Fe content indicate the use of mixtures of Egyptian blue and amphibole, although different proportions of the two minerals were used for each pigment. The results are in accordance with previous investigations since these pigments belong to the third of three types of blue pigment found in Theran wall painting (S. Philipakis et al. 1976); the first is pure Egyptian blue and the second includes amphibole as a major mineral. More specifically, the XRD and SEM analysis of blue pigments of this type have
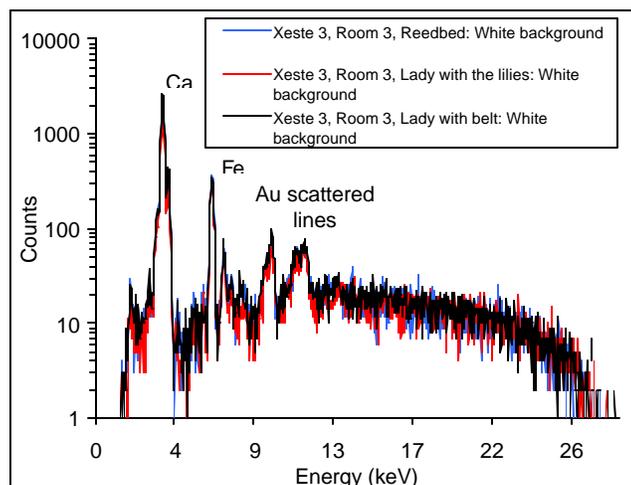

Figure 5. Comparison of three spectra taken from the white background of various wall paintings.

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revealed the presence of Egyptian blue, amphiboles (mostly of riebeckite type), talc, and chlorite (V. Perdikatsis et al. 2000).

The fact that Fe can be used as a fingerprint element for the presence of amphiboles in a blue pigment and Cu for Egyptian blue was used initially (S. Philipakis *et al*. 1976) for grouping the different types of blue pigments found in Thera, Knossos, and mainland Greece. From these data it has been suggested that the introduction of the amphibole group minerals in the color palette of Minoan wall paintings was done by Theran artists (E. Aloupi *et al*. 2000, V. Perdikatsis 1998).

		Analytical data	
Pigment	**Positions analysed *in-situ***	***In-situ* XRF analysis**	**XRD, SEM/ microprobe analysis (V. Perdikatsis *et al.* 2000)**
		Elements	**Minerals**
White Background	Xeste 3, Room 3 : Reed bed, Lady with the lilies, Lady with the belt	Ca (Calcite) with minor amounts of Fe (amphibole)	Calcite, Kaolinite, Chlorite, Amphibole (AKR4)
Blue	Xeste 3, Room 3: Blue pigment on the Lady's belt Shaven Head of the youngest boy	Ca, Cu (Egyptian Blue) and Fe (Amphibole)	Egyptian blue, Amphibole (mostly of riebeckite type), Talc, Chlorite, Calcite (AKR47)
Red	From inside a pot	Fe (Hematite) with traces of Mn and Ti	Hematite (AKR31)
Yellow	From inside a pot	Fe (Goethite) with traces of Mn and Ti	-
Yellow (mustard)	Xeste 3: boy with the yellow base	Fe (Goethite) and Ca (Calcite) as major elements, minor amounts of K (Illite?) and trace amounts of Ti and Mn	Goethite, Calcite, Quartz, Chlorite, Illite, Kaolinite, Amphibole and Talc (AKR16, AKR17)
Brown	Xeste 3: brown pigment from the arm of the boy	Fe (Hematite) and Ca (Calcite) and trace amounts of Ti and Mn	Hematite, Calcite, Kaolinite, Quartz (AKR27)
Green	Lady with Bunch of Lilies	Fe (Goethite), minor amounts of K (Illite?), trace amounts of Ti and Mn and Ca, Cu (Egyptian Blue)	Amphiboles (hornblende) as colorant, possibly painted on top of yellow ochre (AKR50)

Table 4. XRF results of various pigments. XRF can identify only the presence of the elemental form of a pigment constituent. The minerals indicated in the parentheses of the third column are a possible explanation of the color observed and of the semi-quantitative data. For comparison, representative analytical data from XRD/SEM microprobe analyses are shown in the last column, obtained at the locations indicated by the acronym AKR in V. Perdikatsis et al. 2000.

