Journal of Wood Science

NOTE

Coloring mechanisms of ancient buried wood: Japanese cedar trees excavated from the foothills of Mt. Chokai

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Abstract

Spectroscopic characterization of ancient buried Japanese cedar (*Cryptomeria japonica*) woods excavated from the foothills of Mt. Chokai was carried out to investigate the factors governing their color tones. X-ray fluorescence analysis confirmed primary metal elements in the Japanese cedar wood to be Ca and Fe. Infrared photoacoustic spectroscopy revealed that prolonged burial had not caused severe chemical decomposition of the ancient wood. ^{57}Fe Mössbauer spectra of the ancient wood samples suggested that Fe in the Japanese cedar wood was present in the high-spin Fe^{3+} or low-spin Fe^{2+} state. Although the dark color tone of the ancient wood has been assumed to be due to the presence of multinuclear Fe complexes with multidentate ligands such as tannin, no positive correlation was observed between the color depth and Fe content of the ancient wood samples.

Keywords: Ancient buried wood, Color tone, Mössbauer spectroscopy, Raman spectroscopy, Iron, Japanese cedar

Introduction

Umoregi and *jindai-boku* are typical Japanese terms that refer to ancient trees buried or submerged as a result of natural phenomena (e.g., landslides, debris, avalanches, and ground subsidence) more than several centuries ago. These terms are generally applied to the ancient trees that have not been substantially denatured in terms of their physical properties and main constituents. Since, up to the point of their excavation, ancient buried trees have been shielded from sunlight and air, most of them have not suffered severe damage if their burial period time was within several 1000 years. In English, the terms bog wood, fossil wood (or sub-fossil wood), lignite, etc. have been utilized as translations of *umoregi* and *jindai-boku*; however, the meaning of these English terms is not exactly equivalent to that of the mentioned Japanese terms. A scientific definition for the wood identified by these Japanese words does not yet exist. Thus, we here use the term of *umoregi* and define as "*umoregi* wood" the stem of an ancient buried tree that contains neither carbonized nor petrified components. We call the stem of present-day trees "modern wood".

In general, *umoregi* wood turns dark or deep color, so that this wood is treated as a premium woody material for the manufacture of various products, especially furniture, owing to its color tone. Although not so often, *umoregi* wood is even used as construction materials.

Based on studies of iron-gall ink [1–6] and timber color changes associated with Fe contamination [7, 8], the idea that the iron complexes with tannin lead to the characteristic *umoregi*-wood color has been long accepted. Nevertheless, there has been no study that had focused on the coloring mechanism of *umoregi* wood prior to our previous work [9], even though Mössbauer spectra of Fe in *umoregi* wood have been already reported [10, 11]. In our previous report [9], we comprehensively analyzed *umoregi* wood from Japanese cedar (*Cryptomeria japonica*) and from three other tree species using Mössbauer and supplementary spectroscopic techniques, and discussed the chemical states of Fe complexes bringing about the coloring of *umoregi* wood. However, further

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Kurimoto *et al. J Wood Sci* (2020) 66:24

Page 2 of 6

investigations were required to elucidate more clearly the mechanism by which *umoregi* wood samples acquire their colors.

We previously studied the coloring mechanisms of *umoregi* wood and its ash for the four kinds of trees [9, 12]. In this study, our attention was focused on the differences in color tone among the *umoregi* wood samples of the same tree species and among the parts of an *umoregi* tree. As for most of the Japanese cedar *umoregi* trees, the sapwood showed much more lightly color tones compared with the heartwood. Thus, we selected two Japanese cedar *umoregi* trees of which heartwood displayed different colors from each other, and they were characterized using ^{57}Fe Mössbauer spectroscopy and several other analytical techniques. The aim of the present study is to achieve a deeper understanding of the coloring mechanisms of *umoregi* wood.

