The Production Technique of Fine Black Polished Wares from Kaman-Kalehöyük, Part 2

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INTRODUCTION

The so-called Fine Black Polished Ware excavated from the Iron Age layers (Stratum IIa-IIc) of Kaman-Kalehöyük is a pottery type produced by firing under a reducing atmosphere (Matsumura 2000). This ware has a totally black glossy surface and a dark grey clay body (Fig. 1). The grey clay is very fine and the traces of burnishing on the surface are almost invisible. Wares fired under a reducing atmosphere are characteristic of the Phrygian culture (Matsumura 2000). The Lustrous Black Fine Wares excavated from Gordion, the Phrygian royal capital, have a black surface similar to the Fine Black Polished Wares from Kaman-Kalehöyük. A comparison of the production techniques of these two pottery types may shed light on the relation between Kaman-Kalehöyük, a local city and Gordion, a capital city, from the viewpoint of the flow of Phrygian culture. Our previous report concluded that the Fine Black Polished Wares were fired below 800˚C under a reducing atmosphere (Shiraishi *et al*. 2005). XRD, SEM-EDS, XPS and CHN elemental analysis showed that the origin of the black surface of the Fine Black Polished Wares excavated from Kaman-Kalehöyük was carbon.

Fig. 1 Fine Black Polished Ware from Kaman-Kalehöyük.

Further research, presented here, shows that there may be two production techniques for the Fine Black Polished Wares found at Kaman-Kalehöyük. These have been designated Type A and Type B. When samples of Fine Black Polished Ware were refired at 1000˚C under an oxidizing atmosphere, some did not show any color changes due to the firing (Type A), while others underwent a color change showing a difference between the surface and the body (Type B). Type A ware was well characterized in our previous report (Shiraishi *et al*. 2005). Preliminary comparative analysis of the Type A and Type B wares suggested that a slip layer similar to that reported for the Lustrous Black Fine Wares from Gordion (Hendrickson *et al*. 2002) seemed to exist on the surface of the Type B Fine Black Polished Wares of Kaman-Kalehöyük. If this is true, the production technique of this ware may be the same as that for the Lustrous Black Fine Wares of Gordion, suggesting a strong relationship between Kaman-Kalehöyük and Gordion and a flow of Phrygian culture from Gordion. The purpose of the present study is to reveal the production technique of the Type B Fine Black Polished Wares.

The production technique of the Type B wares was investigated by observing the differences in morphology and chemical composition between the body and surface of individual shard samples using a scanning electron microscope equipped with an energy dispersive X-ray spectrometer (SEM-EDS) and by comparing the crystalline materials of the body and surface using X-ray powder diffraction. The possibility of carbon adsorption onto the surface was investigated by quantitative analysis of carbon using CHN elemental analysis.

In addition, Raman microspectroscopy was newly introduced as a powerful analytical method for carbon.

Raman microspectroscopy is a nondestructive technique and usually does not require any sample preparation. Raman spectroscopy uses the light-scattering properties of materials to diagnose the internal structure of molecules and crystals. The capacity to focus the energy source (a laser) on a very small spot (1 mm in diameter), the high lateral resolution and the depth of field are very useful for the study of thin multi-layered samples. These features, together with the ability to identify not only the molecular structure but also the crystalline form of substances present in the sample, are very important for the study of archaeological ceramics (Ospitali *et al*. 2005).

SAMPLE SET

Samples of Fine Black Polished Ware excavated from the Iron Age layers (Stratum IIa) at Kaman-Kalehöyük were analyzed in this study. A sample of imported Greek black glazed ware also excavated from Stratum IIa (Matsunaga *et al*. 1997) and a sample with a black surface reproduced by carbon adsorption were also analyzed as references for comparison. All samples are listed in Table 1.

SAMPLE PREPARATION

Each sample was cut by a diamond-cutter into test pieces of approximately 1 cm × 1 cm, then washed in water and dried. The pieces were refired at 1000°C in an oxidizing atmosphere in order to observe changes in color of the surface and body. The Fine Black Polished Wares of Type B – which undergo changes during this refiring – were identified and then subjected to the following analysis.

