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PIXE ANALYSIS ON URARTIAN BRONZE ARMORS AND HARNESSES IN THE REZA ABBASI MUSEUM, IRAN

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ABSTRACT

Eleven bronze objects in the Reza Abbasi Museum have been analyzed by the Particle-Induced X-Ray Emission (PIXE) technique. The policy of the Reza Abbasi Museum is to house objects rescued from looting or from the antiquities trades, therefore authenticity and period of the objects have been determined by the museum experts. The experts believe that the objects under study, including bronze armors and harnesses, belong to the Urartian period in the first millennium BC and are attributed to the Lurestan province in Central Zagros. The purpose of this work is to characterize and to understand the provenance of them. During the study, besides the major components, including Cu and Sn, trace element that was Fe along with Ti, Zn and Mn were also detected. High amounts of copper and tin and also existence of Fe indicate that Cu and Sn have been extracted separately from their ore minerals (chalcopyrite and cassiterite) and then through bronze making processes they were forged together. Consequently, it can be concluded that extractions were not from one natural ore mineral. This was an important feature of metalworking in that space-time grid.

KEYWORDS: chemical composition, bronze, analysis, PIXE, Urartu

1. INTRODUCTION

For the first time, variant of the term "Uruatri" appears in Middle Assyrian records (Zimansky, 1995). "Urartu" refers to an Iron Age kingdom (860-590 BC) centered in Tushpa around the Lake Van in modern Turkey. This kingdom was developed in mountainous regions in southeast of the Black Sea and southwest of the Caspian Sea. Today the region includes Armenia, Eastern Turkey, and Northwestern Iran. In the 9th and 8th centuries BC Urartu has been considered as a political power in the Middle East (Piotrovskii, 1969). Archaeological studies in Iran between 1968 and 1978 increased the amount of Urartian data in Northwestern Iran (Zimansky, 1990). During those years much information about Urartian culture was collected by Wolfram Kleiss (Jakubiak, 2004). Through further studies in Iran archaeologists were often interested in Urartian architectural remains. Urartian museum objects in Iran have not been completely studied and analyzed yet.

In this study, eleven bronze armors and harnesses in the Reza Abbasi Museum have been studied to gain information about quantitative elemental composition of metal, mineral ores that have been extracted and possible metalworking technology of the time which has been used for making metal alloys. It should be mentioned that the policy of the museum has been to house objects rescued from antiquities trades or looting. These eleven items have been introduced by the museum experts as Urartian bronze objects. Hermann Born and Ursula Seidl have studied these objects in their research on Assyrian and Urartian helmets and they have confirmed these objects' authenticity and their Urartian origin (1995); the same has been confirmed by Ursula Seidl in her study on Urartian bronzes (2010).

In such cases archaeology cannot help in understanding the nature of the objects more profoundly. As knowledge of elemental composition leads to be aware of manufacturing processes, in such cases, archaeologists can use the science of chemistry to identify elemental composition and also the technology of making such works (Rehren and Pernicka, 2008).

Metal objects under study include copper and its alloys. These metals constitute one of the major groups of ancient metals. This was probably because of the availability, quantities, prevalence and also the properties of copper. Unlike most other metals, due to its low chemical reactivity, copper exists in a pure form in nature. Furthermore it should be noted the other properties of this metal such as its color, malleability, shape ability and reusability. These could be the significant factors in designating and using copper and its alloys to make tools (Thantilage, 2008). Alloys containing Cu and Sn are known as bronze, and have been found in Iran since at least the 3rd millennium BC.

2. EXPERIMENTAL

2.1. Sample collection and preparation

In the Reza Abbasi Museum, each object is recorded with a special code. Hence, in this case, objects were marked with these numbers and codes. Eleven bronze objects in the shape of a helmet, pieces of armors and harnesses in the Museum were analyzed here. It should be mentioned that the bronze object no. 148 (Urartian helmet) has previously been restorated by electrochemical method. In addition, the objects nos. 138 and 139 are two parts of an object which has been damaged and separated. For this reason, these two are studied as a single object. Samples' properties are listed in Table 1. In this table, the number of each object stands for its registration in the museum. Dimensions are written based on maximum measurable sizes.

