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Application of PIXE Spectrometry in Determination of Chemical Composition in Ilkhanid Silver Coins

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ABSTRACT

The study of the elemental composition of silver coins of the Ilkhanid period can help explain the locations and identification of coin mines. It also provides information regarding the economic and political conditions of the time period under study. The aim of this work is to study the chemical composition of certain Ilkhanid coins in order to determine any connection between the mines used for extraction of the silver and the actual silver coins minted at that time. Using the PIXE technique, the metallic elements Fe, Cu, Zn, As, Ag, Au, and Pb were analysed.

1. Introduction

The study of ancient coins may serve as an indication of the economic and political circumstances at the time of their production. In connection with the iconography, the archaeological issues concern the dating, provenance, technology and authenticity. Coins play an important role in the Iranian cultural heritage. Those coins which belonged to the kings of Ilkhanid were under study.

Using the proton induced X-ray emission (PIXE) technique to study ancient coins is one of the common methods for determining the chemical composition of ancient metals (Smith 2005, 258–264). This technique served to highlight several aspects of the period under study. These findings can be used as a means to deduce information on the economic conditions and the possible sources of metals. Out of various spectroscopic techniques, PIXE is both a useful and non-destructive approach providing archaeologists with highly fruitful information (Guerra 1995; Torkih 2010; Roumie 2010). PIXE has also been applied non-destructively in order to detect trace elements (Constantinescu 1999). PIXE offers maximum sensitivity for elements ranging from approximately Ar to Zr (Constantinescu 1999; Khademi

Nadooshan 2011; Hajivalei 2012). The variation in the proton beam energy enables the characterization of the layered structures at the surface (Linke 2004: 127–178). Using PIXE as an analytical tool, we have focused on those metals once used in the Ilkhanid periods in Iran.

1.2 Historical Background

In the early 13th century A.D., under the leadership of Genghis Khan, the Mongol Empire expanded out of their original homeland in the eastern zone of the Asian steppe and took over most of Asia. After the death of Genghis Khan, the Empire was divided among his heirs, and consequently Hulagu Khan, Genghis Khan's son, founded the Ilkhanid dynasty of Iran. The Ilkhans consolidated their position in Iran and united the region as a political and territorial entity after centuries of fragmented rule by local dynasties. Hulagu Khan seized the Castle of Alamut, suppressed the Ismaili sect in 1256 and defeated Abbasid Caliph's final army. Al-Musta'sim was captured and executed in 1258, ending 525 years of the Abbasid Caliphate. In 1265 Hulagu Khan died and was succeeded by seven successors: Abagha Khan (1265–1282), Ahmad sultan (1282–1284), Arghun Khan (1284–1291), Gaykhatu (1291–1295), Baydu (1295), Ghazan Khan (1295–1304), Oljeitu (1304–1316), and Abu Said (1316–1335). With the death of Abu Said the Ilkhanid dynasty in Iran virtually came to an end (Figure 1) (Spuler 1986; Alizadeh *et al.* 2002).

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Figure 1. Iran in the Ilkhanid Period.

1.3 Research Background

In light of the historical significance of the coins, there was a need to choose a non-destructive method. PIXE is one of the common methods in such cases as it is completely non-destructive, multi-element, fast and sensitive (Guerra 1998). A number of non-destructive spectroscopic methods, including PIXE, have been used to analyse silver objects (Smith 2005).

Firstly, Bacharach conducted research on Sasanian silver coins (Bacharach 1972) with the results having been consequently compared with those of Rome (Hughes 1979). Meyers (2003) and Gurdus (1967) published two articles

on the cupellation technique which was applied to mineral ores as galena in order to obtain Ag by oxidation of Pb and Zn. The presence of Au and Zn along with Pt, as trace elements, had been reported by both authors. In these cases, trace elements were used to find locations of silver origin during the Sasanian period. It was also mentioned that coin thickness had been determined empirically (Gordus 1967).

When re-melting and re-using operations are carried out, however, the Au contents might not be representative of the provenance. Kontos (2000) has demonstrated that Bi may be present as an indicator for the silver mine location in the case of silver coins from Athens. Guerra (Guerra 1995; 1998;

Figure 2. Silver coins of the Ilkhani and the concentration of Au/Ag Vs. Cu% with the PIXE technique.

Table 1. Percentage of elements present in the Ilkhanid coins by PIXE.

Sample	King Name	Weight	Cl	Ca	Cr	Mn	Fe	Cu	Zn	As	Ag	Au	Pb	Au/Ag
1	Ghazan	2.51	1.7	1.8		0.0	0.08	5.2	0.0	0.1	89.2	1.0	0.8	0.01
2	Ghazan	3.62	2.1	1.1		0.1	0.1	25.8	0.4		68.6	0.7	1.1	0.01
3	Arghun	2.31	1.2	1.1			0.1	21.0			74.5	1.0	1.1	0.01
4	Ghazan	2.66	6.2	1.0			0.3	4.3			85.7	1.2	1.3	0.01
5	Ghazan	2.46	4.5	1.0	0.2		0.8	8.9			83.3	0.9	0.5	0.11
6	Ghazan	2.72	8.5	1.2	0.1		0.8	15.7			71.7	1.1	1.0	0.02
7	Arghun	2.65	1.0	2.1	0.1		2.3	5.3			87.5	0.8	0.9	0.01
8	Hulaku	2.39	8.5	1.2		0.2		20.7	0.4		67.3	0.6	1.3	0.01
9	Ghazan	3.28	5.6	1.2		0.1	0.1	14.8	0.2		75.8	0.8	1.4	0.01
10	Arghun	2.46	7.5			0.1		18.4	0.6		70.6	0.8	1.0	0.11
SUM			39.3	11.7	0.4	0.41	4.58	121.7	1.05	0.1	703.6	8.1	9.4	
AVERAGE			4.37	1.3	0.13	0.0	0.57	13.52	0.0	0.1	78.17	0.9	1.04	
STDEV			0.38	0.38	0.06	0.0	0.76	7.97	0.0	37.0	8.38	0.19	0.28	
S E			0.54	0.57	0.0	0.0	0.02	1.64	0.0	0.03	28.21	0.32	0.25	

2004; 2008) revealed that several elements may characterise Au mines and gold coins. Throughout this study, there has been an attempt to discover the connections between the silver which was used for issuing coins in the Ilkhanid period and the probable sources of metal used at that time.

