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A COMPREHENSIVE APPROACH OF XRF AND ANALOGICAL STUDY OF A PHRYGIAN FIBULA

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ABSTRACT

In this study, an archaeological and archaeometric research of a fibula in the Sivas Archaeological Museum was conducted. One of the purposes of choosing this material is to archaeologically identify this fibula, one of the fibula types identified with Phrygians, and to determine which century it belongs to. Another purpose is to determine which mining sites the Phrygians had contact with, who were mainly located in the middle and west of Anatolia during the period in question (8^{th} – 7^{th} centuries BC). In determining the first aim, that is, the period to which the object belongs, literature review and analogical comparison were selected as methods. The second objective, namely the determination of the mining sites that Phrygs come into contact with based on the fibula, covers two methods. The first method is the determination of the elemental composition of the fibula by the p-XRF method. In the process of associating the fibula with the Anatolian mining sites, a comparative literature review was used. Cadmium in the elemental composition of the work triggered the interest associated with the second aim. Cadmium, has also been detected in a mining site under the control of the Hittites. Although it is known that the mining site in question had been used since the 3^{rd} millennium BC, including the Hittite period, the question of when it was last used has been updated within the scope of this study. In fact during the second quarter of the 1^{st} millennium BC, the Phrygians, who lived in a contemporary period with the Late Hittites, imported raw materials from the mining sites under the control of the Late Hittites in the said period and produced metal works with this raw material. As a result, the Late Hittites are among the last identifiable owners of the mine site, which was determined within the scope of the research on the origin of tin in Anatolia in the 3^{rd} millennium BC. Based on this information, it has been proven for the first time that Phrygian fibulas are produced with ores obtained from the mining site in the north of the Taurus Mountains.

KEYWORDS: Phrygian mining, copper, cadmium, elemental analysis, provenance analysis, tin, alloy, Hittites, mines, ores

1. INTRODUCTION

One of the aspects that need to be addressed for an archaeological artifact to be placed in the context and chronological frame is the archaeological assessment which includes literature review and typology. Then, archaeometric studies is vital in any material culture investigation (Liritzis et al., 2020). Many non-destructive analytical methods are used in these studies (Çakaj, et. al., 2016; Caponetti, et. al., 2017; Liritzis et. al., 2020; Kousouni, et. al., 2021; Belfiore, et. al. 2021; Krueger, et. al., 2021; Pehlivan, 2022; Zlateva, et. al., 2022). Non-invasive methods, such as p-XRF, is a must in the context of preserving the structure of the work (Janssens and Van Grieken, 2004; Shrestha, et. al., 2022).

Within the scope of the study, a fibula called Phrygian type XII in the collection of the Sivas Archaeological Museum was discussed. Fibula entered the inventory of the Sivas Archaeological Museum through purchase in 1979. For this reason, when the museum records are examined, no question about the place of the find and the origin of the artifact can be answered. This situation brings with itself a number of difficulties in terms of operation. One of these difficulties is that the time capsule of the work is broken. The loss of context data, which we care about in the name of an archaeological data, makes it difficult to determine the period of the archaeological work.

Archaeological literature review and style criticism of the fibula, which constitutes the material of this study, and the century in which the artifact was made, could be determined. Then, the questions about the origin of the work were tried to be answered with an archaeometric approach. The elemental structure of the work was determined by the non-destructive p-XRF analysis used at this stage. The elemental analysis provides information about the internal structure of the artifact. From this information, an idea was put forward about the raw material sources of Phrygian mining and the origin of the artifact.

Fibula is a Latin word; that means "clasp, buckle, brooch, needle, vice, pincer, clamp" (Kabaağaç, et. al., 1995). It is also among the most produced artifacts in Phrygian mining.

According to a study carried out by Muscarella, fibulae first appeared in Europe during the Bronze Age about the 3rd millennium BC. (Muscarella, 1964). In the 2nd millennium BC, fibula specimens began to be seen in Asia Minor. It is possible to say that from the 1st millennium BC onwards, it became widespread enough to be seen on embossed plastic elements. (Tekin, 2018; Alexander, 1973). In order to understand the way, the fibula is used, these sculptural works are of great importance (Akurgal, 2003).

Blikenberg (1926) who made a comprehensive study of Phrygian fibulae, states under the Type XII heading that the two ends of the fibula are symmetrical and that the hook and the spring can be easily attached to each other and it has the form of a semicircle in his descriptions. (Blikenberg, 1926). Blikenberg divided fibulae into 17 types in his typology. It evaluated all 17 of these types in 128 separate variants. (Blikenberg, 1926). It is also seen that he has created a geographical classification and divided this geographical classification into 6 regions. These are (1) Asia Minor, (2) Syria, Palestine, (3) Islands, (4) Peleponnesos, (5) Continental Greece, (6) Albania, Bosnia, (7) unknown origin. (Blikenberg, 1926).

Muscarella, on the other hand, used the typological infrastructure created by Blikenberg in his study of Phrygian fibulae published in 1967. In the study conducted by Ertuğrul Caner on Anatolian fibulae, Anatolian-originated fibulae were examined comprehensively (Caner, 1983).

The aim of this study is to propose a methodological approach for recovering the lost data of archaeological artifacts brought to the museum through purchase.

2. MATERIAL - METHOD

2.1. *Material*

The fibula with inventory number 79/12 in the Sivas Archaeological Museum constitutes the material of the study. The needle length of the fibula is 23.7 mm, the body thickness is 0.35 mm, the molding widths are 0.43 mm, the hook width is 13.6 mm, the height is 24.4 mm, the width (including the hook) is 36.4 mm (excluding the hook) is 33 mm, the needle thickness is 1.3 mm. The weight of the artifact is 170 grams. Compared to other fibulas with similar characteristics in the literature, the work is thought to be mold-made. According to our point of view, on the left side, there is a needle handle made to resemble a battering ram. On this needle handle, a decoration formed with torus and discs is seen. It is seen that this decoration is repeated in full symmetry. Between the symmetrical decorations at the starting and ending points, there are three decorations formed with three toruses each. Under this decoration, there is a spring part that forms a spiral. From a mechanical point of view, this spring part allows the needle to spring and move accordingly. At the end of the spring part with double winding, there is a needle section. It is possible to say that the artifact is protected well (Fig. 1).

Figure 1. Sivas Museum 79/12 Inventory Numbered Fibula Photograph and Drawing

2.2. *Method*

At the point of archaeometallurgical identification of the fibula, the Niton brand XL3 model p-XRF device was used. The work done with this calibrated device allows for contactless analysis (Pehlivan, 2022, 98). The study was carried out in the Sivas Archaeological Museum Laboratory, in an area away from light and moisture. The data collected after this reading process was transferred to the computer environment with the device's own software. Following this procedure, the second stage of archaeometric application, the literature review stage, was started. The data obtained after the transfer were compared with the samples in the literature. Graphics and various visuals have been created to make this comparison understandable.

