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Mössbauer spectroscopy technique: How to characterize Fe oxides in the pottery

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1. Introduction

Mössbauer spectroscopy is a radiation-based analytical technique used to characterize Fe oxides in pottery. This non-destructive method provides valuable insight into the oxidation state and coordination environment of Fe atoms in the pottery matrix. By analyzing the Mössbauer spectrum, researchers can determine the types of Fe oxides present, their relative proportions, and potentially provide information about firing conditions and historical aspects of pottery making. This technology makes a significant contribution to the study of archeology and materials science, enhancing our understanding of ancient technologies and artistic practices.

The excavated archaeological Beakje potteries collected from Pungnap- and Seokchon-dong were subjected to spectroscopic studies. The archaeomagnetic dating of the samples were established which belongs to 250–475 CE. The production technology of archeological materials indicates the level of potter's background skills and can be used as an indicator. The microscopic analysis of the Fe-bearing minerals can be carried out by Mössbauer spectroscopy, which is used in the determination of Fe-state, firing condition and temperature, and coloring mechanism.

2. Methods and Results

All pottery samples were studied by Mössbauer spectroscopy on a conventional constant-acceleration spectrometer equipped with a room-temperature Rh matrix ^{57}Co source. The spectra were fitted with a least square minimization method, assuming Lorentzian line shapes. The Mössbauer parameters were derived from the peak positions of the spectra.

Mössbauer spectra were recorded for the sample black and red pottery and are shown in Figure 1. The observed spectra consist of fitted doublets without sextet such as hematite, magnetite, and goethite. The spectrum of black pottery shows the two Fe(III) and one Fe(II). The Fe(III) site indicate nano-sized Fe oxides and/or oxyhydroxide, and other Fe(III) site is illite (mica group). The Fe(III) site is attributable to Fe(II)-bearing silicate materials. The decrease or disappearance of Fe(II) ion means the oxygen-rich in firing atmosphere. The relative amount of Fe(II) can be used as a basis for comparison with the reduction index

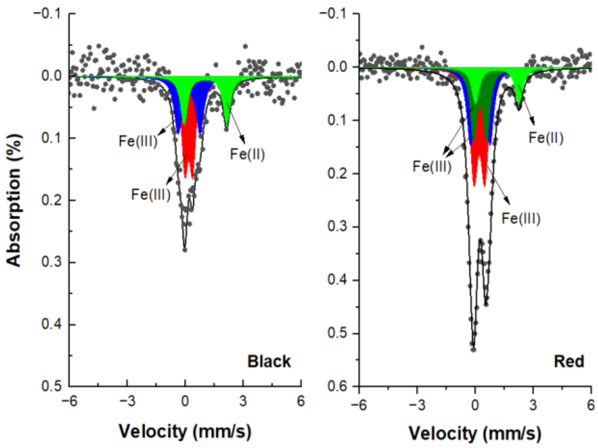

Fig. 1. Mössbauer spectra of black and red pottery samples.

of archaeological pottery to understand their firing atmosphere. The spectrum of red pottery shows the three Fe(III) and one Fe(II). Likewise, the Fe(II) and Fe(III) sites are Fe(II)-bearing silicate and Fe(III) oxide/oxyhydroxide, respectively. Additionally, the other Fe(III) site indicates maghemite. Maghemite is formed from the transformation of magnetite above 200 ºC. Subsequent changes in O_2 fugacity to an oxidizing atmosphere can promote the formation of maghemite.

Figure 2 shows the reduction index (RI) of black and red pottery. The RI value indicates FeO/Fe_{tot} as concerns the oxidation state of Fe. The redox conditions

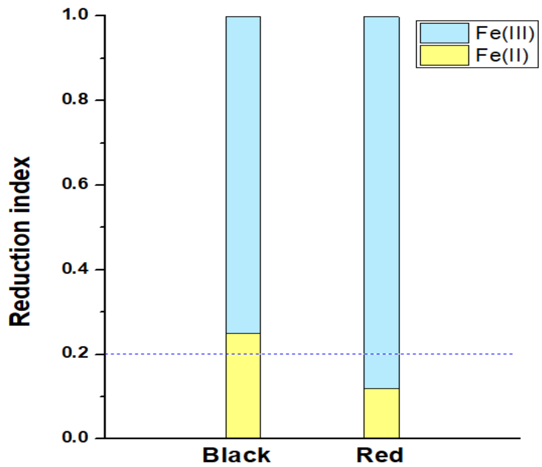

Fig. 2. Reduction index of black and red pottery samples.

of firing may be deduced from the RI. The RI values indicate moderate to strong reducing conditions during firing, supporting the presence of magnetite. The value of 0.20 indicated by the dotted line in the graph represents the upper limit for the amount of Fe(II) in the analyzed clay. If the value exceeds 0.2, it is close to a reducing atmosphere, and if it is lower than 0.2, it indicates a rich oxidizing atmosphere. Black pottery has an RI value above 0.2, while red pottery is below 0.2. This also means that there was a reducing atmosphere process in the process of making black pottery. A reducing atmosphere can actually promote the formation of Fe(II)-containing oxides above a certain temperature. Maghemite can be considered as the fully oxidized counterpart of magnetite. Small magnetite particles, which may have been formed in non-oxidizing conditions, are easily transformed into maghemite. From the presence/absence of paramagnetic Fe(III) and Fe(II), the firing condition and temperature and coloring mechanisms of the archaeological potteries can be deduced.

3. Conclusions

The physical and chemical processes occurring in clay during firing under different conditions can be evaluated by Mössbauer spectroscopy. The Mössbauer spectra of black and red pottery at room temperature consist only of doublets with no sextets. Additional maghemite was recognized in red pottery. From the presence of maghemite and the RI values, it can be inferred that the red pottery was fired in an oxygen-rich oxidizing atmosphere. On the other hand, it can be inferred that black pottery was fired at a higher firing temperature than red pottery and in some reducing atmosphere.

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