2. Material and methods

2.1 Experimental set-up

The analyses were carried out in a van de Graff accelerator at the Atomic Energy Organisation of Iran (AEOL). A 2 MeV proton beam with a current of 2–3 nA was used to bombard the coins. The coins were consequently inserted into a multi-purpose scatter chamber maintained in a high vacuum (10–5 Torr). The emitted characteristic X-rays were detected with an ORTEC Si (Li) detector (FWHM 170 eV at 5.9 keV). The GUPIX (Campbell *et al.* 2000) software was employed in order to analyse the obtained spectra. The results are shown in Table 1. Major elements are those contributing with a more than 10% to the overall composition, minor elements 0.1–10% and trace elements less than 0.1% down to detection limits. The overall uncertainty for the PIXE method was 5% for the major elements; 5–10% for the minor elements and 15% for the trace elements. The uncertainties are not only statistical, but also originate from the roughness of the coin surface and from the chemical corrosion and wear to the objects, altering the accuracy of the result (Khademi Nadooshan 2011).

2.2 Selection of Samples

Due to the long duration of rule, Ilkhanid silver coins, which were produced during the reign of Hulago Khan, Ghazan Khan and Arghun Khan, were selected. These coins belong to a private collection. All of the coins have been cleaned as follows: they have been kept in 3–5% formic acid solution for several minutes, scrubbed with a toothbrush and finally cleaned with alcohol soaked cotton.

3. Results and discussion

The metallic elements Ag, Au, Pb, Cu, Fe, Cl, Ca, Cr, Zn, Mn and As were detected in the studied coins (Table 1). Approximately half of the silver metals were in all probability produced from lead ores (Tylecote 1962). As in antiquity lead ores were largely exploited to produce silver, the proportion of Pb must have been relatively high (Hugges 1979). It is commonly accepted that silver metallurgy developed out of lead smelting technology and that the metal silver was extracted from silver-bearing lead ores (Meyer 2003). Recently, there has been a consensus that oxidized ores such as cerussite (PbCO_3) may have been the primary source for silver in the earliest stages (Craddock 1995). It is also assumed that among the various lead ores argentiferous galena (PbS) was the main source in antiquity for the production of silver (Meyer 2003). The presence of Pb in the alloys indicates the usage of lead and zinc in minting coins (Uzonyi 2000); and the lower Pb content in a number of the coins can indicate the quality silver refining process (Tripathy 2010). The results, which are shown in Table 1, can indicate that only the cerussite (PbCO_3) mine had been explored for extraction of silver in the coins under study. According to Meyers (2003), if the silver was produced from cerussite, the gold content would vary from approximately 0.25% to 1.0% which is valid for our case (Harper, Meyer 1981; Meyer 1993). Therefore, one might argue that it corresponds to the ratios which should be found for the ores from which the silver was extracted. In the spectra obtained by the PIXE technique, the Au is a trace element. Based on the results, a comparison of the Au/Ag ratio with the Cu content of the coins (Figure 1) reveals that one mine of the cerussite type had been explored for production of coins by Ilkhanid metalworkers. Variations in the Cu amounts in the silver coins of the Ilkhanid kings (Hulako Khan, Ghazan Khan and Arghun Khan) reveal that their reign was faced with an eco-political problem and that Cu was deliberately added to silver, not only for hardening purposes but also for economic reasons (Tripathy 2010). Coins No. 2, 3, 6, 8, 9 and 10

Figure 3. Obverse and reverse sides of Ilkhanid coins (Hulako Khan, Ghazan Khan and Arghon Khan).

have a higher percentage of copper which may indicate a debasement during the reigns of Hulako Khan, Ghazan Khan and Arghun Khan. Coins No. 1, 4 and 7 with less Cu, are indicative of an improved eco-political condition at the time during the Ghazan Khan and Arghon Khan periods.

The presence of Ca in the cleaned silver coins is due to the fact that its removal was impossible at that time during the

metallurgical process. Furthermore, the presence of Fe may be attributed to surface contaminations (Kantarelou 2011; Flament 2004). The results indicate a strong negative correlation between Ag and Cu, the more the Ag content, the less will be that of Cu. Moreover, a negative correlation between Ag and Pb can also be seen. The obverse and reverse of the Ilkhanid coins are shown in Figure 3.

4. Conclusion

In light of the absence of S in the analysed Ilkhanid coins, it can be concluded that the extractions of silver were not from Sulfide ores such as galena (PbS). In these cases, extractions seem to have been made from cerussite mineral ores (PbCO₃). The low amounts of Pb and Zn indicate their comparative purity and can indicate that Ilkhanid mineralogy as well as metallurgy was relatively developed. The presence of Cu in the samples is evidence of the eco-political problems during that era. One can thereby argue that metalworkers had deliberately added Cu to these silver alloys in order to reduce the costs. Based on this piece of evidence, these problems were more prevalent in the reigns of Hulako Khan, Ghazan Khan and Arghun Khan than Ghazan Khan and Arghon Khan.

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