Another method used in this article is the literature review and typological comparison method applied during the archaeological approach. Thanks to this method, the typology and chronology of the fibula have been determined.

3. ARCHAEOLOGICAL APPROACH

Analogy

Similar aspects of the work subject to study were compared with the fibulas in many settlements of Anatolia. Hogarth, in his study published in 1908, focused on metal artifacts found at Ephesus. Among these artifacts, there are also a large number of fibulae. Some of the fibulae are in great typological similarity with the artifact that constitutes the subject of the study (Hogarth, 1908: plate XVII – fig 6-7). Hogarth states that the artifact is of the Asia Minor type. However, he adds that it is similar to the Zincirli specimens found in Southeastern Anatolia and dates these artifacts to the end of the 7th century BC. (Hogarth, 1908).

Typological analogues of the artifact are also included in Blikenberg's publication. Blikenberg uses this artifact to describe the type XII–14, the type of fibula body decorated with both ends and the middle. He divides type XII – 14 into sub-variants. A sub-variant, Blikenberg XII-14g, has torus-disc decoration in the quarters of the semicircle, as in the artifact that is the subject of the article (Blikenberg, 1926). The fibula, called Blikenberg XII-14g, was found in the archaic layer in the city of Ephesus and is dated by Blikenberg to the end of the 7th century BC (Blikenberg, 1926).

In a study of fibulae, Muscarella evaluated this type of torus-disc decoration positioned evenly spaced on a semicircle with similar characteristics to the artifact under examination as Lydia Fibulas. He mentioned that this type was among the finds found in Ephesus and Sardis. This information is important in terms of revealing Phrygian – Lydian relationships. He also says that it was produced from precious metals found in Sardis and Ephesus. Muscarella dates the work from the end of the 7th century BC to the beginning of the 6th century, adding that this type of fibula was mold-made (Muscarella, 1967).

A fibula in the Tire Museum is also analogously similar to the artifact. Since the fibula in question was added to the museum collection through purchase, there is no data on its origin. Based on its typological features alone, it has been dated to the 8th-7th century BC (Erdan, 2020). Another example, which has similar features to the artifact that constitutes the subject of the study and is dated to the middle of the 8th century BC, was found in Kaman – Kalehöyük. It seems that no comprehensive information is given about the artifact called the Phrygian type (Paterakis, 2018). The 3 artifacts in the Bolu museum called Bolu type IVa have a close similarity with the artifact subject to the examination. The works in question are dated to the end of the 8th century BC – the beginning of the 7th century BC (Bilir, 2019). While the location of the discovery of the artifacts with inventory numbers 2051 and 2053 was recorded as Alan village of Göynük district of Bolu province; the discovery location of the artifact with inventory number 4281, is unknown. The work called Kocaeli Type IIa, which is found in the Kocaeli Museum with inventory number 398, is in close resemblance to the artifact that is the subject of the study. The work in question is dated to the end of the 8th century BC or the beginning of the 7th century BC (Bilir, 2020).

Another artifact that bears great resemblances with the artifact subject to the examination is the artifact registered in the Ereğli Museum with inventory number 1450. The artifact was brought to the museum in 1973 from the Armağanlı Neighborhood of Ereğli District of Konya province and dated to the end of the 8th century BC and the beginning of the 7th century BC (Çay, 2019). Another example with close similarities with the artifact that constitutes the subject of the article is in the Akşehir Museum in Konya. The work has an inventory number 79-139 and was brought to the museum in 1973. The location of the discovery is unknown. The artifact is dated to the last quarter of the 8th century BC and the beginning of the 7th century BC (Tekocak, 2012). A publication published by Muscarella contains a close analogue of the artifact that is the subject of the study. The artifact in question was recovered from the Gordian MM tumulus. It is dated to between 725 and 700 BC (Muscarella, 1967). It is seen that there are examples of fibulas produced in a similar style in Ankara Beştepeler tumulus (Mellink, 1990). In an article published by Schmidt, a fibula found within the scope of the Kerkenes excavations is shown among the finds. It is seen that the fibula coded as K88 is similar to the artifact that constitutes the subject of the article (Schmidt, 1929). In the Aydın Archeology Museum, there are 4 fibulas with similar characteristics to the artifact that is the subject of the article. The works were brought to the museum collection through purchase. Their inventory numbers are 4314, 5648, 6764, and 6765 (Erdan, 2018). The works were evaluated by Erdan in a wide range such as between the 9th and 6th century BC. There are ornamental elements at all 5 points of the artifacts. The artifacts are typologically classified as Aydın Archeology Museum Fibulas Type VI – 14. An example found in Sardis bears a great resemblance to the artifact that constitutes the subject of the study. It is seen that the fibula which is the subject of the article, is called Variant J, II, I, by Ertuğrul Caner. This designation was used by Caner to describe the type with ornaments at 5 points of the fibula. Ornament may consist of beads, discs, or both discs and beads together. The work is dated by the author from the end of the 7th century BC to the beginning of the 6th century BC (Caner, 1983). The two fibulas found in Boğazköy are similar to the fibula that is the subject of the article. (Caner, 1983). There is no chronological information about the samples discovered in Boğazköy. Another example with a similar nature to the artifact subject of the article was found in Gordion (Caner, 1983), (Figures 1 - 2).

In addition, it is possible to say that the molds of fibulas are usually made of terracotta and stone. When the Kaman – Kalehöyük fibula mold from the Central Anatolia region is examined, it is seen that it is produced from terracotta (Paterakis et. al., 2017). It is known that the use of fibula decreased in the ongoing process.

Figure 2. Map of Excavation Sites and Museums in Anatolia where Type XII – 14g are found

4. ARCHAEOMETALLURGICAL APPROACH

Anatolian Mining: It is known that there was an important change in Anatolia and the Near East with the Neolithic period. Of course, this change is also seen in the field of mining. Undoubtedly, the control of fire in this period accelerated the development of metallurgy (Tekin, 2015). While the forging technique was frequently applied in the early stages of metallurgy, it is seen that the casting technique has been used since 5000 BC (Tekin, 2015; Yalçın, 2000).

