A Study on Magnetic Properties and Role of the Iron Oxides in Ancient Baekje Black Burnished Pottery by Mössbauer Spectroscopy

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The magnetic properties and mineral composition of black burnished pottery and reddish-brown pottery with soot unearthed from Pungnaptoseong, and restored black burnished pottery were investigated to determine the black coloring mechanism and firing condition. Results indicate that an increase in the amount of magnetic iron oxide (especially Fe_3O_4) by the thermal reduction reaction of hematite influences the development of black color on the surface. Furthermore, for each sample, the black surface was determined to contain the highest amount of magnetic iron oxide, followed by the black to dark gray matrix, and then the brownish matrix. These results suggested that the ancient black burnished pottery was produced by a stronger reduction reaction on the surface, as compared to the matrix during the firing process. Further, the pottery with a black to dark gray matrix was produced through intense and prolonged reduction firing, compared to the pottery with a brownish matrix.

Keywords : Iron oxide, Mössbauer spectroscopy, black burnished pottery, firing condition, coloring mechanism

1. Introduction

Pottery is the scientific and archeological evidence that indicates that mankind could realize and utilize the physical and chemical changes of natural matter. It has been a part of human life since the Neolithic era, when agriculture began. The production methods and styles of pottery that developed along with the flow of time reveal information about the technical expertise, art styles, and lifestyles during the different eras. Thus, characterization studies of pottery can provide useful information about the era and living environment at the archeological sites where the corresponding pottery was unearthed and dated.

Black pottery with a brilliant luster on the surface has been among the types of pottery excavated from ancient archeological sites. The luster of such pottery was achieved by a polishing technique that induces light reflection by smoothly rubbing the surface, and imparting a black color different from the color of raw material soil was a high-end manufacturing technique in the ancient times. Further-

more, black burnished pottery is believed to have been manufactured for special purposes because of its scarcity compared to the other types of pottery, as well as being usually found in the graves of the ruling class [1-3].

Previous archeological studies in Korea on the development of black burnished pottery reported various factors responsible for the black coloring, such as iron oxide reduction, smoke adsorption, and black pigmentation [4-6]. Most of the recent scientific research verifying the above factors that were conducted in Korea indicated that the black color on the surface and in the matrix is due to surface coating and internal penetration by carbon and carbon-related substances [7, 8]. Further, there has been no research on the black coloring technique by the reduction of iron oxide. By contrast, studies on ancient pottery in the other cultural circles suggested that black color was achieved via the reduction of iron oxides covering the raw material soil particles [9-12]. Thus, there is a need to study about the iron oxide composition on the surface of black burnished pottery unearthed in the Korean cultural circle. Such research makes it possible to confirm whether the black burnished pottery that was manufactured in the ancient Korean peninsula is a unique type of black pottery produced through a manufacturing

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technique that is different from those in the other cultural circles.

In this study, Mössbauer analysis was conducted on various types of black pottery unearthed from the Pungnaptoseong site, a site dated to the Hanseong Baekje period (AD 270 to AD 475). We examined the magnetic properties of the pottery to ascertain the possibility that the black color development was caused by the conversion of iron oxides to other mineral phases in the raw material soil during the firing process.

2. Experimental Method

The samples used in this study are shown in Fig. 1. These samples included three pieces of black pottery shards unearthed from the 197 Pungnap-dong archeological site located in Pungnaptoseong, where the royal palace of the Baekje Kingdom once stood. The samples were identified as PN1: black burnished pottery that has a black surface and black matrix; PN2: black burnished pottery that has a black surface and a brown-colored matrix; PN3: red-brown pottery with a black layer covered with carbon-based soot; and RES1; a restored specimen of black burnished pottery manufactured by the Archaeological Research Center at the National Research Institute of Cultural Heritage in 2015 through the "Research on the reconstruction of pottery production in the Hanseong phase of Baekje" program [13].