A cross-section of each pottery shard was prepared in order to characterize the surface layer using SEM-EDS. For X-ray powder diffraction analysis, the surface materials were isolated from the body of the ware using a needle under the microscope. For elemental analysis and Raman analysis of carbon, the samples were pre-treated with acid and alkali (Acid-Alkali-Acid treatment: cf. Shiraishi *et al*. 2005) to remove any contamination of carbonate and humic acid.

ANALYTICAL INSTRUMENTS

The morphologies of the samples were observed using SEM-EDS (JEOL JSM-6700F). The acceleration voltage was 10 kV. X-ray powder diffraction data were measured using a BRUKER MXP3 under the following measurement conditions: Cu X-ray tube operated at 30 kV and 15 mA, 2θ range 4 - 80°, 1 or 2°min^{-1} , step size = 0.05°.

Raman spectroscopy was performed using JASCO NRS-3200 with a LMPL microscope and a charge-coupled device (CCD) thermoelectrically cooled detector. A laser diode (532 nm) was used as a radiation source with a nominal laser power of approximately 1 mW.

Table 1 List of studied samples.

	Year No.	Date	Area	Sector	Grid	PL	Layer
Fine Black Polished Ware	–	920831	North	XVII	XLI-57	⑤	IIa
	86000790	860813	North	V	XXXVII-55	⑮	IIa
	87001044	870625	North	III	XL-55		IIa
	04000500	040810	North	XIX	XXXVI-56	㊿	IIa
	04000513	040901	North	XIX	XXXVII-56	(67)	IIa
	04000519	040818	North	XX	XXXV-57	㉕	IIa
	04000520	040823	North	XX	XXXV-57	㉕	IIa
Greek black glazed ware	–	920828	North	XVII	XL-56	⑥	IIa
	–	920820	North	XVII	XLI-57	④	IIa

RESULTS AND DISCUSSION

Refiring of the samples

When the Fine Black Polished Ware samples were refired at 1000˚C under an oxidizing atmosphere (Fig. 2), the two different ware types (Type A and B) became apparent (Fig. 3(a), (b)). Type A showed no difference between the surface and body of the sample by refiring, as in Fig. 3(a). This indicates that there is not an applied surface layer on the Type A pottery. On the other hand, the Type B pottery underwent changes as shown in Fig. 3(b): the surface changed color from black to red while the body changed from gray to cream.

The effects of refiring on the Fine Black Polished Wares were compared to the effects on two other black wares of known production techniques: a sample reproduced by carbon adsorption and a sample of Greek black glazed ware excavated from the Iron Age layer (Stratum IIa) of Kaman-Kalehöyük. The results are shown in Fig. 4(a) and (b). In the case of the sample reproduced by carbon adsorption, the original black surface color became equal to the body color (red) after firing because the surface adsorbed carbon (Fig. 4(a)). On the other hand, in the case of Greek black glazed ware, the original black surface color became reddish brown, which was different from the body color (red) after firing (Fig. 4(b)). According to Mirti *et al*. (1996), iron-rich materials were applied to the surface of Greek black glazed wares and the wares were produced by a unique iron-reduction technique, in which only the glaze containing iron on the surface changed to black under reducing conditions. It stays black even under a certain oxidizing conditions, although the core becomes red (Mirti *et al*. 1996). In order to produce the black glossy surface by the characteristic firing process, some flux containing iron-rich material should be applied to the surface.

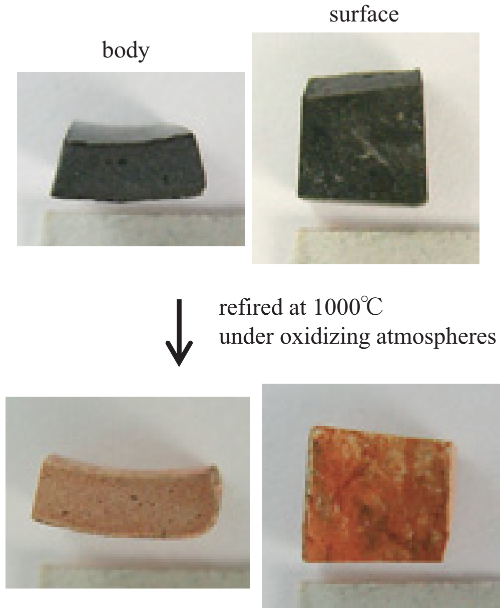
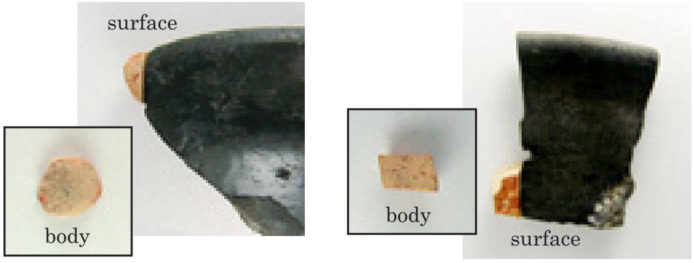