Table 1. Elemental Composition of Fibula. Note the high Sn (~23%), Pb (5.5%), Cu (28.6%)

No	Element	ppm	No	Element	ppm	No	Element	ppm
1	Fe	6241	9	Mn	2778	17	Rb	38
2	Si	195063	10	P	7314	18	Sr	64
3	Al	114957	11	Cl	13658	19	Ag	1641
4	Ca	18117	12	V	180	20	Cd	129
5	Mg	12948	13	Ni	1305	21	Sn	226387
6	S	34722	14	Cu	286709	22	Sb	465
7	K	11785	15	Zn	1886	24	W	839
8	Ti	1964	16	As	6215	24	Pb	54584

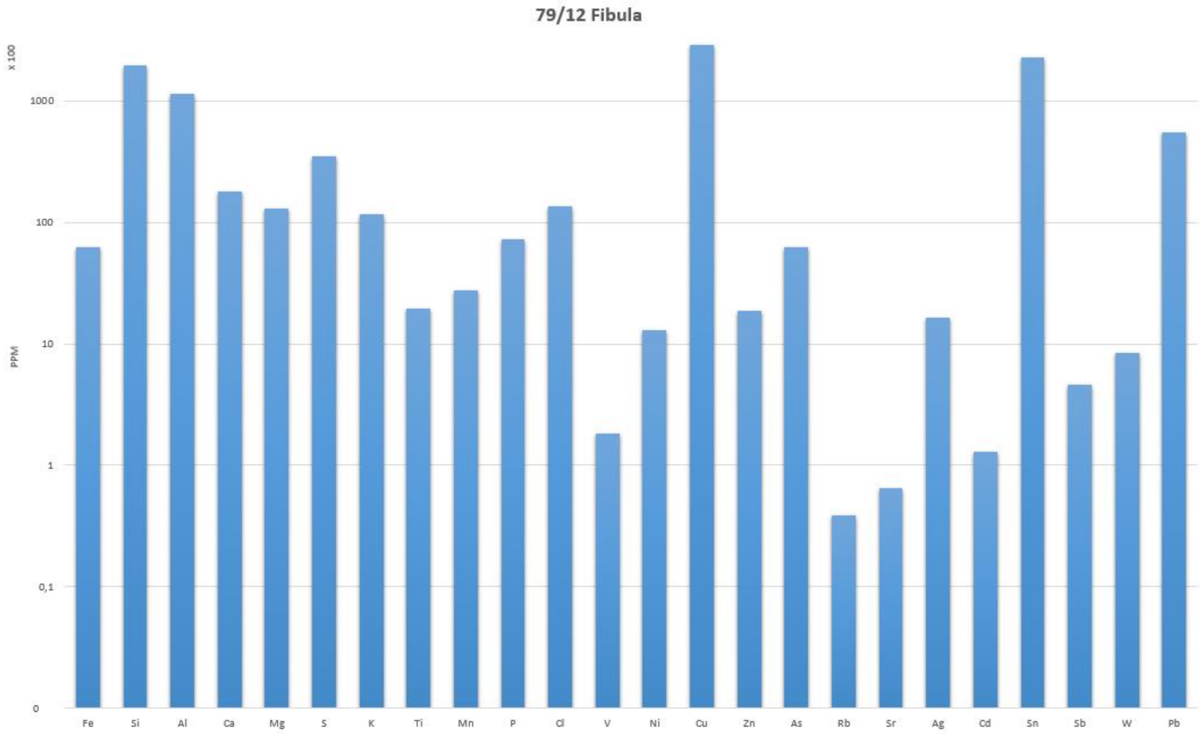

Figure 3. Logarithmic Elemental Concentrations Chart in ppm values

When the elemental structure of the fibula is examined, copper emerges as the main element. Copper has a value of 2867 ppm. Another main element that proves that the work is a bronze alloy is tin with a value of 2263 ppm (Table 1, Fig. 3).

When this alloy ratio is evaluated in terms of fibulas, although it seems to be low, the data seen in the graph is not raw data but concentration data. In addition, proper cleaning is an important condition in bronze works. Due to the difference in cleanliness, it is seen that there is an average of 11% variability in each of the copper and tin ratios. Twiley (1996) in his study on the fibulas found in Kaman – Kalehöyük, states that the microenvironment has an effect on metals. This is a catalyst that accelerates the oxidation and therefore degradation process of metals. In addition, it is seen that there is an element transition between the microenvironment and the artifact. This makes it possible to explain the high silicon content caused by the improper cleaning of the fibula, which has been under the ground for years (Figures 4 - 5).

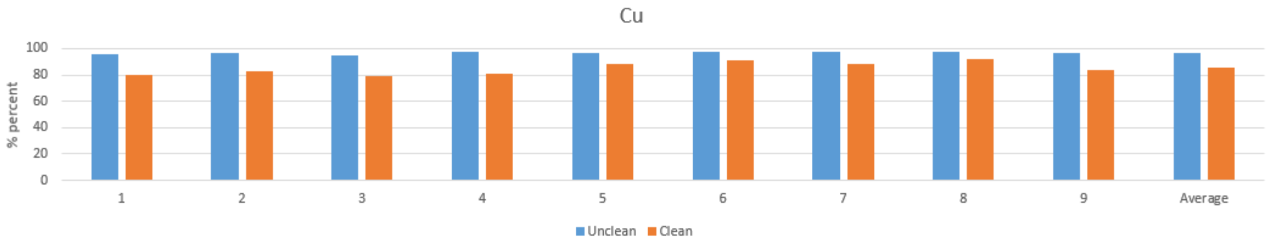

Figure 4. Graph showing the change in the copper level before and after cleaning in copper-tin objects in Charalambous et al.'s article (graph based on Charalambous et al., 2014: 205-216)

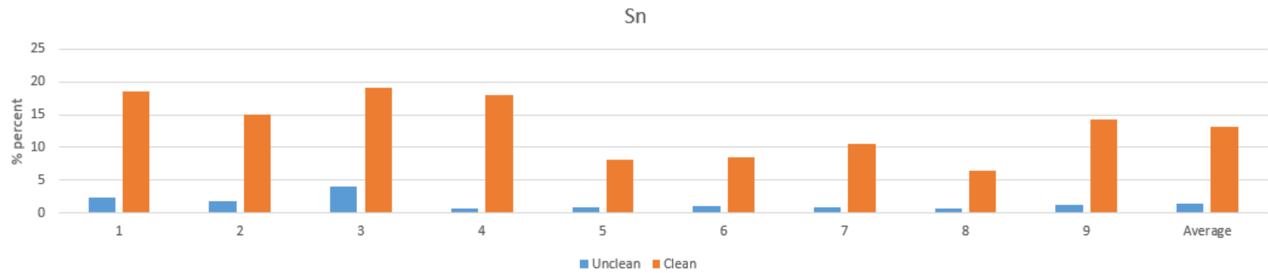

Figure 5. Graph showing the change in the tin level before and after cleaning in copper-tin objects in Charalambous et al.'s article (graph based on Charalambous et al., 2014: 205-216)