Because the color development patterns on the surface and in the core of the samples are different, the separation of the mineral particles for analysis was performed by magnifying and observing the samples with a loupe and carefully collecting a powdery sample from each part using a knife. An automatic trace element analyzer (TruSpec

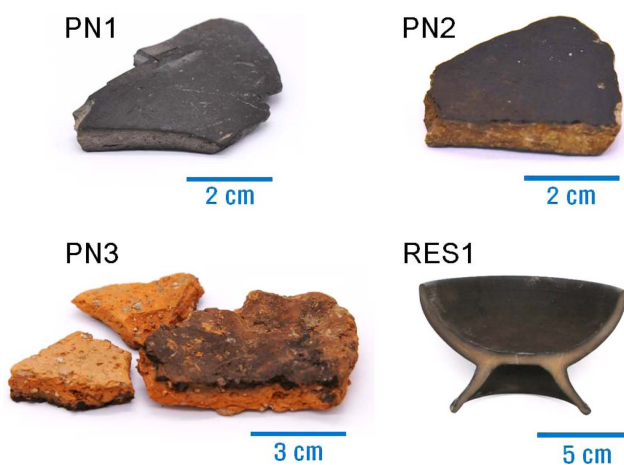**Fig. 1.** (Color online) Pottery shard samples unearthed from Pungnaptoseong and restored pottery.

Micro, LECO) was used to measure the organic content of the samples and Mössbauer spectroscopy and X-ray diffraction analysis (XRD) were performed to determine the magnetic properties and mineral composition of the iron oxide present in the samples. Mössbauer spectra were recorded using ^{57}Co of 60 mCi that was diffused in rhodium as a γ-ray source at 295 K. The XRD spectra were recorded with a Cu-Kα diffractometer (EMPYREAN, Malvern Panalytical) scanning with a range of 30-40° 2-theta at 45 kV and 40 mA with a scanning interval of 0.02° 2-theta.

3. Results and Discussion

3.1. Organic element analysis

Table 1 summarizes the elemental composition (carbon, hydrogen, nitrogen, and sulphur) of the organic compounds present on the surface and in the matrix of each pottery sample.

Carbon (1.88 %) was detected on the black surface of PN1, while no carbon was detected in the black to dark gray matrix. The PN1 surface had 0.7138 % hydrogen, while the matrix was composed of 0.7276 % hydrogen. The carbon and hydrogen contents of the black surface in the case of PN2 were determined to be 2.6101 % and 0.534 %, respectively, and 0 % and 0.5274 % in the brownish matrix, respectively. The amount of hydrogen present on the surface and in the matrix were nearly equal for both PN1 and PN2 samples. This can be due to the homogeneous moisture content and hydrous mineral distribution on the surface and matrix of the two samples. Carbon was present on the black surface of both PN1 and PN2, whereas carbon was not detected in the matrix of both samples. In particular, it is possible that substances other than carbon could have imparted the black color because carbon was not detected in the black or dark grey matrix of PN1. This was interpreted as due to the penetration of carbon into the matrix in the previous studies

Table 1. Organic compound contents of pottery samples (wt.%).

Sample	C	H	N	S
PN1-surface	1.8844	0.7138	-	-
PN1-matrix	-	0.7276	-	-
PN2-surface	2.6101	0.5340	-	-
PN2-matrix	-	0.5274	-	-
PN3-blackish part	10.9470	0.7237	-	1.2310
PN3-reddish part	0.2958	0.1382	-	1.0248
RES1-surface	-	-	-	-
RES1-matrix	-	-	-	-

[7, 8].

PN3 was found to have a higher carbon and hydrogen content in the black region (10.947 % and 0.7237 %, respectively) than in the reddish-brown region (0.2958 % and 0.1382 %, respectively). Further, approximately 1 % of sulfur was detected in the reddish-brown and black parts. These results reflect the characteristics of the coating of secondary raw materials, like carbon and hydrocarbon-based substances. In particular, the much higher carbon content in PN3, as compared to the surface of PN1 and PN2, is considered as a quantitative characteristic factor that can be used to determine the mechanism for black surface development between the original black burnished pottery and the soot coated black pottery (Table 1).

In case of the restored black burnished pottery RES1, organic elements were not detected in either the black surface or the dark brown matrix. This result could be attributed to the characteristics of the raw material and suggested that there was no surface coating or internal penetration of carbon-based material. The restoration experiments for RES1 were performed without surface coating by additional material or contact with a carbon-based material. Moreover, the combustion chamber, which may have been the only carbon source in the kiln, was fired at a distance greater than two meters from the sample RES1 [13]. Compared to the surface of the black burnished pottery unearthed from Pungnaptoseong, where carbon was detected on the surface, contact with organic raw materials may have occurred during the firing. More-over, these results suggested that there were other factors responsible for the black color apart from the surface coating by a carbon-based material.