Table 1
The properties of the Urartian bronze objects, Reza Abbasi Museum

Row	Object No. & Type	Dimension	Sampling Date	Image
1	139 Armor (shoulder cover)	Width: 11.5 cm Length: 24.5 cm	8/6/2011	
2	788 Armor (shoulder cover)	Width: 23 cm Length: 24.4 cm	8/6/2011	
3	789 Armor (shoulder cover)	Width: 25 cm Length: 29.4 cm	8/6/2011	
4	138 Armor (shoulder cover)	Width: 14.8 cm Length: 24.5 cm	11/6/2011	
5	791` Armor (shoulder cover)	Width: 13 cm Length: 29 cm	11/6/2011	
6	134 Armor	Diameter: 29 cm	11/6/2011	
7	799 Armor	Width: 11 cm Length: 13.5 cm	11/6/2011	
8	796 Armor	Width: 17.4 cm Length: 30.6 cm	11/6/2011	
9	137 Harness	Length: 33 cm	11/6/2011	
10	792 Harness	Width: 25 cm Length: 29 cm	11/6/2011	
11	148 Helmet	Diameter: 21.4 cm Height: 31.7 cm	20/6/2011	

Considering the conservation principles, metal cores sampling was carried out. Sampling was done by Museum restoration specialist during three days. Samples were obtained from the damaged and marginal parts of the objects by scalpel. One of the important aims in sampling was not to let corrosion products and metal cores to be mixed together.

2.2. PIXE measurement

Regarding low amount of samples and possible requirement of re-analyzing, it was necessary to choose a non-destructive method. PIXE is one of the common methods in such cases because it is completely non-destructive, multi-element, fast and sensitive (Guerra, 1998).

Eleven samples in the form of tiny pieces obtained by scalpel from the Urartian alloys have been selected and after transferring samples to the Van de Graaff laboratory of Atomic Energy Organization of Iran (AEOI), spectroscopic studies were carried out on them. The analysis was performed by using PIXE. The 2 MeV, 0.5 mm diameter proton beam with a current of 2–3 nA from AEOI, Van de Graaff accelerator was used. The characteristic X-rays emitted from the samples, were detected by a Si (Li) detector from ORTEC with an energy resolution of 170 eV at 5.9 keV. The detector was placed in the beam direction at 135°. Results of spectroscopy have been demonstrated in Table 2 and Fig.1. In the Table 1, in each row, percentages of selected elements, including Ti, Fe, Cu, Sn, Zn and Mn, have been shown. Subsequently, based on the mentioned percentages, a diagram has been made (fig.1), then a tack plot (fig.2) has been drawn, according to percentages of major components.

Table 2
Percentage of selected elements by PIXE on the Urartian bronze objects, Reza Abbasi Museum

Others	Sn (%)	Cu (%)	Fe (%)	Ti (%)	Object Code	Row
-	10.10	89.75	0.15	-	138-139	1
-	3.85	95.74	0.34	0.07	788	2
-	7.57	91.88	0.55	-	789	3
-	9.24	90.02	0.74	-	791	4
Mn: 0.51%	15.73	82.00	1.55	0.21	134	5
-	7.70	90.76	1.45	0.09	799	6
-	7.01	91.55	1.35	0.09	796	7
-	12.17	87.69	0.14	-	137	8
-	6.15	91.38	2.29	0.18	792	9
Zn: 0.49%	13.11	86.31	0.09	-	148	10

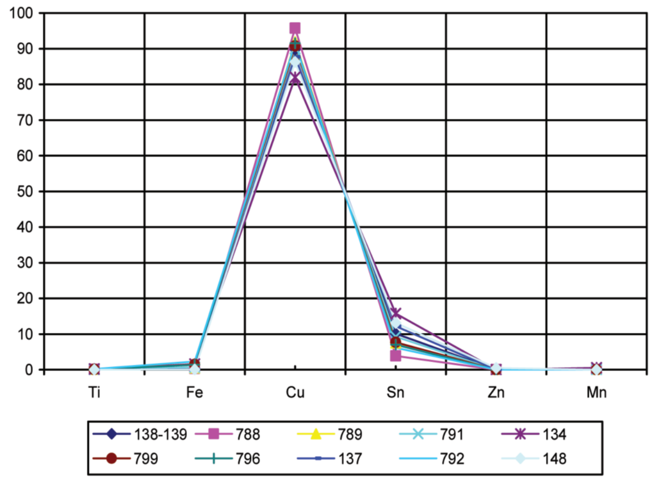

Figure 1. Results of PIXE analyses on the Urartian Bronze objects, Reza Abbasi Museum.

