

The Production Technique of Gold Wash Wares from Kaman-Kalehöyük

Chiemi KUMAZAKI and Izumi NAKAI

Tokyo

ABSTRACT

The Iron Age Gold Wash Ware excavated from Kaman-Kalehöyük can be divided into two types: one with gold colored particles and the other without visible particles. The gold colored particles and the firing temperature of both ware types were studied using XRD and SEM-EDS techniques. The gold colored particles were identified as muscovite and the particles without visible gold colored appeared to be typical of tri-octahedral mica, close to a phlogopite composition. The XRD and SEM analyses suggest that the firing temperature of both groups was below 900°C.

INTRODUCTION

The Iron Age Gold Wash Ware of Kaman-Kalehöyük has a glossy surface and was produced by firing in an oxidizing atmosphere. This type of ware can be divided into two types: one has clearly visible gold colored particles (called type 1 here) and the other (type 2) has no visible gold colored particles (Matsumura 2000). Figure 1 shows the two types of Gold Wash Ware. These wares have been found mostly in second millennium B.C. contexts at Kaman-Kalehöyük, but some have also been found in the first millennium B.C. layers. In the second millennium B.C. in western Anatolia, Gold Wash Ware and so-called Plumbeous Ware with a glossy silver surface appeared at the same

time. The Plumbeous ware was fired under reducing conditions and is gray in color. The silver lustrous materials on the Plumbeous Ware surface have been analyzed and identified as either muscovite or another type of mica with a crystal structure and chemical composition similar to muscovite (Matsunaga and Nakai 1998 ; 2000). Since the gold particles on the surface of the Gold Wash Ware are also thought to be mica, it has been proposed that Gold Wash Ware and Plumbeous Ware were produced using a similar micaceous wash surface treatment technique but produced under different firing conditions (Matsumura 2000).

Other wares from sites in Turkey have a similar surface treatment. The surface coating of Gökeyüp (Manise) cooking pottery is reported to be biotite, which is also a type of mica. Gökeyüp golden mica cooking pottery is a particular type of pottery produced according to ancient craft tradition in western Turkey. The pottery is fired by a simple bonfire technique. The mica coating turns a golden color due to the oxidation of the biotites during firing. The raw materials are 75% gneiss and 25% clay. The gneiss is crushed to obtained small temper grains. By sieving, a mica-rich gneiss fraction is obtained and is used for the surface coating (Çolak, Maggetti and Galetti 2006).



Fig. 1 The Gold Wash Ware excavated from Kaman-Kalehöyük
(a) With gold colored particles on the surface (type 1)
(b) Without visible gold colored particles on the surface (type 2)
(bar = 2 cm)

The glossy surface of North Black Polished Ware (NBPW) is also reported to be mica. North Black Polished Ware was produced at the height of the Iron Age in India, *ca.* the sixth to second centuries B.C. The surfaces, although typically glossy black, are a “bronze metallic” surface overlying a glossy black slip. The surface of NBPW was analyzed and the black coloration is due to the presence of an iron-rich biotite or related mica, and the surface gloss is attributed to the alignment of the mica platelets parallel to the slip surface. The “bronze metallic” surface is considered to be due to a similar mica that has been oxidized during heating (Gillies and Urch 1983; Lambert, McLaughlin, Shaw, and Xue 1999).

The Gold Wash Ware and Plumbeous Ware from Kaman-Kalehöyük both have a similar glossy surface, but they are different in color. The former shows a gold color and the latter a silver color. Chemical characterization of both wares is thus necessary to determine if the applied mica is the same type of mica. Different types of mica have different colors, and it is possible that the mica was selected to obtain the desired color. The present study was conducted to identify the particles in the Gold Wash Ware.

The firing temperatures of the two types of Gold Wash Ware were also estimated in this study through refiring experiment. The firing temperature of the Plumbeous Ware has been estimated to be 800 or 900°C (Matsunaga and Nakai 2000).

The gold colored particles on the surface were examined by X-ray powder diffraction analysis (XRD) to identify the crystalline material. A scanning electron microscope equipped with an energy dispersive X-ray spectrometer (SEM-EDS) was used to investigate

the component elements. The firing temperature was evaluated using XRD to determine the change in the crystal structure of the component minerals after the wares were refired (Higashimura 1990: 171-184). SEM was used to observe the changes in morphology developed during the refiring (Tite 1969; Maniatis and Tite 1981).

Finally, we tried reproducing Gold Wash Ware and Plumbeous Ware using the types of mica identified in our analyses, muscovite and phlogopite.