According to pedological studies, the color of soil is influenced by the oxidation and reduction reactions of iron oxides that cover the constituent mineral particles; in particular, the color becomes darker as the amount of magnetic phase minerals, such as magnetite $\{[Fe_3O_4]\}$ and maghemite $\{[\gamma\text{-}Fe_2O_3]\}$, that are generated by thermal reduction reaction increases [14-16]. Furthermore, there are cases from the other cultural circles that point to the reduction of iron oxides contained in the soil raw material as a coloring factor in black pottery [9-12]. Thus, it is necessary to examine the possibility that the black color in the no-carbon and low carbon-containing black areas of the samples that are used in this study developed due to the reduction of iron oxides.

3.2. Mössbauer spectroscopy

Samples for Mössbauer spectroscopy were selected considering the amount that can be collected and the purpose of comparison. To compare the magnetic pro-
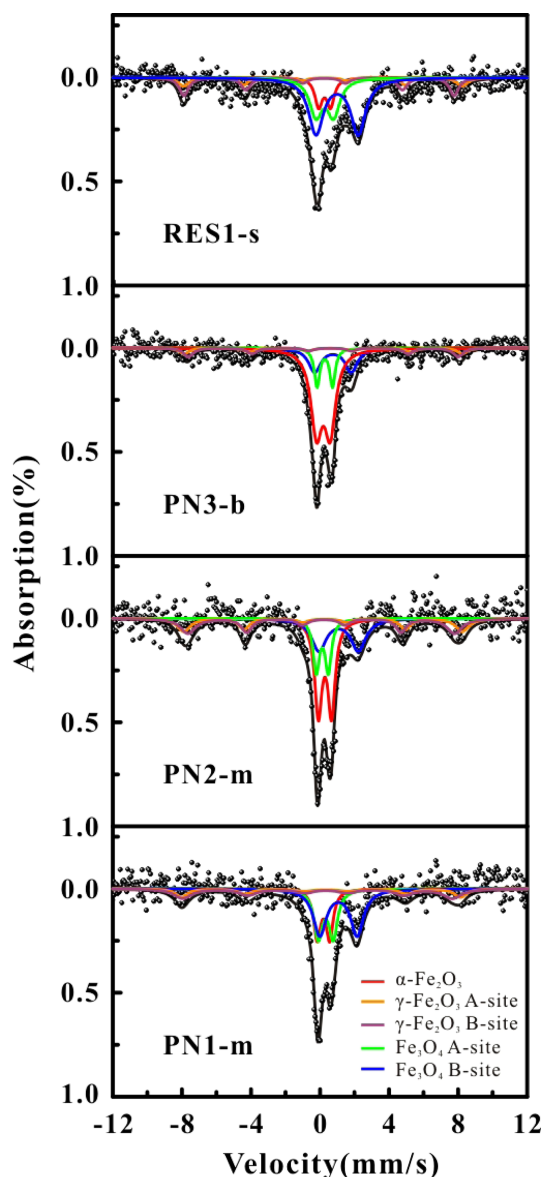

Fig. 2. (Color online) Mössbauer spectra of pottery samples at 295 K.

perties of iron oxide by color in the matrix without carbon, the black or black-gray matrix of PN1 (PN1-m) and the yellowish-brown matrix of PN2 (PN2-m) were used. Moreover, to examine the coloring factor on the black surface, the magnetic properties of the soot-coated black part of PN3 (PN3-b) and the black surface of the restored specimen of the black burnished pottery RES1 without carbon (RES1-s) were compared.

Figure 2 shows the Mössbauer spectrum for each sample, and Table 2 compiles the magnetic hyperfine field, electric quadrupole splitting, and isomer shift of the Mössbauer spectrum according to the state of the iron compound as well as the composition and ratio of each

Table 2. Mössbauer parameters of pottery samples. H_{hf} = magnetic hyperfine field, E_Q = electric quadrupole splitting, δ = isomer shift, A = area ratio.