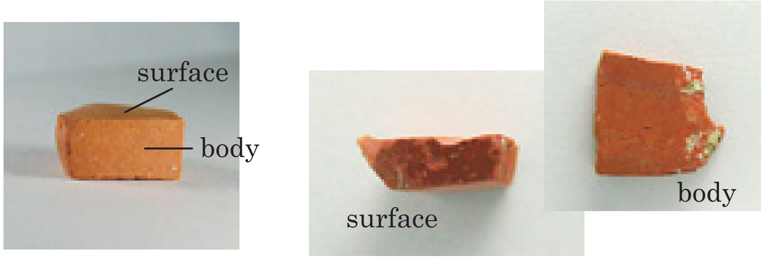
Fig. 2 A shard of Fine Black Polished Ware, as excavated, and a sample refired at 1000˚C in an oxidizing atmosphere.



(a) The surface color is equal to the body color after refiring.

(b) The surface color is different from the body color after refiring.

Fig. 3 Refiring of samples showed that there are two ware types for the Fine Black Polished Wares.



(a) A reproduced sample by carbon adsorption refired.

(b) The Greek black glazed ware refired.

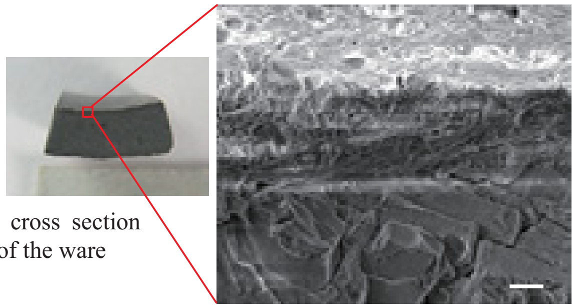
Fig. 4 A comparison of samples refired at 1000˚C under an oxidizing atmosphere.

The changes seen in the refiring of the Type B Fine Black Polished Ware in Fig. 3(b) are consistent with the changes seen in the refiring of the Greek black glazed ware, in that they indicate a difference between the surface and the body of the wares. Our previous study revealed that the origin of the black surface of the Type A pottery shown in Fig. 3(a) was carbon adsorption. It is presumed that the Type B ware in Fig. 3(b) was produced by a different production technique, such as application of a slip or pigment. Figure 5 shows the

Fig. 5 View of the cross-section of a shard of the Type B Fine Black Polished Ware under a microscope (bar = 40 μm).

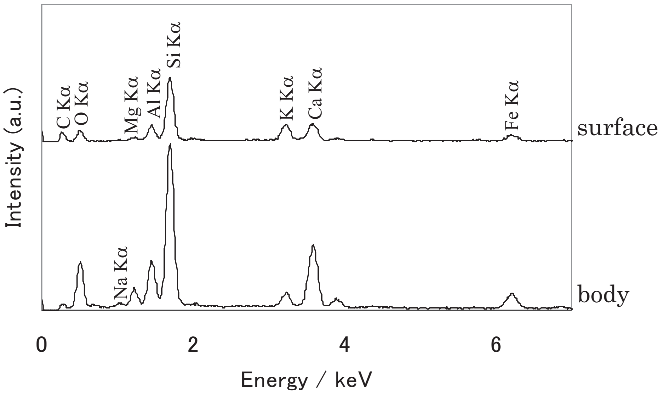
cross-section of a refired Type B shred observed with a microscope, which clearly shows the existence of a surface layer, whose color is different from the body.

The surface material on the Type B pottery was investigated using SEM-EDS to compare the component elements and to observe the difference in morphology between the body and surface. X-ray powder diffraction was used to identify the crystalline material.