EXPERIMENTAL

(1) Identification of the gold colored particles

Optical microscopy: First, the surfaces of all the pottery sherds were examined using an optical microscope. Gold colored particles on the surfaces were sampled from the sherds using a needle under the microscope.

X-ray powder diffraction (XRD) analysis: The samples were ground in ethanol using an agate mortar. Since the amount of each sample was very small, the measurements were carried out using diffraction-free quartz plate. The XRD patterns were measured using a RIGAKU RINT with a Cu-K α X-ray tube operated at 50 kV and 100 mA. The diffraction pattern was measured from 4° to 80° in 2 θ , at a scan rate of 4° min⁻¹ (step size = 0.2° 2 θ , time = 3 sec).

SEM-EDS analysis: The chemical composition of the samples was examined by an energy-dispersive X-ray spectrometer (EDS). The samples were coated with graphite before EDS analysis. The EDS investigations were carried out using a HITACHI S-5000 coupled with

Table 1 List of studied samples

	Date	Area	Sector	Grid	Layer	PL	Structure
Type 1 Gold Wash Ware	0400707	North	XXXII	XLIII-51	II a	⑰	
Type 1 Gold Wash Ware	0400810	North	XXXII	XLIII-50	II a	⑰	P2802
Type 1 Gold Wash Ware	-	North	-	-	II a	-	
Type 1 Gold Wash Ware	9500815	North	XXX	XLIK-51	II a	⑤	P1279
Type 2 Gold Wash Ware	9200827	North	XXII	XLIK-55	II a	⑩-e	
Plumbeous ware	0400729	North	XXXII	XLII-50	II a	⑳	

an energy-dispersive detector; analysis condition 20 kV; measurement time 100 s (live time).

(2) Estimation of firing temperature

The samples were cut from the sherds with a diamond-cutter. Refiring of the sherds was done at 500, 700, 800, 900 and 1000°C using a programmable furnace. The heating rate was 3.3°C per minute, and holding time at the highest temperature was one hour. The furnace was then cooled at 3.3°C per minute.

The refired samples were then crushed and ground in an agate mortar. They were analyzed by XRD under the same measurement conditions used for the identification. The SEM observations were carried out using the JEOL-7000F. A fragment of each sample was coated with platinum-palladium before the SEM observations. The accelerating voltage was 3 or 5 kV.

(3) Reproduction of Gold Wash Ware and Plumbeous Ware

A natural muscovite from Shiraishi, Fukushima, Japan was used in the reproduction of type 1 Gold Wash Ware and Plumbeous Ware. A natural phlogopite from Russia and biotite from Bear Lake, Ontario, Canada were used in the reproduction of type 2 Gold Wash Ware.

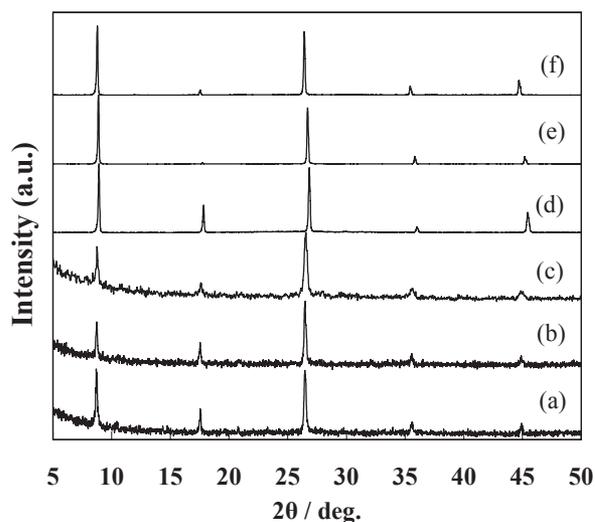


Fig. 2 The X-ray powder diffraction pattern of the gold colored particles (a), (b), (c) and reference minerals (d), (e), (f) (a) The gold colored particles on the type 1 Gold Wash Ware, (b) The gold colored particles on the type 2 Gold Wash Ware, (c) The silver lustrous material on the Plumbeous Ware, (d) muscovite, (e) biotite, and (f) phlogopite

A clay from Shigaraki, Shiga, Japan was used for the substrates. A fragment of mica was cut from the mineral specimen and crushed in an agate mortar. The ground mica was applied on the surface of the clay block with a finger when the block was in semidry condition.