Sample	Component	H_{hf} (mm/s)	E_Q (mm/s)	δ (mm/s)	A (%)	Fe-oxide phase ratio (%)
PN1-matrix	α-Fe_2O_3	-	0.72	0.19	13.5	13.5 α-Fe_2O_3
	γ-Fe_2O_3 A-site	501.51	0.00	0.20	17.4	46.4 γ-Fe_2O_3
	γ-Fe_2O_3 B-site	485.04	0.00	0.10	29.0	40.1 Fe_3O_4
	Fe_3O_4 A-site	-	0.86	0.33	16.3	
	Fe_3O_4 B-site	-	2.16	1.07	23.8	
PN2-matrix	α-Fe_2O_3	-	0.76	0.28	22.5	22.5 α-Fe_2O_3
	γ-Fe_2O_3 A-site	500.75	0.00	0.22	20.7	50.1 γ-Fe_2O_3
	γ-Fe_2O_3 B-site	479.62	0.00	0.14	29.4	27.4 Fe_3O_4
	Fe_3O_4 A-site	-	0.69	0.13	11.6	
	Fe_3O_4 B-site	-	2.27	1.07	15.8	
PN3-blackish part	α-Fe_2O_3	-	0.79	0.19	45.2	45.2 α-Fe_2O_3
	γ-Fe_2O_3 A-site	500.23	0.00	0.39	12.2	29.7 γ-Fe_2O_3
	γ-Fe_2O_3 B-site	485.24	0.00	0.39	17.5	25.1 Fe_3O_4
	Fe_3O_4 A-site	-	0.89	0.27	10.4	
	Fe_3O_4 B-site	-	2.11	0.75	14.7	
RES1-surface	α-Fe_2O_3	-	0.68	0.26	8.1	8.1 α-Fe_2O_3
	γ-Fe_2O_3 A-site	500.29	0.00	0.21	15.0	41.6 γ-Fe_2O_3
	γ-Fe_2O_3 B-site	485.37	0.00	0.09	26.6	50.3 Fe_3O_4
	Fe_3O_4 A-site	-	1.02	0.27	18.1	
	Fe_3O_4 B-site	-	2.44	0.99	32.2	

type of iron oxide obtained from them.

Three iron oxide phases, namely α-Fe_2O_3, γ-Fe_2O_3, and Fe_3O_4, were obtained from the spectra of all samples (Fig. 2), and their volume fractions were determined to be 13.5 %, 46.4 %, and 40.1 %, respectively, in PN1-m. The volume fractions of α-Fe_2O_3, γ-Fe_2O_3, and Fe_3O_4 were determined to be 22.5 %, 50.1 %, and 27.4 % for PN2-m; 45.2 %, 29.7 %, and 25.1 % for PN3-b; and 8.1 %, 41.6 %, and 50.3 % for RES1-s, respectively (Table 2).

The amounts of magnetic iron oxide (γ-Fe_2O_3 and Fe_3O_4) in PN1-m, PN2-m, and RES1-s, were relatively higher than that of PN3-b, and the amount of α-Fe_2O_3 was found to be relatively lower (Table 2). These results suggested that the black burnished pottery samples (PN1, PN2, and RES1) were fired in a relatively reduced environment compared to the soot-coated reddish-brown pottery PN3 [17-19].

In the case of comparing the magnetic properties of samples with different colored matrices, the amount of Fe_3O_4 in black PN1-m was found to be higher than that of yellowish-brown PN2-m, whereas α-Fe_2O_3 showed the opposite pattern (Table 2; Figs. 2a and 2b). Moreover, both samples did not contain carbon (Table 1). This suggests that the relatively higher concentration of ferromagnetic iron oxide in the sample functions as a black color-

ing factor. Furthermore, these results indicate that PN1-m experienced relatively intense and prolonged reduction reaction during firing than PN2-m.

By comparing the characteristics of the samples with black surfaces, even though the surface of PN3-b was black, its magnetic iron oxide content was found to be 54.8 %, which is significantly lower than that of RES1-s (91.9 %). In contrast, the PN3-b α-Fe_2O_3 content was 45.2 % and significantly higher than RES1-s (8.1 %) (Table 2; Figs. 2c and 2d). As a result, the black color of PN3-b was primarily affected by the surface coating of carbon-based materials rather than the firing condition. However, RES1-s, which did not have any carbon-based material, was presumed to have a black color because it contained a higher quantity of magnetic iron oxide during the reduction firing (Tables 1 and 2).