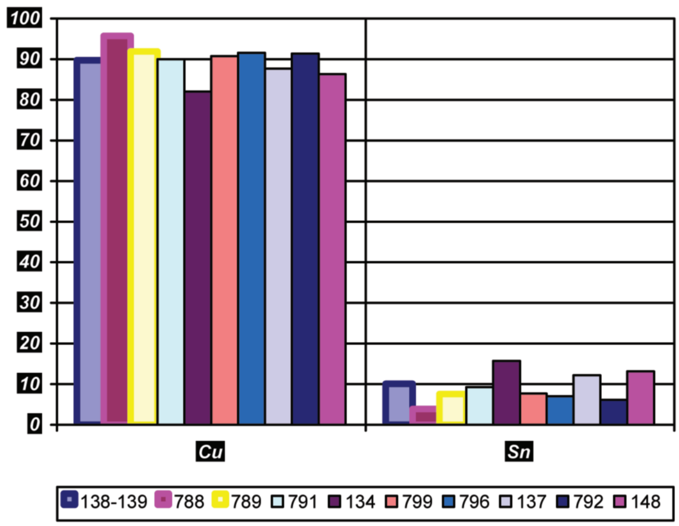

Figure 2. Tack plot for major components, Cu and Sn of the Urartian Bronze objects, Reza Abbasi Museum.

3. RESULTS AND DISCUSSION

All the pieces are made of a copper-tin bronze alloy (fig.2). The percentage of Cu varies from 82 to 95.74 wt% and that of Sn varies from 3.85 to 15.73wt%.

Copper-tin bronzes are classified as low-tin bronze (up to about 14 wt % tin) or high tin bronze (about 19-27 wt% tin). Therefore these samples can be considered as low-tin bronzes. The amount of tin justifies the samples' colors. Copper-tin alloys with less than 10 wt% tin are reddish and those with 10-20 wt% tin are more orange-yellowish (Selwyn, 2004).

The elements Fe, Ti, Zn and Mn were detected in the objects along with the major components Cu and Sn. It is worth mentioning that iron (trace element) was in all objects, but Ti was detected in five samples and Mn as well as Zn were observed just in one sample (Table 2). In none of the samples, arsenic was detected. This element was commonly used as minor component in bronze making processes in the western regions like Oriental Mediterranean and the South East (S.E.) of the Iberian Peninsula. From Early Bronze Age to Iron Age, the amount of arsenic was gradually reduced by the time but it has been still exist in the bronze samples in Iron Age (Fortes et al, 2005).

As it is shown in Table 2 and Fig. 1, Fe was detected in all analyzed samples. The amount of Fe was greater than 0.09 wt% and less than 2.29 wt%. Existence of Fe can show that the extraction of Cu was from an ore mineral called chalcopyrite ($CuFeS_2$). According to the formula it can be expected that sulfur should also be present in the samples, while sulfur was not observed. In such cases sulfur is evaporated during the heating and ignition process in the form of SO_2, SO_3 and SO_4, thus causing the absence of sulfur in the results.

There are not many elemental analyses of Urartian armors and harnesses, but some shields that have been found at Ayanis Fortress in the Van region were analyzed. These analyses were carried out by EDS on the shields. Barring the differences between analytical techniques, and minor elements (Zn and Pb), in these samples Fe was also detected. The percentage of Fe was up to 0.57 wt% (Ingo et al, 2009). Therefore it can be concluded that copper in these objects was also extracted from chalcopyrite ores.

There is Ti in five samples. Presence of Ti in some and not all samples shows that parageneses are usually in the type of poly-metals and therefore Ti appeared as an impurity of the ore.

4. CONCLUSION

Urartian mineralogy as well as their metallurgy were relatively developed. The high percentage of Cu (82-95.74 wt %) and Sn (3.85-15.73 wt %) in the eleven analyzed samples was a surprising result. These amounts show that extractions were not accidentally from one natural ore mineral like stannite (Cu_2FeSnS_4). High amounts of copper and tin indicate that these two had been extracted separately from their ore minerals. Existence of Fe may be a good clue that Cu had been extracted from chalcopyrite alone. Tin is almost found in nature exclusively as cassiterite (tinstone), therefore it is clear that in this case Sn had been also recovered by melting cassiterite (SnO_2). Subsequently these two had been mixed in the type of copper-tin bronzes. This was an important feature of metalworking in that space-time grid.

Variation of Sn amounts illustrates that the ratio of tin to copper was not determined by exact calculations. It shows that the ratio of Sn to Cu has been determined experimentally which implies a skillful procedure. Other elements, such as Ti, Mn and Zn were not added to the alloy deliberately and in fact, they were ore impurities.

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