The blocks were then fired in a furnace to 800°C at the rate of 2.2°C per minute, and held at the highest temperature, 800°C, for one hour. The furnace was then cooled at 100°C per hour. The firing atmosphere was oxidizing for reproduction of the type 1 and type 2 Gold Wash Wares, but reducing for reproduction of the Plumbeous Ware. To create a reducing atmosphere, the samples were placed in a clay box, which was then placed in another bigger alumina box filled with activated charcoal.

RESULTS AND DISCUSSION

(1) Identification of the gold colored particles

The gold particles on the surfaces of the type 1 and type 2 Gold Wash wares were identified as one of the mica group minerals (Fig. 2). The chemical composition of the type 1 sample was very similar to that of muscovite (Fig. 3). The gold particles on

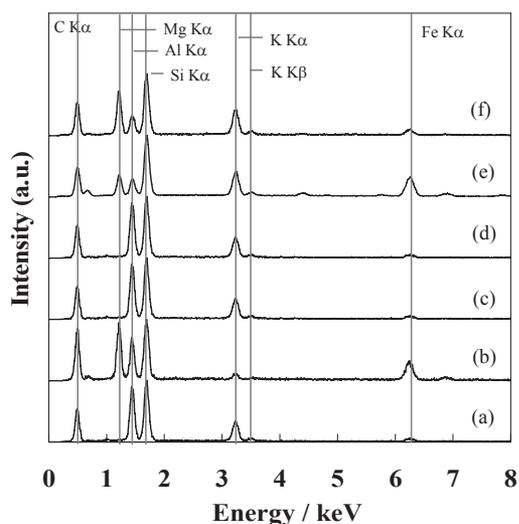


Fig. 3 The EDS spectrum of the gold colored particles (a), (b), (c) and reference minerals (d), (e), (f) (a) The gold colored particles on the type 1 Gold Wash Ware, (b) The gold colored particles on the type 2 Gold Wash Ware, (c) The silver lustrous material on the Plumbeous Ware, (d) muscovite, (e) biotite, and (f) phlogopite

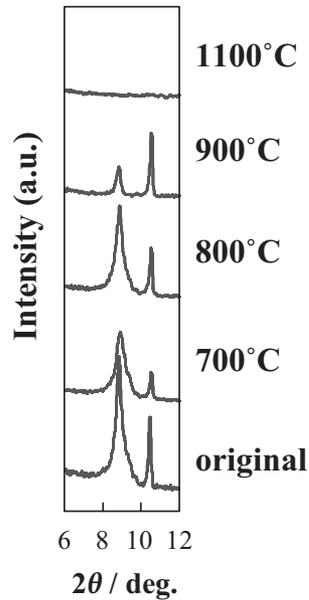


Fig. 4 X-ray powder diffraction pattern of the original sample and the sample refired at several temperatures

the surfaces of the type 1 ware were identified as muscovite. The chemical composition of the type 2 sample was different from those of the type 1 ware and the Plumbeous Ware, and similar to biotite or phlogopite (Fig. 3). The gold particles on the surfaces of the type 2 ware were assumed to be tri-octahedral mica that is close to phlogopite. Biotite has a high iron content and is a very common member of the mica group, forming a series with phlogopite. The 3T and 1M polymorphs in the phlogopite-biotite series are not distinguishable by powder diffraction patterns. The term biotite used here denotes an iron-rich tri-octahedral mica which is arbitrarily differentiated from phlogopite in having $Fe/Mg > 1/2$ (Deer, Howie, and Zussman 1967).

(2) Estimation of firing temperature

The X-ray powder diffraction patterns of the original samples and refired samples are shown in Fig. 4.