(a) cross section of the ware

(b) SEM image of the cross section （ bar = 10 μm ）



(c) EDS spectra of surface and body

Fig. 6 Cross-section of the Type B Fine Black Polished Ware (a), SEM image of the cross section (b), and EDS spectra of the surface and body (c).

Analysis of the surface material

SEM-EDS analysis

A photomicrograph, the SEM image and the EDS spectra of the surface and body of a sample of Fine Black Polished Ware of Type B are shown in Fig. 6(a), (b) and (c), respectively. A layer of approximately 20 μm thickness can be observed in Fig. 6(b), which shows the difference in the structure between the surface and the body: the surface structure is composed of fine, flakey clay particles, while the underlying body shows a more regular alignment of the large clay platelets parallel to the surface of the ware. The results of the EDS analysis show that the surface is lower in calcium and magnesium (alkali earth metals) compared with the body. These results suggest the possibility that refined body clay was used as a slip.

X-ray powder diffraction analysis

The results of the XRD analysis indicate that the major component minerals of the surface and body are quartz (△), feldspar (□), calcite (◇), augite (●) and kutnohorite (◎) (Fig. 7). However, minerals of the feldspar group and augite group are more abundant in the body than on the surface. This difference does not explain the origin of the black surface, as no pigment mineral producing a black color, such as magnetite, was found on the surface material of the Fine Black Polished Wares. The origin of the surface red color is due to the oxidation of iron component, which existed in the clay.

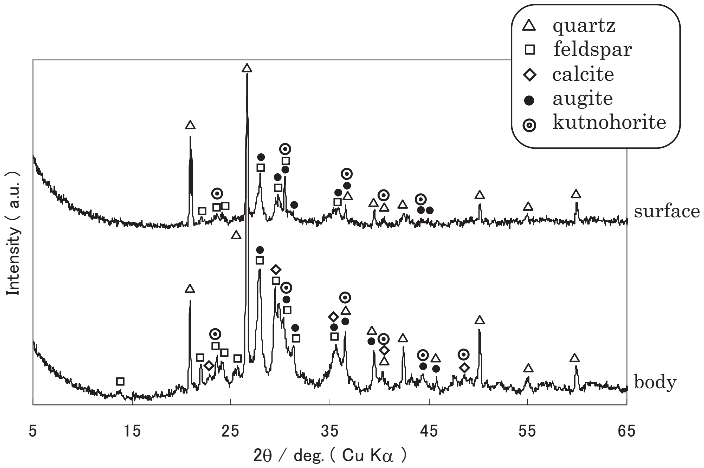


Fig. 7 X-ray powder diffraction patterns of samples of the surface and body material of the Type B Fine Black Polished Ware.

Table 2 Carbon content of the samples measured by elemental analysis.

sample	C (wt. %)	
The Fine Black Polished Ware belonging to the IIa 1	surface	1.20
	body	0.31
The Fine Black Polished Ware belonging to the IIa 2	surface	1.36
	body	0.11
The Fine Black Polished Ware belonging to the IIa 3	surface	2.69
	body	0.52
The reproduced sample by carbon adsorption	surface	0.82
	body	0.06
The Greek black glazed ware	surface	0.10
	body	0.10
The Greek black glazed ware	surface	0.06
	body	0.04

CHN elemental analysis

Quantitative analysis of carbon on the surface and in the body of the Type B ware was carried out using CHN elemental analysis and the results are shown in Table 2. The carbon content was found to be between approximately 1% and 3% at the surface, while it was below 1% in the body (Table 2). The carbon content of the imitation of the black polished ware produced by carbon adsorption gave data similar to those for the Fine Black Polished Wares. On the other hand, the Greek black glazed ware, in which the iron compound was applied to the surface, showed no difference in carbon content between the surface and body.

These results confirm the hypothesis that the origin of the black surface of the Type B Fine Black Polished Ware is also due to graphite carbon adsorbed on the surface.