Two pure pigments, red and yellow, were also analyzed. The red pigment was composed mainly of the iron based mineral hematite, and the yellow pigment of the iron mineral goethite. Traces of Mn and Ti were identified in both pigments. However, the yellow (mustard) pigment measured on the wall painting indicated the presence of calcite (expected from the white background) and minor amounts of K (due possibly to the presence of the mineral illite). Almost the same spectrum, except for the presence of K, was measured from a location with a brown pigment. These results are also in agreement with previous measurements (Table 4).

The XRF analyses support the argument (V. Perdikatsis et al. 2000) that the pure pigments were calcite free. The fact that secondary calcite was always detected in the pigments indicates that the ochre was ground before use to a fine powder and then mixed with lime in variable proportions according to the intensity

Figure 6. Xeste 3, youngest boy head.

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of the required color. Finally, a green pigment was analysed *in-situ* from the Lady with Bunch of Lilies. Although XRF analysis cannot identify, at least under these specific experimental conditions, if there are one or two different layers of pigment material, the estimation is that a yellow ochre and Egyptian blue were used for the green color (either mixed or painted one on top of the other). The trace amounts of Ti and Mn and the minor concentration of K, support the use of a yellow ochre as a constituent of the green pigment.

Further processing of the XRF data can reveal interesting complementary information; the pure pigment weight ratio with respect to specific inert materials (goethite/calcite, hematite/calcite), or the mixing ratio of two pure pigments to produce a composite color (possibly the case for green).

Figure 7. Bichrome jug, Mus. No 8149

Other artifacts

Additional objects were analyzed during this trip to Akrotiri. Four of them are shown below, of which two (photos c and d) date to the Early Bronze Age (3rd millennium BC) and two come from the Late Cycladic I (c. 17th cent. BC) horizon of the city at Akrotiri. These objects have been analyzed only qualitatively.

The "sauceboat" of Figure 9 comes from the Early Cycladic II (c. mid 3rd millennium BC) horizon of Akrotiri. Its black glaze has elevated amounts of manganese. The Early Cycladic III (late 3rd millennium BC) pyxis of Figure 10, found in the Phira quarries, is decorated with impressed concentric circles filled with a white calcite paste. Concerning the bichrome decoration applied to the jug in Figure 7, the red paint of the swallows was found to contain iron, while increased amounts of Mn-based minerals (possibly umbrae) were used for the production of the black color. The alternative use of Mn-rich and Fe-rich black indicates technological traditions concerning firing processes and the use of raw materials. The potential of the *in-situ* XRF analysis to provide a definite answer to the interplay between Mn and Fe rich black was used in a survey of Cypriot pottery at the Nicosia museum (E. Aloupi et al. 2001). Figure 8 illustrates a faience rosette, the surface of which is covered with green glaze abundant in copper.

Figure 8. Faience rosette, Mus. No. 3763

Conclusion

Of the many beautiful and unique objects analyzed on this trip to Santorini, Greece, the ibex is truly a unique artifact. Its origin has been suggested to be from the East. The XRF analysis supports the conclusion that the raw material used was native. At the welding areas, the XRF data show increased copper concentration indicating that the different parts of the ibex were joined by heating the metal under reducing conditions with a copper mineral powder. It is clear that the use of complementary techniques that determine PGEs will help resolve the provenance site of the gold. In addition to the ibex, a bronze dagger and blade were analyzed showing a higher ratio of Sn in the blade to increase strength. The XRF analyses of pigments from wall-paintings confirmed the ability of the technique to identify fingerprint elements of minerals, and therefore indirectly deduce pigment composition. The XRF data were in agreement with published XRD and SEM results.

Figure 9. Sauceboat

The increased need for non-destructive investigations has become a major issue, since sampling is in most cases restricted in view of the importance or uniqueness of the object. *In-situ* XRF analysis can provide answers to specific analytical problems and therefore, in many cases, offer unique data for archaeological research. This type of non-destructive analysis can be conducted very quickly. Software is available for the quantitative analysis of samples with homogeneous composition and no surface corrosion, and can be performed during data acquisition. XRF is becoming an increasingly popular method for chemical analysis, and the portability of the system used here allows for the easy implementation of the method across the varying fields of art and archaeology.

Figure 10. Pyxis, Mus. No. 1352

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