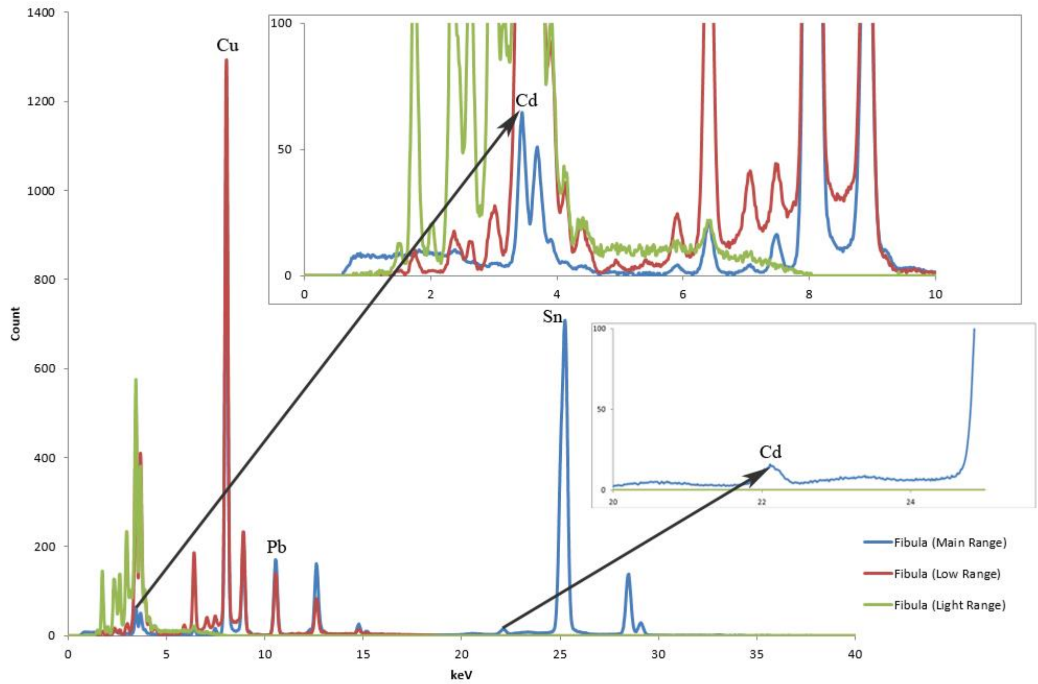

Figure 6. The XRF Spectrum of the Fibula (keV Chart)

As can be seen in the graph, copper, and tin, which make up the main elements, allow the alloy of the fibula to be called bronze. The Ka and Kb values of copper and tin clearly show this. On the other hand, in the analyses we have carried out by considering the La and Ka values, it is clearly seen that the artifact contains cadmium. Cadmium's Ka value is 23.17 and La value is 3.13. These areas, which appear to peak in the graph, are an important data showing the existence of the element Cadmium contained in the work. This situation revealed the necessity of investigating cadmium-containing mines (Fig. 6).

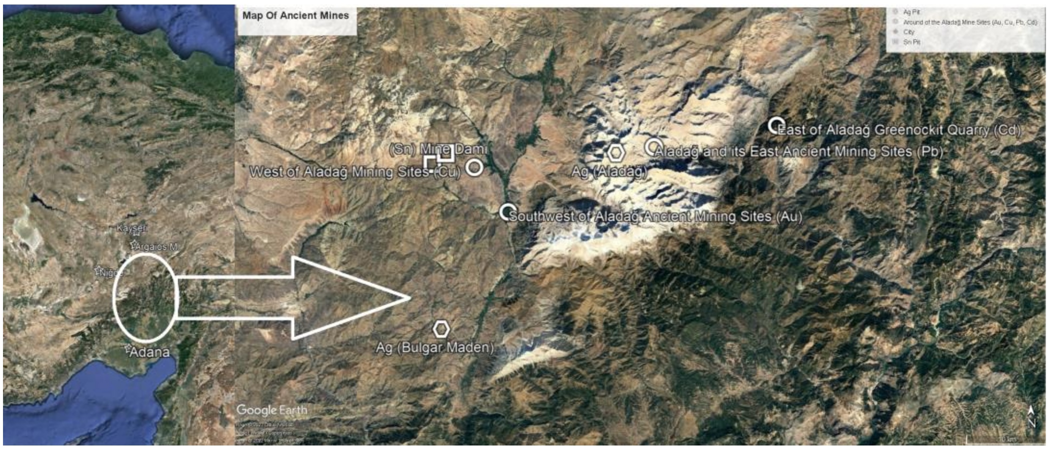

Figure 7. Map of Copper – Tin – Silver – Lead – Gold and Greenockite (Cadmium) areas in Asia Minor. Left the wider region and right the indicated area in white circle expanded.

Tin (Fidan, 2016; Yener, et al., 2015), Copper (Fidan, 2016), Lead (Fidan, 2016), Gold (Fidan, 2016), Silver (Fidan, 2016), Greenockit (cadmium-containing mineral) (Ayhan, 1983) are found in the area seen on the map. This area was called Kizzuwatna in ancient Hittite times (Fig. 7).

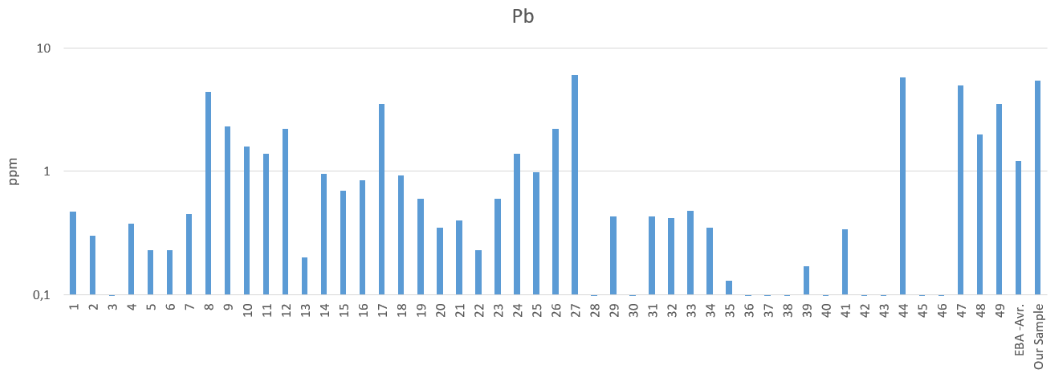

Figure 8. Comparative logarithmic graph showing the proportion of lead in the 1st Millennium BC bronze artifacts (1-49) with the examined Fibula and Early Bronze Age Bronze vessels (graph based on Craddock, 1976).

After the comparison process with a large number of samples, it is seen that the element lead is found in very small amounts in some elements among the comparison samples (Table 2). In the artifact that is the subject of the investigation, it is seen that lead is also found as an important element. However, when the artifacts containing the element of lead and the artifact subject to our study are compared, it is seen that our artifact contains much more lead than the artifacts of the Early Bronze Age. In addition, in terms of lead average, it is clearly seen that it has a similar character to its contemporary artifacts (Fig. 8). Lead is a frequently used mineral in terms of increasing the brightness of an object. At the same time, it allows the object to be used for many years without oxidation (Tekin, 2015).