Raman micro-spectroscopy

The Raman spectra of the surfaces of the Type B Fine Black Polished Ware and the Greek black glazed ware are shown in Figs. 8 and 9. The Fine Black Polished Ware shows the presence of Raman bands at 211, 245, 286, 325, 366, 463, 506, 545, 1376 and 1606 cm^{-1} (Fig. 8). The bands at 211, 366 and 463 cm^{-1} are assigned, as those of quartz and the bands at 245, 286, 325, 506 and 545 cm^{-1} are those of feldspar. It should be noted that the bands at 1376 and 1606 cm^{-1} could be interpreted as being amorphous carbon. These bands are assigned to the sp^3 and sp^2 hybridized carbon, respectively, the so-called D and G bands. The G band is due to graphitic carbon while the D band is due to saturated carbon compounds. A ratio of these bands indicates the ratio of graphitic carbon to amorphous carbon (Legodi and Waal 2003). From the relative intensities of these bands in Fig. 8, it is clear that there is a larger amount of G carbon than of D carbon on the surface of the Type B Fine Black Polished Ware. These findings suggest that the carbon on the surface of this ware has a high graphitic content. This result agrees well with the results of the powder diffraction analysis.

On the other hand, the spectra of the surface of the Greek black glazed ware show the presence of the

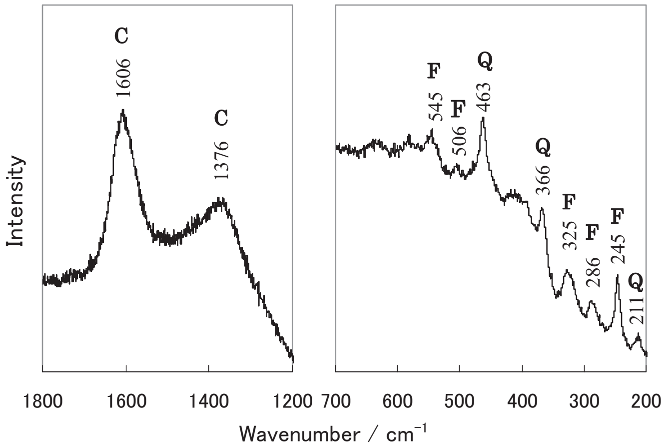


Fig. 8 Raman spectrum of a region on the surface of the Fine Black Polished Ware.
C : carbon, F : feldspar, Q : quartz

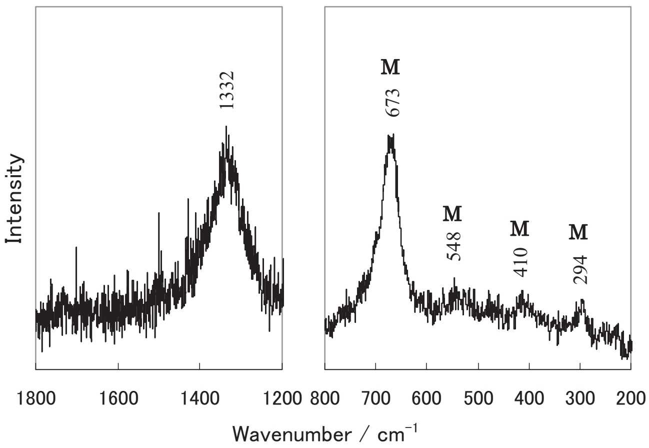


Fig. 9 Raman spectrum of a region on the surface of the Greek black glazed ware.
M : magnetite

Raman bands of magnetite (294, 410, 548, 673 cm^{-1}) (Fig. 9). This is further confirmation that the black surface of the Greek black glazed ware is the result of an applied iron compound on the surface.

The results of the Raman microspectroscopy clearly indicate that the origin of the black surface of the Type B Fine Black Polished Ware was carbon and that this carbon originated from carbon with a graphite structure.

CONCLUSION

It was previously determined that the origin of the black surface of Fine Black Polished Wares excavated from Kaman-Kalehöyük was carbon (Shiraishi *et al.* 2005). The possibility of the existence of another production technique has been discussed in the present study and may serve as an important point when considering the influence of the Phrygian culture.

The results of SEM-EDS and X-ray powder diffraction analysis revealed the existence of slip on the surface of some Fine Black Polished Ware shards (called Type B). Elemental analysis disclosed that carbon concentrations were much higher on the surface than in the body. Moreover, Raman microspectroscopy was introduced as a new analyzing method for carbon and graphite carbon was detected on the surface.

From these results, it appears that there are two types of Fine Black Polished Wares excavated from Kaman-Kalehöyük: those with slip (Type B) and those without slip (Type A). For both types, it can be concluded that the origin of the black surface of these wares is carbon.

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