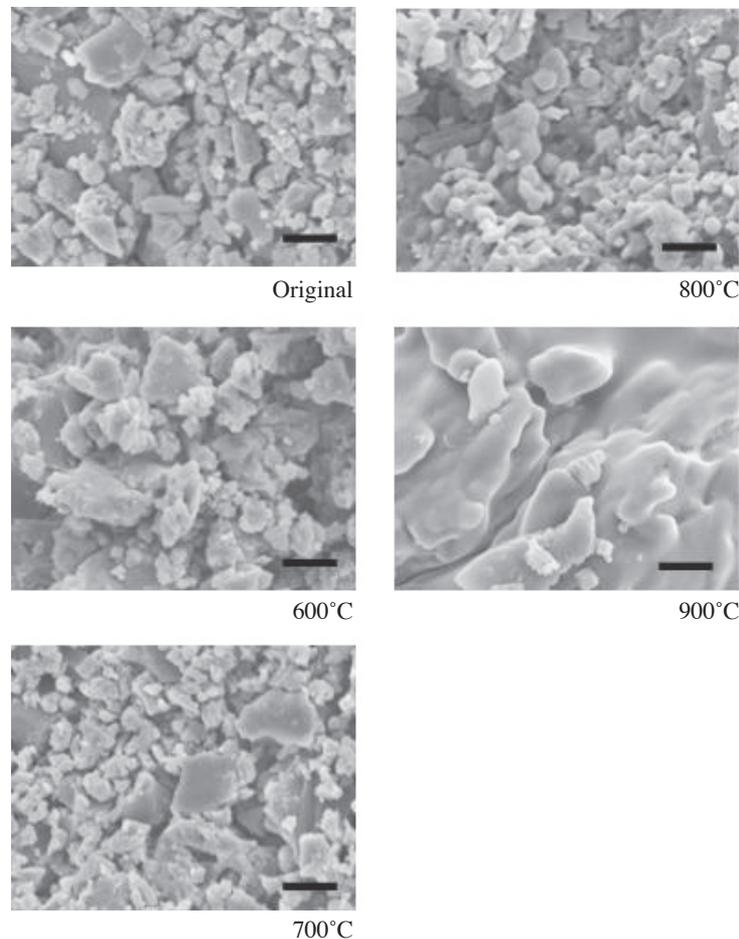


Fig. 5 SEM images of the samples refired at several temperatures (bar = 1.00 μm)

The diffraction peaks of illite in the original sample were reduced in intensity when the sample was refired at 900 °C. This result suggests that the firing temperature was less than 900 °C.

Figure 5 shows the SEM images of the morphologies of the refired samples. The original sample showed no vitrification and is an aggregate of flaky clay particles. These morphologies did not change when refired at temperatures of 500, 700, and 800 °C. In contrast, the morphology of the sample changes at 900 °C. The clay particles began to vitrify, combine, and increase in size, forming a smooth surface in the sample refired at 900 °C. From these observations, the firing temperature of the Gold Wash Ware was estimated to be below 900 °C.

(3) Reproduction of Gold Wash Ware and Plumbeous Ware

We have revealed that the gold colored particles on the surface of the type 1 ware and the lustrous material of the Plumbeous Ware were composed of the same type of mica, i.e., muscovite. The reproduction experiment revealed that the only difference between the two wares was the firing atmosphere.

The reproduced samples with muscovite are shown in Fig. 6. The sample fired under oxidizing conditions contains gold colored particles similar to the type 1 Gold Wash Ware (Fig. 6 (b)). The sample fired under reducing conditions shows a silver luster surface similar to that of

the Plumbeous Ware (Fig. 6 (a)).

As muscovite is white to colorless, the gold color on the surface of the type 1 Gold Wash Ware is created by the mixture of the white muscovite and the red color of the oxidized body; whereas the silver luster of the Plumbeous Ware is caused by the mixture of white muscovite and the gray color of the body obtained under reducing conditions. The different color of the surface luster of each ware is physical between the surface and core, rather than based on chemical properties.

The sample coated with phlogopite has gold particles and a similar glossy surface and coloration (Fig. 6 (c)) as the type 2 Gold Wash Ware, but the sample coated with biotite shows black particles that are different from type 2 (Fig. 6 (d)). The color of the biotite did not turn golden under oxidizing conditions.

The glossy surfaces of type 1 and type 2 Gold Wash Wares and Plumbeous Ware were reproduced with mica. It is concluded from these results that the glossy nature of both ware surfaces is due to the alignment of the mica platelets parallel to the surface.

CONCLUSION

The gold colored particles visible on the surface of Gold Wash Ware (type 1) was identified as muscovite. The gold colored particles on the Gold Wash Ware without visible gold particles (type 2) was found to be

