Transactions of the Korean Nuclear Society Spring Meeting
Jeju, Korea, May 22-23, 2025

Role of Mössbauer spectroscopy in characterization of iron oxides based pigments in the ancient Gaya tumuli

[1]Young Rang Uhm*, [1]Hyungyung Choi, [2]Min-Su Han, and [3]Dong Hyeok Moon
[1]HANARO utilization division, Korea Atomic Energy Research Institute, Daejeon, 34057, Republic of Korea
[2]Department of Cultural Heritage Conservation Science, Korea National University of Cultural Heritage, Buyeo, Republic of Korea
[3]Geological Museum, Korea Institute of Geoscience and Mineral Resources,Daejeon, 34132 Republic of Korea
**Corresponding author: uyrang@kaeri.re.kr*

Keywords : Ancient Gaya tumuli, red pigment, Mössbauer spectroscopy, iron oxides

1. Introduction

Since the prehistoric times, humans used to use mineral-based pigments for paintings, makeup, architectural structures, and the ceramic surfaces for the purposes of coloring, decoration, and incantation [1]. Among all minerals for pigments, iron oxide-based reddish materials, is the most widely used as a pigment in human history around the world [1]. Moreover, recent scientific analysis reveals that Neanderthals also used iron oxide-based red ochre as pigments [2]. The formation of the reddish mineral hematite, well crystalline α-Fe_2O_3 with weak ferromagnetic properties, in ochre by thermal treatment were common in human history, a process was already known in antiquity [3-4]. In Korea, such iron oxides-based red pigments are also found in archaeological sites and cultural heritages throughout all historical periods. In particular, red paint-ceremony, held in the tumulus, is closely related to social ideas and faith of the ancient Kingdoms, established after the Iron Age. Recently, excavated red pigments in ancient tombs of the Gaya cultural circles, the ancient kingdom in the southern region of the Korean Peninsula (1st–6th centuries AD), has been reported. The red pigment is stored in vessels, or painted on the walls. In this study, the variety of mineral composition used as red pigments in five ancient tombs of four renowned Gaya sites in Haman, Gimhae, Hapcheon, and Changnyeong in Gyeongsangnam-do Province, South Korea (Fig. 1), is well identified. Especially, Mössbauer spectroscopy contribute to magnetic characteristics of each iron-oxides phases. Furthermore, they were assessed to determine whether the natural minerals were used, or if they were transformed into artificial iron compounds by pretreatment

2. Experimental Technique

2.1. Archaeological outline for samples

Five red pigment samples for each type from the ancient tombs of Gaya cultural circles of these four archaeological regions were considered for analysis: Haman, Gimhae, Hapcheon, and Changnyeong (Fig. 1 and Table 1). Among the four regions where the tombs are located in this investigation, Gimhae region was the seat of "Garakguk", the leader of the Gaya federation. In addition, Haman, Hapcheon, and Changnyeong were the provenances of small allies such as "Aragaya", "Daraguk", and "Bihwa-gaya" respectively.

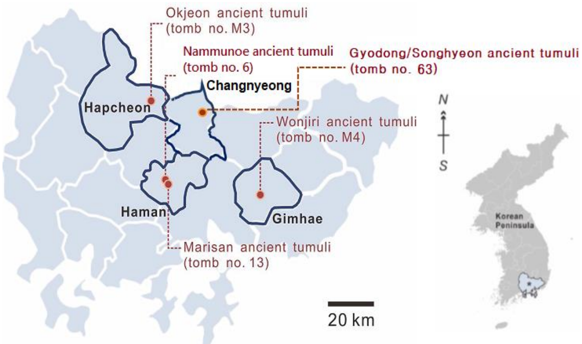

Fig. 1. Location and tomb numbers of the pigment collection sites

Moreover, their archaeological remains excavated from ancient tombs in these regions reflect the powerful authority of the ruling class and the fact that each small allies grew up on a similar cultural basis. As described in Table 1, red pigments were preserved in difference status in each tumuli, and specimens for analysis were collected in powder.