3.3. X-ray diffractometry

XRD patterns of pottery samples, from which the composition of the iron oxide mineral phase was identified, are shown in Fig. 3. There was no difference in the diffraction patterns between the black surface and the matrix of PN1. In the case of PN2, the diffraction pattern differs from the black surface due to hematite was detected in the yellowish-brown matrix. Both the black
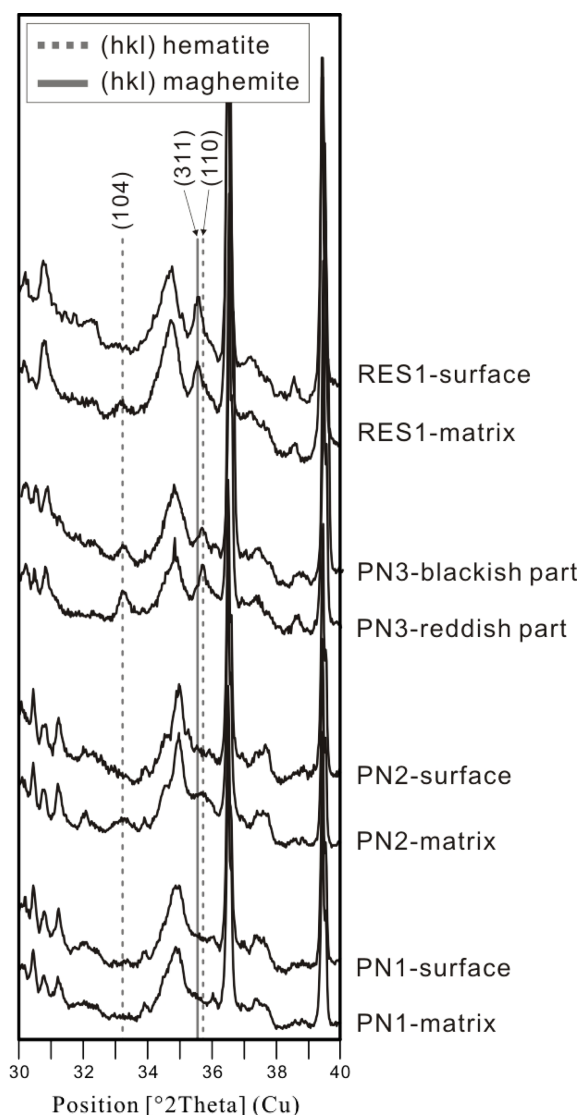
Fig. 3. XRD patterns of pottery samples for surface and matrix.

and reddish-brown parts of PN3 did not show any differences in the diffraction data, and well crystalline hematite was detected in both parts. In the case of RES1, the recorded diffraction pattern could detect well crystalline maghemite from both the black surface and dark brown matrix, while the diffraction pattern for hematite was recorded only in the dark brown matrix.

In the case of black burnished pottery, hematite was detected only in the brownish matrix of PN2 and RES1 (Fig. 3). However, in the case of PN3, hematite was detected not only in the reddish-brown areas but also in the black areas. In addition, the carbon-based soot coated black part of PN3 had a relatively lower magnetic iron oxide to total oxide ratio and a higher α-Fe_2O_3 to total oxide ratio, as compared to the type that underwent

reduction firing (Table 2; Fig. 2 and Fig. 3). These results suggested that hematite, which originally existed in the raw material of the black burnished pottery, was converted into iron oxide of a different composition by the reduction firing. In the case of soot-coated type, the composition of the hematite was preserved.

As discussed earlier, in addition to the carbon content and magnetic properties, the hematite content can be a characteristic parameter for distinguishing between different pottery types, which have been subjected to reduction firing or simple soot coating.

3.4. Firing condition and coloring mechanism

The most abundant iron oxides present in the surface soil, which is a raw material for pottery, are in the form of hematite, goethite $\{[FeO(OH)]\}$, and amorphous ferri-hydrite. Soil that is abundant with these iron oxides is yellowish in color [20-22]. Thermal reactions in the oxidizing environment of the soil induce an increase in the hematite ratio due to the dehydration of iron hydroxide, which causes the soil to change color from red to brown [15, 16]. However, thermal reactions in a reducing environment result in the formation of magnetic iron oxide minerals, such as maghemite and magnetite, and an increase in their amount in the soil renders dark colors, such as dark brown to black [19, 23, 24].

The reduction of iron oxides has been reported to result from thermal reactions in soil that is rich in organic matter [25-28]. In this case, CO gas from the incomplete combustion of carbon in organic matter functions as a reductant, and the following reaction takes place:

$$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2 \qquad (1)$$
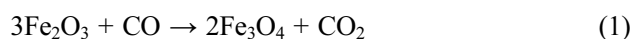
Magnetization resulting from the reduction of hematite in iron ore in the CO-CO_2 environment that is formed by the combustion of fuel has been reported to start from a temperature of at least 500 °C [29]. Furthermore, the magnetization of hematite in red-brown clay has been reported to take place in a reducing environment at approximately 600 °C [18]. Thus, the above-mentioned studies indicate that the temperature range of 700-900 °C, which has been reported as the range of firing temperatures for black burnished pottery of the same type as the ones investigated in our study, is sufficient to induce the aforementioned reactions [7, 8, 30].

