Preliminary Report on the Analysis of an Early Bronze Age Iron Dagger Excavated from Alacahöyük

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1. INTRODUCTION

It is generally understood that smelting of iron requires a higher technology than smelting of copper, because iron smelting requires a higher reducing condition and temperature (Wertime 1968). There are various opinions as to the origins of iron smelting technology (Buchwald 2005, Wertime 1968; 1973). Iron is described as a more precious metal than gold in the Kültepe tablets of 1950 B.C. (Garelli 1963). It is often said that the Hittites were the only people who had iron smelting technology in the middle of the 2nd millennium B.C. From Anatolia, however, several iron finds dated to the 3rd millennium B.C. are reported, well before the Hittite period (Waldbaum 1980; Yalçın 1999). Among the most well preserved and best known is the gold-handled dagger (find number Al.K.14) excavated from grave K of Alacahöyük, dating to the Early Bronze Age (ca. 2400–2300) (Koşay 1938;1951; Wertime 1973).

Where did the iron in this early dagger come from? It is generally accepted that iron was obtained from meteoric iron before iron smelting was invented (Waldbaum 1973). Since meteoritic iron is rich in nickel and smelted iron is not, the two iron sources are often distinguished by the analysis of Ni. The Alacahöyük gold-handled dagger is in the collection of the Ankara Museum of Anatolian Civilizations. Recently, we had the opportunity to analyze the iron dagger for this work, courtesy of the museum. X-ray fluorescence (XRF) analysis was applied to investigate the chemical composition of the iron dagger.

2. EXPERIMENTAL

Analysis was conducted at the conservation laboratory of the Ankara Museum of Anatolian Civilizations. First, the sample was separated into the components of gold decoration and iron blade, whose part was subjected to the X-ray camera to take an X-ray transmission photograph. Nondestructive chemical compositional analysis was conducted with a portable X-ray fluorescence spectrometer, OURSTEX 100FA-II. A view of the measurement conducted at the museum using the portable XRF spectrometer is shown in Fig. 1. This instrument was jointly developed by OURSTEX Co. and the NAKAI laboratory (Nakai *et al*. 2005; Abe *et al*. 2009) and is composed of a high-voltage power supply, a counting circuit controller, a spectrometer, a small vacuum pump, a lap-top computer, and an external water-cooling system. The open-designed measurement head (spectrometer) allows us to analyze a sample of any shape and size. This instrument uses an X-ray tube with a Pd target, and two excitation modes are available: A monochromatic X-ray mode utilized by a pyrolytic graphite (0002) crystal to obtain a Pd-K line X-ray for the analysis of medium to heavy elements, and a white X-ray mode for analysis of both light elements and

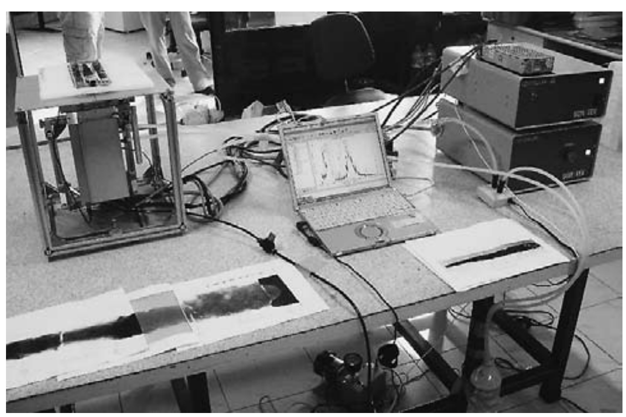

Fig.1 Analysis of the iron dagger using a portable X-ray fluorescence spectrometer.

Table 1 XRF analysis conditions of the iron dagger.

X-ray target	Pd (Monochromatic X-ray)
Detector	SDD
Voltage [kV]	40.0
Current [mA]	0.50
Measurement Time [sec.]	200–2000

heavier elements. Using both modes and 40 kV X-ray tube, highly sensitive analysis of elements with atomic number greater than that of Na can be carried out. The silicon drift detector (SDD) was adapted as a detector and cooled to operation temperature by an internal Peltier device and an external water-cooling system. With these features, this instrument has the world's highest level of sensitivity among such portable instruments. The measurement conditions for the X-ray fluorescence analysis are shown in Table 1.

