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Mineralogical characterization of Baekje pottery using radiation-based analysis

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1. Introduction

During the Hanseong period, Baekje occupied the Han river area, which is currently the location of Seoul, the capital city of Korea. Black pottery, which was used during the peak period of Baekje, was mainly excavated from the fortress and burial sites in Seoul. The most prominent feature that distinguishes black pottery from ordinary pottery is its black coloration. The color of pottery can vary depending on the firing conditions and chemical composition.

Iron in clay turns red or brown when oxidized and black or gray when reduced. With traditional firing methods, it is difficult to maintain a consistent firing atmosphere. Therefore, once-fired pottery has different colors for each pottery, and even within the same pottery, colors vary depending on the area.

Radiation-based analytical techniques have become a standard method for characterizing archaeological materials. X-ray diffraction (XRD) analysis is capable of determining the composition of pottery and Raman and Mössbauer spectroscopy are useful non-destructive analysis techniques for obtaining qualitative information about the samples being investigated. These techniques are commonly employed in studying the pigments used in pottery, and supplementary methods, such as the inclusion of non-iron-bearing minerals and iron oxides like hematite, magnetite, and wüstite, are often used in conjunction with them.

In this study, we have investigated the material characteristics of the excavated black and red pottery from the Hanseong period of Baekje through spectroscopic and mineralogical analysis.

2. Materials and Methods

Through the discovery of excavated pottery, it has been confirmed that the ancient Baekje people constructed Pungnap Fortress and formed settlements in its vicinity. We compared two black pottery fragments and one red pottery fragment that were excavated from residential areas near Pungnap fortress.

XRD was used for the mineralogical analysis of black and red potteries. The outer surface and inner core of each pottery fragment were separated and pulverized, respectively. The degree range was from 10 to 80° and 0.04° step length was set. The PDXL software was used to analyze the diffraction data.

Dispersive Raman spectroscopy were performed using a Horiba LabRAM HR spectrometer. The laser emits light with a wavelength of 785 nm. Additionally, FT-Raman experiment was conducted using a Bruker MultiRam model with a 1064 nm excitation line (ND:Yag laser) to minimize fluorescence.

The Mössbauer spectra of the potteries were recorded in transmission geometry using ^{57}Co(Rh) source. The drive velocity was calibrated with metallic iron foil. Isomer shifts are given relative to a-Fe. The MOSS program was fitted with Lorentzian lines grouped into the magnetic sextet and quadrupole doublets.

3. Results and Discussion

The XRD analysis results can reveal the crystalline phase composition of Baekje pottery, providing supplementary information for investigating the firing methods used for these pottery fragments. However, the pottery measured by XRD only showed the crystalline phase composition of quartz, feldspar (plagioclase), and mica, and other composition or metal oxides that may occur in natural clay mineral were not detected, probably due to weak crystalline and low content. The crystallographic information obtained from XRD is not sufficient to fully characterize the pottery. Therefore, obtaining molecular structural information through Raman spectroscopy is necessary for a comprehensive characterization of theses pottery.

Raman spectrum of black pottery shows in Fig. 1 for the Raman shift range 100-2000 cm^{-1}. The result shows that the pottery was mainly characterized by amorphous carbon and quartz. It was difficult to distinguish other peaks in the sample, except for the Raman spectrum of amorphous carbon, due to the background caused by

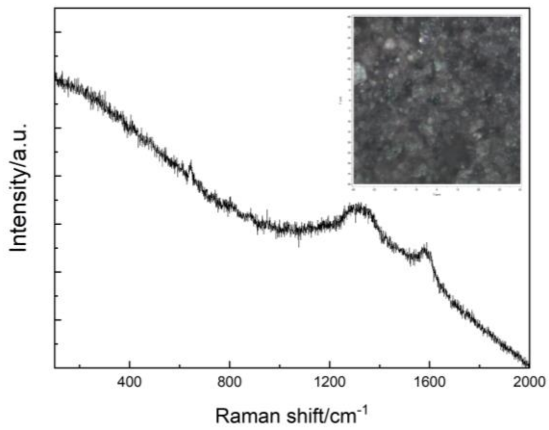

Fig. 1. Raman spectrum obtained from the black pottery for on charcoal grey particles.

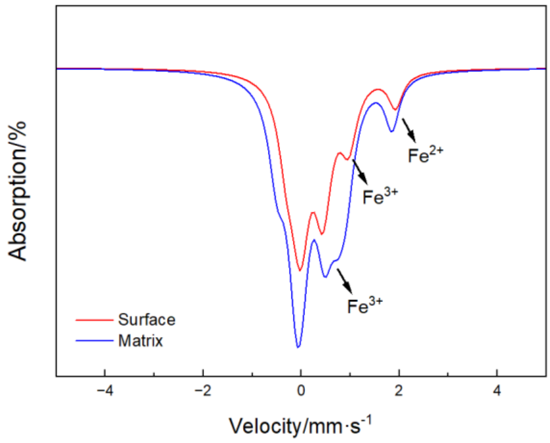

Fig. 2. Mössbauer spectra of the red pottery (surface/ matrix).

fluorescent materials. The most fluorescent mineral, probably, is calcite, a carbonate mineral that can be found worldwide. The pigment of black pottery shows the presence of amorphous carbon possibly obtained carbonized vegetable material.

Mössbauer spectra were recorded for the red pottery and are shown in Fig. 2. The parameters were derived from the peak positions of the spectrum. Based on the presence or absence of magnetic Fe^{3+} and Fe^{2+} in archaeological pottery, inferences can be made about the firing conditions/temperature and coloring mechanisms. The coexistence of Fe^{3+} and Fe^{2+} indicates an out-of-equilibrium state between oxidation and reduction conditions that can arise due to atmospheric changes. The fitting of spectrum was made with two different quadrupole doublets associated with the presence of Fe^{2+}, which have relatively a large quadrupole splitting, and a quadrupole doublet associated with the presence of Fe^{3+}, which are characterized of clay minerals or iron oxides of superparamagnetic state. The pigment of red pottery is associated with the presence of hematite goethite, and/or ferrihydrite. The presence of a high concentration of Fe^{3+} indicates that cooling has occurred in an oxidizing environment.

4. Conclusions

The Raman and Mössbauer spectroscopy allowed to determine the coloring factors present in black and red pottery. Through analyzing the type of Mössbauer spectrum, it is possible to obtain information regarding the firing conditions of pottery, which can then be compared with XRD results to determine the environmental conditions during the firing process. These techniques provide valuable insight into how the pottery was fired and the conditions it was exposed to during the process.

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