Previous studies on black burnished pottery had proposed the adsorption and penetration of carbon-based soot as the main coloring factors [5-8, 13]. Based on this assumption, an experiment, recreating these conditions, was conducted [13]. In the experiment, the seven specimens that were fired at 850-900 °C were placed inside a jar

filled with natural fuels, such as rice husks and sawdust. These heated specimens were covered in fuel material, sealed, and held for 2 min, 5 min, 30 min, 1 h, 2 h, 3 h, and 4 h, respectively [13]. As a result, a black layer developed from the surface to the matrix core, whose thickness increased proportionally with time. In the archaeological research field in Korea, this phenomenon has been reported as a result of the adsorption and penetration of carbon-based soot in proportion with the firing time [13, 30].

However, such a coloring pattern also suggested the possibility that organic carbon acted as a reductant, causing a reducing atmosphere in a closed space with a high temperature. Furthermore, the reducing atmosphere could also cause the reduction of iron oxides. In other words, the high-temperature environment with CO induced by the incomplete combustion of organic matter in a sealed kiln or jar accelerated reaction (1). Moreover, this reaction could continue until the raw material that generated CO gas was completely exhausted, or the temperature dropped below 600 °C [18]. As a result, the ratio of magnetic iron oxide and residual α-Fe_2O_3 in the soil, which was produced during the above-mentioned process, could influence the color of the pottery [14].

From the Mössbauer spectroscopy results for the black burnished pottery samples used in this study, the Fe_3O_4 content was determined to be high, in the order of RES1-s (black surface), PN1-m (black to dark gray matrix), and PN2-m (brown matrix). Additionally, the α-Fe_2O_3 to total oxide ratio showed the opposite pattern (Table 2 and Fig. 2). This result indicates that a stronger reduction reaction occurred on the surface compared to the matrix of the pottery. It also suggested that the color of each sample could be influenced by the magnetic characteristics of iron oxides in the raw material. In particular, the increase in the amounts of Fe_3O_4 and α-Fe_2O_3 was considered to be a factor affecting the development of black and brown colors, respectively (Table 2).

In conclusion, the black burnished pottery unearthed from Pungnaptoseong is considered to have been produced through firing and cooling processes in an atmosphere that supports thermal reduction reaction. In this case, the reduction reaction of iron oxides in the raw material occurs strongly from the surface, which suggests that the increase in the magnetic iron oxide content results in black coloration. Moreover, it is estimated that the black layer gradually develops towards the matrix core in proportion to the duration of the reduction reaction [13, 18, 29]. These results indicate that a more intense or prolonged reduction firing is required to manufacture black burnished pottery, which has a black matrix (same type as PN1) instead of a brown matrix (same type as PN2).

4. Conclusions

The magnetic properties, mineral composition, and carbon content of black burnished pottery and reddish-brown pottery that were coated with soot unearthed from Pungnaptoseong, and restored black burnished pottery were investigated to determine the black coloring mechanism and firing condition. It was found that an increase in the amount of magnetic iron oxide (especially Fe_3O_4) influenced the development of black color on the surface of the black burnished pottery. The increase in magnetic iron oxides resulted from the magnetization of hematite in the raw material during the reduction firing. These results were similar to the cases researched in other cultural circles. However, they were distinct from the previous studies, which proposed that the black color of the pottery was due to the coating or penetration of carbon-based materials. In the case of the soot coated black part on reddish brown pottery, lower quantities of magnetic iron oxide and higher quantities of α-Fe_2O_3, well crystallined hematite, and carbon were detected, as compared to that of the black burnished pottery. These results helped in distinguishing the mechanisms for black color development between black burnished pottery and carbon-based black material coated pottery. Furthermore, the amount of magnetic iron oxide in black burnished potteries were determined to be higher, in the order of black surface, black to a dark gray matrix, and brownish matrix for each sample. These results suggested that the ancient black burnished pottery was produced with a stronger reduction reaction from the surface to the matrix core during the firing process. Therefore, it was estimated that the pottery type with a black to a dark gray matrix was produced through an intense and prolonged reduction firing, as compared to the pottery type with the brownish matrix.

Acknowledgments

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