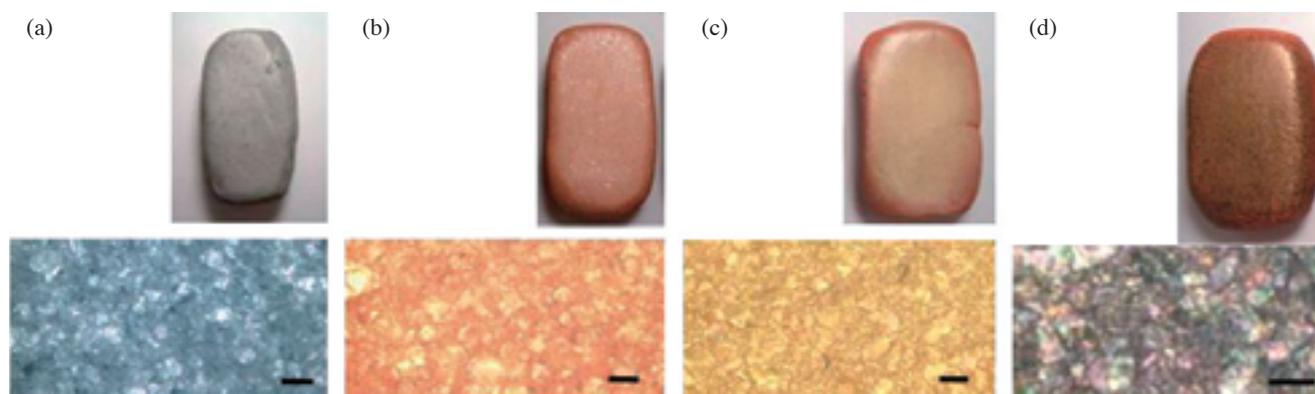


Fig. 6 The reproduced samples using muscovite, phlogopite, and biotite
 (a) Using muscovite firing under reducing conditions, (b) Using muscovite firing under oxidizing conditions
 (c) Using phlogopite firing under oxidizing conditions, (d) Using biotite firing under oxidizing conditions

Upper: photograph of the samples

Lower: optical micrographs of the samples (bar = 100 μ m)

another kind of mica, but not muscovite; it is assumed to be tri-octahedral mica close to a phlogopite composition. The estimated firing temperature of both types of Gold Wash Ware was lower than 900°C.

It was confirmed that the surfaces of the type 1 Gold Wash Ware and the Plumbeous Ware were produced with the same material, *i.e.*, applied muscovite, but by using different firing conditions; the firing temperatures of both were similar, but each was produced under a different atmosphere.

The surface gloss of the Gold Wash Ware and Plumbeous Ware is attributed to the alignment of the mica platelets parallel to the surface and the coloration developed in the firing atmosphere.

ACKNOWLEDGEMENTS

We are grateful to Dr. S. Omura for giving us the opportunity to perform this research, for the kind support and comments on our study, and for providing samples. We express our sincere thanks to Dr. K. Matsumura for directing our attention to this problem and for joining in the discussion of the results.

BIBLIOGRAPHY

- Çolak, M., M. Maggetti and G. Galetti
2006 “Golden mica cooking pottery from Gökeyü (Manisa), Turkey,” *Geological Society*, London, Special Publications 2006, v. 257, pp. 141-150.
- Deer, W.A., R.A. Howie and J. Zussman
1967 *Rock Forming Minerals*, Vol. 3, London.
- Gillies, K.J.S., and D.S. Urch
1983 “Spectroscopic Studies of Iron and Carbon in Black Surface Wares,” *Archaeometry* 25, pp. 29-44.
- Higashimura, T.
1990 *Archeology and Physicochemistry*, Gakuseisha (in Japanese).
- Lambert, J.B., C.D. McLaughlin, C.E. Shawl, and L. Xue
1999 “X-ray Photoelectron Spectroscopy and Archaeology,” *Analytical Chemistry News & Features*, Sept. 1, pp. 614-620.

- Maniatis, Y. and M.S. Tite
1981 “Technological Examination of Neolithic-Bronze Age Pottery from Central and Southeast Europe and from the Near East,” *Journal of Archaeological Science* 8, pp. 59-76.
- Matsumura, K.
2000 “On the Manufacturing Techniques of Iron Age Ceramics from Kaman-Kalehöyük,” AAS IX, pp. 119-136.
- Matsunaga, M. and I. Nakai
1998 “The Study of Material Science about the pottery excavated from Kaman-Kalehöyük (3) – production of Plumbeous Ware,” AAS VII, pp. 285-291 (in Japanese).
2000 “Study on Origin of the Silver Luster on Gray Iron Age Pottery,” AAS IX, pp. 29-44.
- Rice, Prudence M.
1987 *Pottery Analysis*, The University of Chicago Press.
- Tite, M.S.
1969 “Determination of the Firing Temperature of Ancient Ceramics by Measurement of Thermal Expansion,” *Nature* 222, p. 81.

Chiemi Kumazaki and Izumi Nakai
Department of Applied Chemistry
Tokyo University of Science
1-3 Kagurazaka, Shinjuku, Tokyo 162-8601
Japan
E-mail: inakai@rs.kagu.tus.ac.jp (Izumi Nakai)