Studies of the degraded state of excavated archaeological silk fibers using infrared microspectroscopy

Several kinds of textile fabric made of silk fibers have been found in many archaeological sites in Japan. However, almost all of them were heavily degraded owing to their long-term exposure to the elements underground. Therefore, the identification of textile materials is often difficult. Besides, only a small amount of sample is available.

The objective of this research is to enable the characterization of degraded archaeological silk fibers using FTIR microspectroscopy. The samples used were excavated from the *Fujinoki* tumulus (6th century AD) and the *Shimoikeyama* tumulus (3rd century AD) in Nara Prefecture. Both archaeological sites are famous for several excavated remains including textile fabrics. Since organic subjects are almost all in a heavily degraded state, it is very difficult to identify the original textile fibers.

The degraded archaeological silk fibers of the Fujinoki tumulus (6th century AD) are shown in Fig. 1 and were gifted by the Kashihara Archaeology Institute, Nara Prefecture. The degraded silk fibers show diverse characteristics: collapsed fibers, absolutely pulverized, etc. First, suitable fiber samples were selected using a stereomicroscope. All of the selected fibers showed a distinct direction of the fiber axis and a clear cross-sectional pattern.

The infrared microspectroscopy of beamline **BL43IR** was used. To identify the fiber material, a stereomicroscope and a super high-resolution scanning electron microscope were also used. A high-brilliance infrared synchrotron radiation beam was focused on the surface of a very small amount of sample fibers.

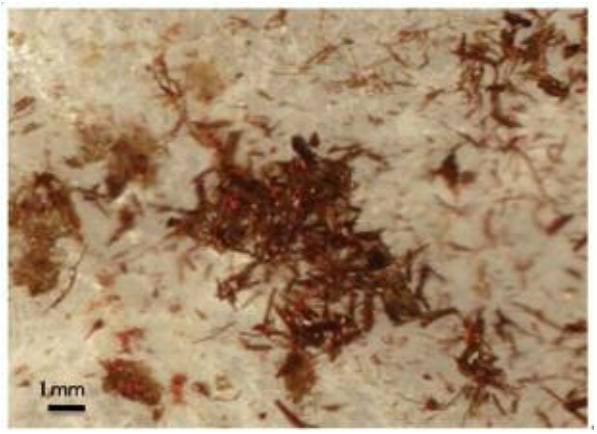

Fig. 1. Photograph of degraded archaeological silk fibers of the *Fujinoki* tumulus.

FTIR microspectroscopy was used since it requires only a small amount of sample, and its sample preparation is easy. The infrared spectra obtained show deformed profiles due mainly to the degradation of the silk fibers. The second derivative of the spectrum is useful for the analysis of the change in the secondary structure of silk fibroin molecules. Curve fitting analysis was also performed by combining established procedures for research.

Prior to the measurement, the silk fibers were pressed on a diamond cell to produce a thin-film sample. The sample prepared on the diamond cell was transferred to the measurement compartment, and measured by the transmittance mode. The measurement conditions are as follows: resolution, 4 cm^{-1}; numbers of scans, 1024 or 2048; wavenumber range, 4000-700 cm^{-1} for several absorption peaks in which each peak is further composed superposed component peaks.

As a preliminary identification of the fiber material, the infrared spectrum of each sample was measured. Since all of the samples showed distinct absorption peaks of the secondary amide, the samples were unequivocally determined to be animal fibers. The observation using a scanning electron microscope showed that the diameter of the cross section of the fibers was about 20 μm, and that their forms were oval or distorted triangles. In summary, the fiber material was identified as silk even in its degraded state.

The FT-IR spectra of reference modern silk samples and ancient silk samples are shown in Fig. 2. As a result of the analysis of the excavated silk fibers, with the advance of the degradation from the peak intensity ratio of each spectrum, it turned out to be that amides **II** and **III** are preferentially decomposed rather than amide **I**. In the spectra of the excavated silk, the peaks of amides **I** and **II** are overlapped and appear as one broad peak. This is due to the effect of oxidation or hydrolysis in the environments where the fibers were found buried [1,2] because amides **II** and **III** belong mainly to the N-H and C-N combinations and amide **I** belongs mainly to the C=O combination.