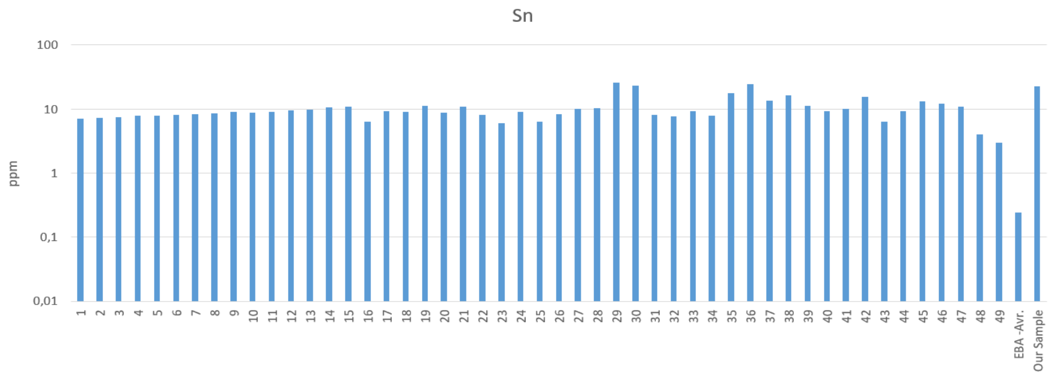

Figure 9. Comparative logarithmic graph showing the proportion of tin in the 1st Millennium BC bronze artifacts (1-49) with the examined Fibula and Early Bronze Age Bronze vessels (graph based on Craddock, 1976).

According to the evaluation made with a large comparison sample of the tin element, it is seen that the Early Bronze Age tin average is below the tin average of the 1st millennium BC. The work, which is dated to the 1st millennium BC, seems to contain the same amount of tin as its contemporaries (Fig. 9, Table 2).

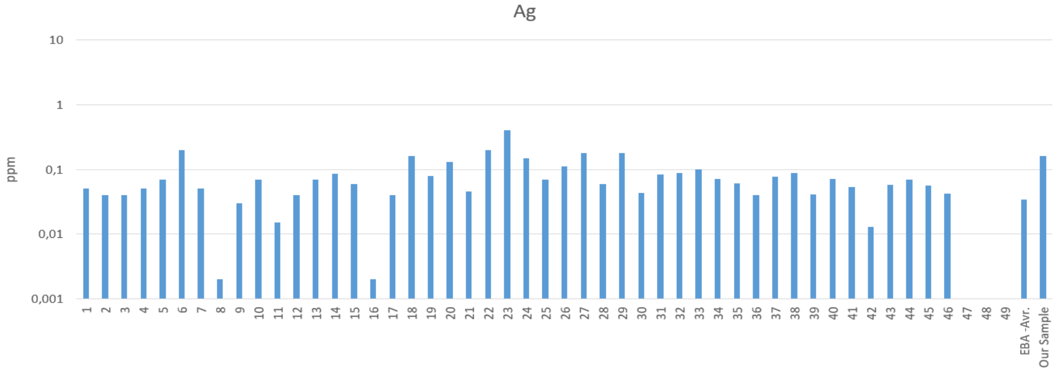

Figure 10. Comparative logarithmic graph showing the proportion of silver in the 1st Millennium BC bronze artifacts (1-49) with the examined Fibula and Early Bronze Age Bronze vessels (graphed based on Craddock, 1976).

When the situation regarding the silver element is examined, although it is not possible to talk about the conscious addition of a silver element, it is possible to say that domestic mines are generally used by looking at the silver ratios in the samples in the comparison group and therefore some silver could be seen in bronze objects. Silver quantities in the comparison universe show a ratio between 0.01 ppm and 0.1 ppm (Fig. 10, Table 2).

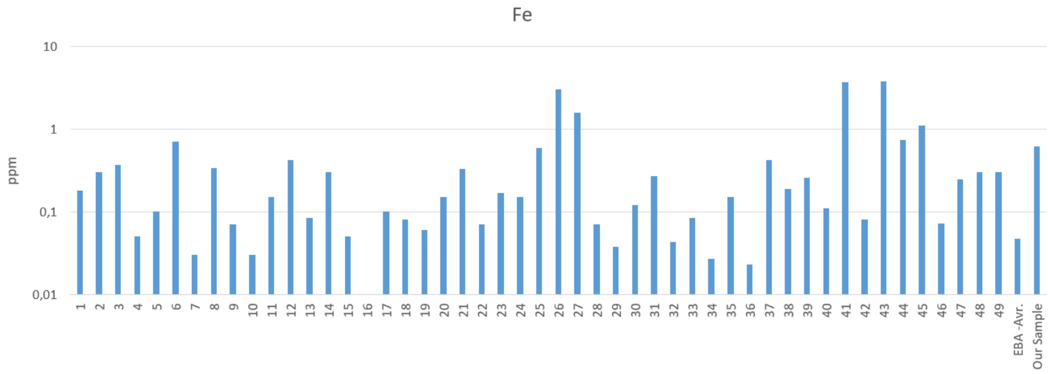

Figure 11. Comparative logarithmic graph showing the proportion of iron in the 1st Millennium BC bronze artifacts (1-49) with the examined Fibula and Early Bronze Age Bronze vessels (graphed based on Craddock, 1976).

When examined in terms of iron element, it is seen that the EBA average has a rate below the general average. On the other hand, the artifact under review offers an average value close to the universe of comparison (Fig. 11, Table 2).

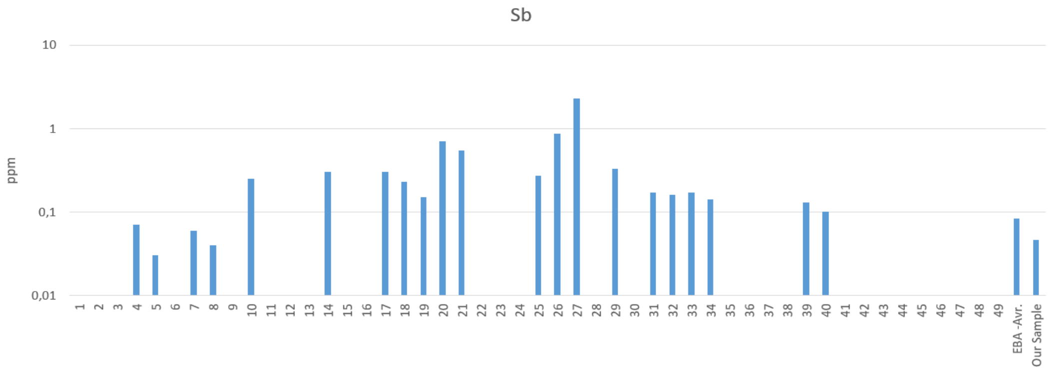

Figure 12. Comparative logarithmic graph showing the proportion of antimony in the 1st Millennium BC bronze artifacts (1-49) with the examined Fibula and Early Bronze Age Bronze vessels (graphed based on Craddock, 1976).

Although antimony is not an element expected to be encountered in mining works, it appears in trace amounts in some of the works in the comparison universe, and the artifact subject to examination. The rate of antimony in the artifact subject to review is below the EBA average and the average of the artifacts produced in the same period. In some works, it is absent at all (Fig. 12, Table 2).