3. RESULTS AND DISCUSSION

The iron part of the dagger is totally corroded; an X-ray photograph suggests that no metallic iron remains in the sample. An example of the XRF spectrum of the iron dagger is shown in Fig. 2. It shows that the major components of the dagger are iron (Fe) and nickel (Ni), with trace amounts of cobalt (Co). The other minor elements such as Ca, Zn, As, and Sr are mostly due to the components of iron corrosion, contaminated soils, and conservation materials. In order to estimate the original composition of the iron, it is necessary to exclude the elements introduced by the corrosion process. We carefully analyzed 22 sample points on the dagger, on both sides, to reveal the elements that originally existed in the iron dagger. It is expected that the elements that originally existed in the dagger should show a positive correlation with the concentration of iron. The analysis showed that nickel and cobalt have a positive correlation with the iron, indicating that these two elements are original components of the dagger.

Quantitative analysis of iron, nickel and cobalt were carried out by the calibration curve method; the data expressed as oxide components are shown in Table 2. The NiO content showed significantly high values ranging from 3.08 to 7.59 wt%. We also analyzed several samples of meteoric iron as well as an iron of the Hittite period at the same time for comparison. The Hittite iron was excavated from a Hittite stratum at Alacahöyük and would be a fragment of fibula, or horseshoe. The Ni content of the Hittite iron is extremely, lower than detection limit of the spectrometer. Fig. 3 compares the shapes of the nickel and iron peaks in the XRF spectra of the dagger and the meteoritic iron. The spectra closely

Table 2 Chemical composition expressed as oxide form.

		NiO [%]	CoO [%]
Iron dagger	Point 1	3.08	0.20
	Point 2	5.16	0.31
	Point 3	7.59	0.29
	Point 4	5.70	0.24
Hittite iron	AI.D 225	Not detected	0.24

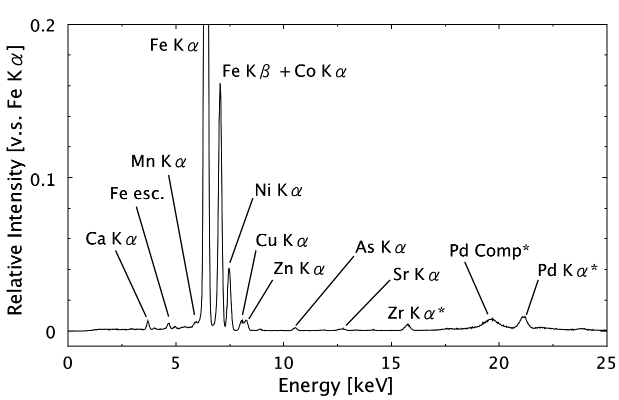

Fig.2 An example of the XRF spectrum of the iron dagger.

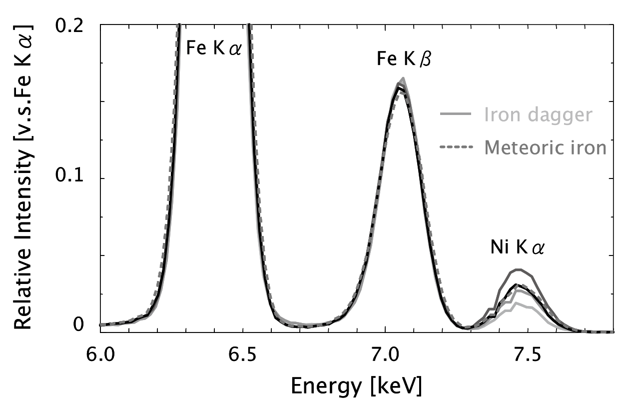

Fig.3 Comparison of the shape of Fe and Ni peaks for the XRF spectra of the iron dagger and meteoritic iron.

resemble each other. From these observations it is reasonable to conclude that the iron dagger was produced using meteoritic iron. This paper is a preliminary result of the study; detailed results will be reported in a scientific journal in the near future.

4. ACKNOWLEDGEMENTS

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