2.2. Instrumentation and measurement

Commission International d'Eclairge (CIE) L*, a*, and b* values were recorded to quantify the brightness and saturation of the red pigment. Chromaticity measurements were conducted on the uncontaminated sections of the red pigment, averaging over 10 measurements

2.3. Mössbauer spectroscopy

Mössbauer spectra were obtained for the samples

Table 1. The collection site, description, Lab CIE color coordinates of the pigment samples

Collection Site	Sample	L*- a*- b*	Visualized hue
Ancient tomb no. 6 in Nammunnoe tumuli, Haman	Trace of the reddish-orange pigment, remaining on the mound wall	60.3-18.8-30.3	
Ancient tomb no. 13 in Marisan tumuli, Haman	Fine reddish-brown powder, painted on the rock fragment brick	48.8- 9.9-15	
Ancient tomb no. M4 in Wonjiri tumuli, Gimhae	Black of red pigment paste, stored in vessel	44.1-28.6-26.1	
Ancient tomb no. M3 in Okjeon tumuli, Hapcheon	Finely ground red pigment (no information on storage conditions)	39.9-29.5-20.2	
Ancient tomb no. 63 in Gydong/Songhyeon tumuli, Changnyeong	Trace of the reddish-orange pigment, remaining on the mound wall	50.55-15.07-24.86	

from 4.2 to 295 K under transmission geometry using a conventional constant-acceleration spectrometer with a ^{57}Co in Rh matrix source and Wissel transducer.

3. Results and discussion

Mössbauer spectrum for H1(Haman) shows a superparamagnetic behavior, which dominated by three quadrupole doublet; whose parameters are consistent with superparamagnetic Fe^{3+} of iron oxides (D1) and Fe^{3+}in the phyllosilicate structure of fine clay minerals (D2 and D3) [3-4]. In addition, two sextets of hyperfine magnetic splitting were also contained magnetite (S1 and S2) [3]. The Mössbauer spectrum of H2 appears as four distinct doublets (D1, D4, D5, and D6) and a single magnetically split sextet (S3). D1 corresponds to Fe^{3+} in super-paramagnetic iron oxides. D4, D5, and D6 are assigned to paramagnetic Fe^{2+} and Fe^{3+} in chlorite group minerals (clinochlore), respectively. S3 is identified as a hematite [3].

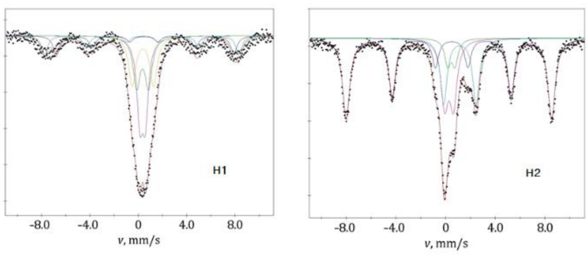

Fig. 2 Mössbauer spectra for H1 and H2 at 295 K

In the hematite rich and deep reddish-brown pigments of G (Gimhae), the Mössbauer spectrum appears as the sum of almost fully sextet with relatively sharp lines, attributable to weakly ferromagnetic hematite, and some trace of a central doublet which is associated to paramagnetic iron oxides. For the Mössbauer data in HP(Hapcheon), the spectrum consists of a single sextet with sharp lines, and the parameters are fitting with those expected for weakly ferromagnetic hematite [4]. Mössbauer spectra of the red pigment layer for the C(Changnyeong) sample exhibited weak ferro magnetic behavior.

4. Conclusions

These results suggest that the ancient Gaya people produced various types of iron oxides-based pigments according to purpose, by selective application of raw materials and thermal process. A method for detailed identification of iron oxides-based pigments was successfully improved using the Mössbauer spectroscopy. These provide crucial insights into environmental changes within the tomb and demonstrate the effectiveness of Mössbauer spectroscopy in distinguishing iron mineral phases in complex soil matrices.

Acknowledgement

This work was supported by the National Research Institute of Cultural Heritage grant funded by the Korea Heritage Service (No. RS-2021-NC100301).

REFERENCES

[1] M. Kawano, T. Minami, T. Tateishi, S. Shoda, S. Imazu Review on the archaeological studies on red pigment in Japan. J. Kor. Field Archaeol. vol 21 pp.103–121(2014).

[2] DL. Hoffman, DE. Angelucci, V. Villaverde, J. Zapata, J. Zilhão, Symbolic use of marine shells and mineral pigments by Iberian Neandertals 115,000 years ago. Sci Adv., vol. 4, pp. 5255 (2018)

[3] D. H. Moon, N. R. Lee, W. R.Han, S. J. Kim, Y. R.Uhm, Characterization of iron oxides-based red pigments in the ancient Gaya region, South Korea, JRNC vol. 332, pp.5175-5184 (2023).

[4] H. Choi, M.S.Han, D. H. Moon, C.S. Kim, S. W. Nam andY. R.Uhm A study on the characteristics of the excavated pottery in Hanseong and Sabi periods of the Baekje Kingdom (South Korea): mineralogical, chemical and spectroscopic analysis, Heritage Science vol. 12(236) pp.1-13 (2024).