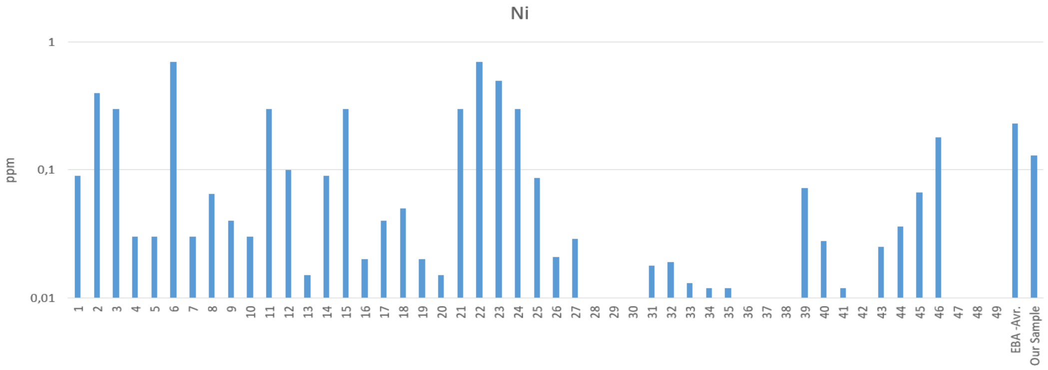

Figure 13. Comparative logarithmic graph showing the proportion of nickel in the 1st Millennium BC bronze artifacts (1-49) with the examined Fibula and Early Bronze Age Bronze vessels (graphed based on Craddock, 1976).

According to the examination between the comparison universe and our sample, it appears that the element nickel is not added in a stable amount. It is seen in the graph that it is below 1 ppm. It is also noticeable that some of the comparison examples do not have nickel at all (Fig. 13, Table 2).

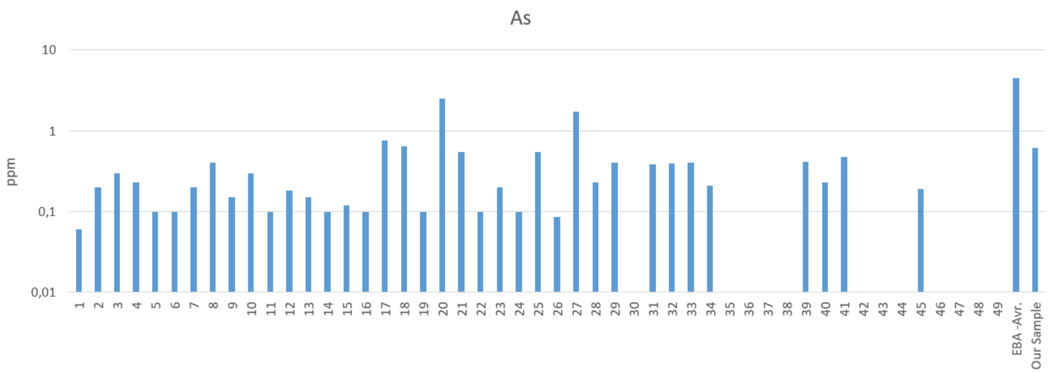

Figure 14. Comparative logarithmic graph showing the proportion of arsenic in the 1st Millennium BC bronze artifacts (1-49) with the examined Fibula and Early Bronze Age Bronze vessels (graphed based on Craddock, 1976).

When the state of the element arsenic is examined, it is seen that some works in the comparison universe contain it. When looking at the EBA arsenic average, it is seen that it offers a rate above the general average. It is possible to say that our example is below the EBA average, in parallel with the mining works of the 1st millennium BC (Fig. 14, Table 2).

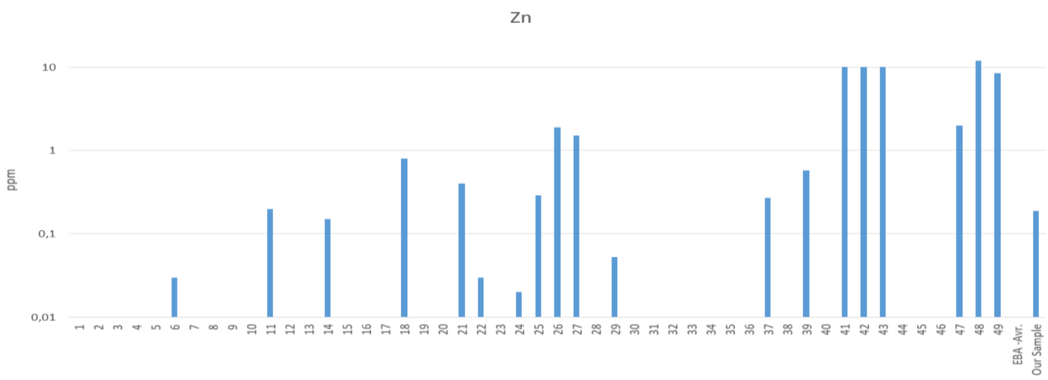

Figure 15. Comparative logarithmic graph showing the proportion of zinc in the 1st Millennium BC bronze artifacts (1-49) with the examined Fibula and Early Bronze Age Bronze vessels (graphed by quoting from Craddock, 1976).

Zinc, which Strabo refers to as "false silver" (Strabon, 2000), is less than in other samples than in the EBA average. Since zinc has been used in the production of metal goods since the 1st millennium BC, some of these samples contain zinc. The amount of zinc in the artifact subject to examination is low compared to the metals of the Roman Imperial Period (Fig. 15, Table 2).

Table 2. Elemental Composition of the Comparison Samples (Count) (Craddock, 1976)