The second derivative spectra of the (a) reference modern silk and (b) ancient silk samples are shown in Fig. 3. It was found that the amides **II** and **III** peaks preferentially decrease in area as compared with the amide **I** peak with progress of the degradation.

The difference between the behaviors of amides **II** and **III** is due to the difference in binding energy, namely, amides **II** and **III** (N-H and C-N) are relatively

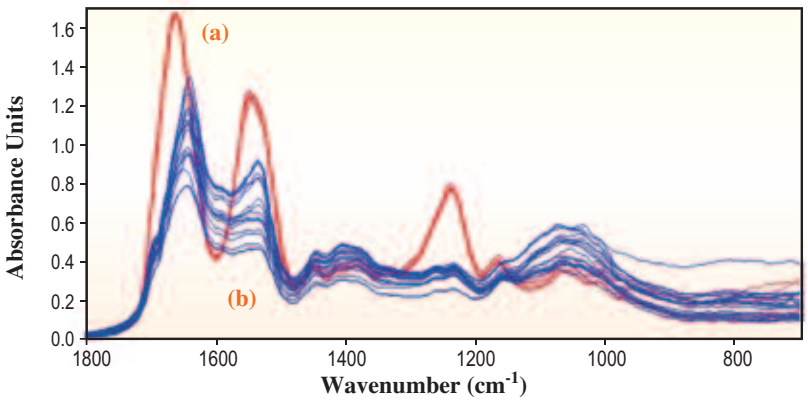

Fig. 2. FT-IR spectra of **(a)** reference modern silk samples and **(b)** ancient silk samples.

weaker than amide **I** (C=O); hence, their bonds degrade relatively easily by oxidation or hydrolysis in environments under long-term burial. Although the apparent form of the amide **I** peak showed no remarkable change with degradation, it was found that the analysis of secondary component structures showed an evident increase in the amount of crystalline components (1660 and 1650 cm^{-1}, β-sheet /disorder), as compared with that of modern reference silk fibers.

As the sample amount that can be used for the analysis is severely limited, it is usually difficult to obtain sufficient data by repeating the measurements using an IR microscope with a glover-lamp light source [3]. Throughout the IR research on the organic archaeological samples, the availability of the synchrotron radiation infrared microscope used was approved.

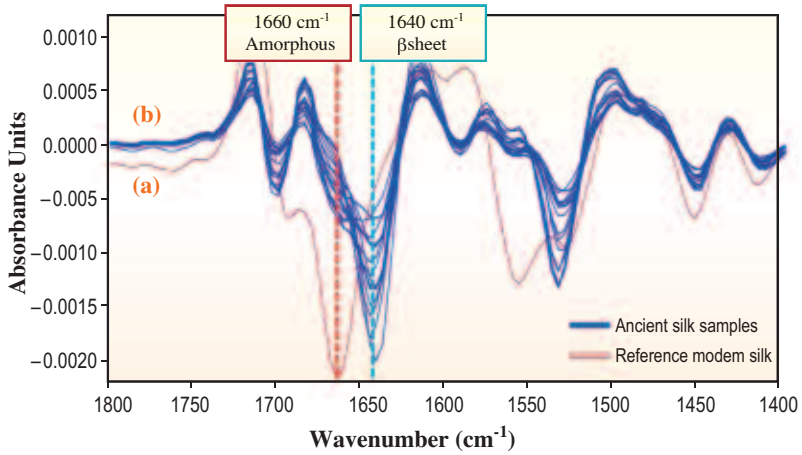

Fig. 3. Second derivative spectra of **(a)** reference modern silk and **(b)** ancient silk samples.

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