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Analysis of Japanese Jōmon period red lacquerwares by pyrolysis gas chromatography/mass spectrometry

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ABSTRACT

Sixteen lacquerwares excavated from the Minamikonuma ruins located in Saitama City, Saitama Prefecture, Japan, were analyzed by mean of cross-section observation, attenuated total reflection Fourier transform infrared spectroscopy (ATR-FT/IR), energy dispersive X-ray fluorescence (EDXRF), and pyrolysis gas chromatography/mass spectrometry (Py-GC/MS). The results showed that Fe_2O_3 was used as a red pigment in the relatively cheap lacquerwares or in the under layers, and HgS was used as another red pigment in an advanced stage. The characteristic urushiol products were detected in direct and derivative pyrolysis GC/MS of all sixteen lacquerwares and suggested that these Jōmon period lacquerwares were coated with lacquer sap collected from *Toxicodendron vernicifluum* lacquer trees.

1. Introduction

Many historically important products, especially lacquerwares, have been excavated from ancient ruins all over the world (Wei et al., 2012; Igo et al., 2015; Miyazato et al., 2013; Honda et al., 2016). Analysis of these relics can reveal an ancient culture and technology. In general, archeology entails observation of relics and reference to the record of the ruins, but the obtained information is usually limited and lacks accuracy. Therefore, chemical analysis is necessary to clarify historical materials and fabrication techniques of relics (Kumanotani, 1995; Lu et al., 2013a).

Lacquerwares dating from the Jōmon period have been examined, and the results indicated that lacquer was first used in the Jōmon period (approximately 14,000 BC to 500 BC) (Sakaguchi, 2009; Hall, 2004; Habu et al., 2011). Because the Jōmon period is very long and different periods should have different properties, it is important to analyze a series of samples to understand the history of Japanese lacquer craft techniques and technology. Previously, we reported the analysis of several Japanese Jōmon period lacquerwares, and the lacquer craft technique and technology were discussed (Lu et al., 2013b; Yuasa et al., 2015; Lu et al., 2015). In order to completely understand the lacquer culture of the long Jōmon period and confirm the previous results, in this study, 16 kinds lacquerwares excavated from the Minamikonuma ruins located in Saitama City, Saitama Prefecture, Japan, were analyzed by cross-section observations, attenuated total reflection Fourier transform infrared spectroscopy (ATR-FT/IR), energy dispersive X-ray fluorescence (EDXRF), and pyrolysis gas chromatography/mass spectrometry (Py-GC/MS), and the results are discussed.

2. Experimental

2.1. Materials

Sixteen samples belonging to different eras of the Jōmon period excavated from the Minamikonuma ruins (5000–2300 BC) were analyzed in this study as shown in Fig. 1. These samples were supplied by the Saitama City Board of Education and Saitama City ruins investigation committee, and the shapes of samples were earrings, bowls, and scoops (see Table 1).

2.2. Cross-section observation

Cross-sections of all samples were observed using an optical microscope (ECLIPSE LV100N POL, Nikon) as previously reported (Lu et al., 2006; Yuasa et al., 2015; Lu et al., 2015; Honda et al., 2016).

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Fig. 1. Photos of 16 samples.

2.3. Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FT/IR)

ATR-FT/IR spectroscopy was performed using a Nicolet iN 10 instruments (Thermo Fisher Scientific Co., Ltd., Japan). The measurement range was 675–4000 cm^{-1}, the resolution was set to 8 cm^{-1}, and the ATR estimation frequency was 128 Hz using a Ge tip.

2.4. Energy dispersive X-ray fluorescence (EDXRF) and scanning electron microscope (SEM)

The elements of the cross section were analyzed by energy