Art. Number	Cu	Sn	Pb	Ag	Fe	Sb	Ni	As	Bi	Zn
EBA – 1	91	0,4	5,1	0,06		0,07	0,65	3	0,15	-
EBA – 2	92,5	0,12	0,25	0,015	0,06	0,16	0,06	6,2	0,015	-
EBA – 3	94	0,25	0,02	0,01	0,015	0,02	0,07	6,2	0,004	-
EBA – 4	95	0,3	0,25	0,06	0,15	0,13	0,32	2,4	0,5	-
EBA – 5	96	0,15	0,45	0,025	0,01	0,04	0,05	4,5	0,001	-
1st Mill. – 1	92,5	7	0,47	0,05	0,18	-	0,09	0,06	0,012	-
1st Mill. – 2	92,5	7,3	0,3	0,04	0,3	-	0,4	0,2	-	-
1st Mill. – 3	92	7,4	0,05	0,04	0,37	-	0,3	0,3	-	-
1st Mill. – 4	91,5	7,9	0,38	0,05	0,05	0,07	0,03	0,23	-	-
1st Mill. – 5	92,5	7,9	0,23	0,07	0,1	0,03	0,03	0,1	0,005	-
1st Mill. – 6	90	8	0,23	0,2	0,7	-	0,7	0,1	-	0,03
1st Mill. – 7	90	8,3	0,45	0,05	0,03	0,06	0,03	0,2	0,002	-
1st Mill. – 8	87	8,5	4,4	0,002	0,34	0,04	0,065	0,4	0,007	-
1st Mill. – 9	88	9	2,3	0,03	0,07	-	0,04	0,15	0,001	-
1st Mill. – 10	88,5	8,7	1,6	0,07	0,03	0,25	0,03	0,3	0,011	-
1st Mill. – 11	90	9	1,4	0,015	0,15	-	0,3	0,1	-	0,2
1st Mill. – 12	87	9,6	2,2	0,04	0,42	-	0,1	0,18	-	-
1st Mill. – 13	88,5	9,8	0,2	0,07	0,085	-	0,015	0,15	0,006	-
1st Mill. – 14	88	10,6	0,95	0,085	0,3	0,3	0,09	0,1	0,01	0,15
1st Mill. – 15	88,5	10,9	0,7	0,06	0,05	-	0,3	0,12	0,003	-
1st Mill. – 16	91,5	6,3	0,85	0,002	0,01	-	0,02	0,1	-	-
1st Mill. – 17	83,5	9,3	3,5	0,04	0,1	0,3	0,04	0,75	-	-
1st Mill. – 18	87,5	9,1	0,93	0,16	0,08	0,23	0,05	0,65	0,008	0,8
1st Mill. – 19	87	11,2	0,6	0,08	0,06	0,15	0,02	0,1	0,002	-
1st Mill. – 20	86	8,8	0,35	0,13	0,15	0,7	0,015	2,5	0,02	-
1st Mill. – 21	85,5	11	0,4	0,045	0,33	0,55	0,3	0,55	0,025	0,4
1st Mill. – 22	90	8	0,23	0,2	0,07	-	0,7	0,1	-	0,03
1st Mill. – 23	93	6	0,6	0,4	0,17	-	0,5	0,2	-	0,01
1st Mill. – 24	90	9	1,4	0,15	0,15	-	0,3	0,1	-	0,02
1st Mill. – 25	90,9	6,3	0,98	0,069	0,59	0,27	0,087	0,55	-	0,29
1st Mill. – 26	82,9	8,3	2,2	0,11	3	0,87	0,021	0,085	-	1,9
1st Mill. – 27	75,2	10	6	0,18	1,6	2,3	0,029	1,7	-	1,5
1st Mill. – 28	89,1	10,4	0,051	0,06	0,07	-	0,01	0,23	-	-
1st Mill. – 29	73	25,5	0,43	0,18	0,038	0,33	0,01	0,4	-	0,053
1st Mill. – 30	76,4	23,4	0,046	0,043	0,12	-	0,01	-	-	-
1st Mill. – 31	90,6	8,1	0,43	0,083	0,27	0,17	0,018	0,38	-	-
1st Mill. – 32	91,2	7,7	0,42	0,087	0,043	0,16	0,019	0,39	-	-
1st Mill. – 33	89,7	9,3	0,48	0,099	0,085	0,17	0,013	0,4	-	-
1st Mill. – 34	91,3	7,9	0,35	0,072	0,027	0,14	0,012	0,21	-	-
1st Mill. – 35	82,2	17,6	0,13	0,061	0,15	-	0,012	-	0,01	-
1st Mill. – 36	75,7	24,2	0,074	0,04	0,023	-	-	-	0,01	-
1st Mill. – 37	85,9	13,6	0,03	0,077	0,42	-	0,01	-	0,01	0,27
1st Mill. – 38	83,7	16,1	0,02	0,089	0,19	-	0,01	-	0,01	-
1st Mill. – 39	87,2	11,2	0,17	0,041	0,26	0,13	0,072	0,41	-	0,58
1st Mill. – 40	90,1	9,3	0,092	0,072	0,11	0,1	0,028	0,23	-	-
1st Mill. – 41	75	10	0,34	0,054	3,7	-	0,012	0,47	-	10
1st Mill. – 42	75	15,6	0,039	0,013	0,081	-	-	-	-	10
1st Mill. – 43	75	6,3	0,094	0,057	3,8	-	0,025	-	-	10
1st Mill. – 44	84,2	9,2	5,8	0,07	0,74	-	0,036	-	-	-
1st Mill. – 45	85,2	13,3	0,032	0,056	1,1	-	0,067	0,19	-	-
1st Mill. – 46	86,9	12	0,072	0,042	0,073	-	0,18	-	-	-
1st Mill. – 47	82	11	5	-	0,25	-	-	-	-	2
1st Mill. – 48	81	4	2	-	0,3	-	-	-	-	12
1st Mill. – 49	86	3	3,5	-	0,3	-	-	-	-	8,5
Our Sample	**28**	**22,63**	**5,45**	**0,16**	**0,62**	**0,046**	**0,13**	**0,621**	**-**	**0,188**

5. ASSESSMENT

When we look at the ores used since 5000 BC, copper ores come first. It is known that these can be classified as Kuprit, Melakonite, Malahyde, Azurite, Calcocyte, Covallite, Bornite, Chalcopyrite, Enargit and Tetrahydrite. Tetrahydride, cuprite, and melaconite ores, which contain trace amounts of zinc and iron elements, can be associated with the sample examined. Tetrahydride, which is weak in terms of copper, seems to be a more likely ore. Anatolian mines have a polymetallic characteristic. Since it is not possible to use copper alone in every field, it is known that it is used in alloys. Among the types of alloys used in Anatolian mining, Copper-Arsenic alloy is also included.

(Tekin, 2015). When we look at the areas where copper arsenic ore is found, it is possible to talk about the geography of Cyprus, Iran, and Anatolia (Jesus, 1980; Heskel et. al., 1980; Panayiotu, 1979). Another alloy known to be used later is the Copper-Zinc alloy (Tekin, 2015). This alloy is also called brass (Tekin, 2015). The earliest examples of brass use appear in Urartian metallurgy (Pernicka, 1995). It is known that brass was a metal that was also used in coin minting during the Roman Early Empire (Tekin, 2015). Another type of alloy is Copper – Silver alloy. This alloy is known to be used in items produced for both prestige and religious purposes (Hauptman et. al., 2000). Another alloy that forms the material of the fibula, which is also the subject of the study, is the Copper-Tin alloy. Analysis is needed to determine whether tin and copper are consciously alloyed or they are together due to ore when producing an object. While ore-sourced tin is below 2%, the rates above 2% allow us to consider willing bronze production (Tekin, 2015).

The melting point of copper differs according to the tin ratio in its content. As the tin rate increases, the melting point decreases (Lucas, 1962). If we look at the areas containing copper ore of Anatolian origin, it is known in the light of written sources that Kizzuwwatna and Ankuwa are the regions used in copper supply (Tekin, 2015; Kosak, 1982:).

To evaluate the information on the use of tin, there are findings of the use of tin at the alloy level in Afghanistan in the middle of the 4th millennium BC (Lamberg-Karlowsky, 1967; Penhallurick, 1986). It is known that tin was used in Anatolia from the 2nd half of the 3rd millennium BC. (Tekin, 2015; Eaton et. al. 1976; Gurney, 1952; Selimkhanov, 1962; Penhallurick, 1986; Stech et. al. 1986).

6. DISCUSSION

A clear answer to the question of where the tin came from in Anatolia could not be found. Afghanistan is seen as a possibility at this point. The basis for this is that in the 2nd layer of Troy there are also stones of Central Asian origin such as jade and nephrite (Schmidt, 1902). In this case, it was used as data to support the hypothesis that tin is originated from Central Asia, which was the common view of the period. By synthesizing this information, the view that tin came to Anatolia by imported means was tried to be brought to the forefront (Belli, 1991). It is known through written sources that in the 13th century BC the Hittites procured tin from Kizzuwatna (Kosak, 1982). Archaeometallurgical surveys conducted throughout the country in the past also show that this region contains tin mines (Yener, 1992; Yener et. al., 1993). The issue of Kizzuwatna's boundaries is still a matter of debate among Hittithologists. However, the region that we will compare in terms of analysis data is located within the region called Kizzuwatna (Goetze, 1940; Ünal, 2002). Kizzuwatna is the area west of the Kayseri, Adana line (Ünal, 2002). When the mines and geological formations in this area are examined, answers have been produced to the question of whether there is tin as mentioned above (Yener et. al., 2015). These answers, which contain certainty that tin is found, seem insufficient when the conditions of the reserves are evaluated in the face of today's need (Dinlen, 2021). However, this answer is given from today's perspective and does not even allow the production of ideas about their adequacy or inadequacy, let alone proving that these deposits were insufficient in the past. Among the tin fields identified in Turkey, the mines of Çamardi / Celaller and Ulukışla / Bolkardağı located in the east of Niğde city center are noteworthy (Dinlen, 2022, Drahor, 1993). These areas are located within the boundaries of the Kizzuwatna region described above. In addition, Ayhan, in an article about Çamardi carbonated zinc-lead deposits, states that there are greenockite deposits rich in iron, and poor in cadmium inside Aladağ - Delikkaya region (Ayhan, 1983). According to the analyses made in the samples taken from Aladağ – Delikkaya region, it was determined that 0.1% cadmium was found (Ayhan, 1983).

The reason why the temporal limitation is limited to the 1st millennium is that the fibula, which is the subject of the article, belongs to this period. In this period, the knowledge of human beings to be able to use tin and gold was reflected even in literary texts (Homer). With the end of the Hittite empire in 1200 BC, it is seen that the peoples loyal to the empire continued to exist in what we call the Late Hittite City-States. The Late Hittite City States were located south of the Kızılırmak arc in the area we call Kizzuwatna. (Pınarcık, 2018). The city-states, located on the rich mineral deposits in Kizzuwatna, continued to exist for a while by controlling these mines as well as other advantages of the region.

The Phrygians, who were located in a location where the provinces of Kütahya, Eskişehir, and Afyon were the focus, were among the peoples who settled in Anatolia after the collapse of the Hittite State in the 12th century. (Sams, 2007). Their capital was Gordion in the Polatlı district of Ankara (Sams, 2007). Phrygians would inevitably take an active role in this region. It seems possible that there was a relationship between Phrygia and the mining sites held by the Late Hittite city-states. (Küçükbezci, 2019). However, it is not yet archaeologically proven. In many parts of Anatolia, works in the Phrygia style are encountered. (Conka, 2012, 59). This may have been due to the fact that Phrygian mining was at the top of its period and that Phrygs exported finished products. There are important studies for the determination of the mining sites of this period. However, there is a gap in the literature in terms of raw material-work matching. For this reason, the study has also undertaken the responsibility of filling an important gap in this direction. It has been proven for the first time that Phrygian fibulas are produced by metals procured from the mining site in the north of the Taurus Mountains.

The geography in which the Phrygians lived was one of the important production centers of the period since the 1st millennium BC in the field of mining. As a result of the excavations carried out in the capital Gordion, a large number of metal works were uncovered in different groups. The Phrygians, who are known to have used many alloys, used the copper-tin alloy that is bronze, which was used in Anatolia after the 3rd millennium BC. (Vassileva, 2012). Phrygian metallurgy is also known to influence surrounding cultures. The fact that phiales with Phrygian omphalos influenced the phiales of Greek omphalos is one of the best examples of this (Vassileva, 2012). One of the first artifacts that come to mind when it comes to Phrygian metal artifacts is undoubtedly Phrygian fibulae.

7. CONCLUSION

The work that is the subject of the study is dated to the 8th-6th century BC thanks to other examples dated by context through analogical comparison. When the political conjunctural structure of this period is examined, it is seen that the Hittite empire collapsed and the Late Hittite City States, which we can consider as their successors, were located in the south of the geography once under the Hittite Domination. Their location in this region gave the Late Hittite City States a great advantage in terms of mineral raw materials. This situation strengthened the Late Hittite city-states economically and increased their resistance against Assyria on the stage of history. This role they played in mining allowed the Late Hittite City States to be in contact with other Anatolian peoples.

The amount of antimony seen in the archaeometric analysis is in line with the Early Bronze Age average. While this situation allows suggesting the use of mineral resources of Anatolian origin in the Early Bronze Age, it can be explained that imported products were brought from mines outside Anatolia as of the 2nd millennium BC (increasing in the 1st millennium BC). It can be argued that tin imports have increased in order to meet the increasing need for tin in the mining sector.

It can be said that mineral deposits of Anatolian origin are used intensively in terms of copper, lead, zinc, and silver. The fact that the trace amounts of lead, nickel, and silver elements in the fibula subject to this study are close to the Early Bronze Age average supports the hypothesis of using raw material resources originating from Anatolia. It is possible that the increasing need for tin was met from outside Anatolia.

Elements such as zinc, lead, copper, and silver in the content of the artifact may be related to the Aladağlar (Niğde – Kayseri) mining site as mentioned above. The most important data supporting this hypothesis is the Greenockit deposits seen in the west of the same field. When the Greenockit deposits in this field are analyzed, it is seen that they contain a trace amount of cadmium.

It is not possible for cadmium, which is a mineral found in small quantities in the world, to be brought by imported means and used in the production of the fibula subject to examination, that is, to be added consciously. It is thought that it came among the ores brought to the Phrygian geography from the Aladaglar mine site under the Late Hittite Control and was used in the production of the fibula.

As a result, it was possible to produce an answer to the question of the mineral origin of the fibula thanks to the element cadmium found on the Phrygian fibula, stylistically dated to the 8th-6th centuries BC. Non- destructive archaeometric analysis on the fibulas recovered in the museums and excavation areas shown on the map will make it possible to follow a new way thanks to the use of trace element data in determining the origin of the artifacts.

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