Experimental

Japanese cedar *umoregi* trees
The Japanese cedar *umoregi* trees used in this study were dug up in 2018 from Nikaho City in Akita Prefecture, Japan, in a location to the north-west of Mt. Chokai. The excavation point was located at 39° 13′ 44″ north latitude and 139° 58′ 4″ east longitude. The *umoregi* trees were probably buried by the heavy landslides occurring around the north-west foothills of Mt. Chokai about 2500 years ago [13].

Umoregi wood
The log of *umoregi* wood was cut into small blocks after air-drying in door for several months. *Umoregi* wood blocks were then ground to powder, which could be made to pass through a 40-mesh sieve, using a cutting mill. The *umoregi* wood powder samples obtained were submitted for the spectrometric measurements.

Bleaching with oxalic acid
The *umoregi* wood blocks were cut into smaller blocks ($15 \times 15 \times 15$ mm^3) and dried at 105 °C for 24 h in an electric oven. These dried blocks were immersed in aqueous oxalic acid solution (3 w/w%) of special-grade oxalic acid purchased from Fujifirm Wako Pure Chemical, Corp., and then a glass beaker holding the solution and blocks was placed in a vacuum desiccator. The blocks were kept at room temperature for 15 min in the desiccator, inside which the pressure was sufficiently reduced using a water-jet pump. They were taken out from the solution and dried in air for 2 days.

X-ray fluorescence spectrometry
The content of elements from Mg to Sr present in the Japanese cedar *umoregi* wood was determined by X-ray fluorescence (XRF) spectrometry using a compact spectrometer (MESA-500, Horiba, Ltd., Japan). *Umoregi* wood powder samples (~ 0.12 g) were placed in a cylindrical polytetrafluoroethylene (Teflon) cell with a diameter of 20 mm. The sample chamber of the compact spectrometer was evacuated using an oil-sealed rotary vacuum pump during measurements. X-ray irradiation was performed at room temperature for a total measurement time of 2000 s. The X-ray tube voltages were 15 kV (1000 s) and 50 kV (1000 s). Relative mass percentages of elements to total elements detected were estimated using a standardless fundamental parameter method [14, 15] from characteristic X-ray intensities.

Infrared photoacoustic spectroscopy
Infrared photoacoustic (IR-PA) spectra were recorded at room temperature using a spectrometer (JIR7000W, Jeol, Ltd., Japan) connected with an IR-PA spectroscopy module (IR-PAS 1000, Jeol, Ltd., Japan). The spectra were obtained from 300 accumulations with a spectral resolution of about 4 cm^{-1}. A thin cell (diameter, 5 mm) was filled with the wood powder, and photoacoustic signals were collected upon, flowing helium gas (10 mL/min) through a cell bench. The moving-mirror velocity was fixed at 1.6 mm/s. Amorphous carbon was used as a reference.

Mössbauer spectroscopy
^{57}Fe Mössbauer spectra were recorded using a Mössbauer spectrometer (Model-222, Topologic System Inc., Japan) with a ^{57}Co (Rh) source (925 MBq) in an ordinary transmission mode. Measurement temperatures were 298 K and 78 K, and they were regulated using an Oxford cryostat DN-1726 with a temperature controller of ITC-601. On the assumption that all spectra were composed of Lorentzian-shaped peaks, curve fitting of the Mössbauer spectra was performed by a nonlinear least-squares method using the MossWinn 4.0Pre. program. The isomer shift (*IS*) values and Doppler velocity scale were calibrated with respect to a set of sextet due to α-Fe at room temperature.

The thicknesses of Japanese cedar *umoregi* wood samples were in the 64–70 mg/cm^2, and these allowed us to discuss Mössbauer absorption intensities semi-quantitatively.

Results and discussion

Color tone of Japanese cedar *umoregi* woods and bleaching with oxalic acid
Figure 1 shows photos of two Japanese cedar *umoregi* wood samples characterized in this study. These samples a and b were obtained from the different individuals of Japanese cedar. As shown in Fig. 1, the sample a
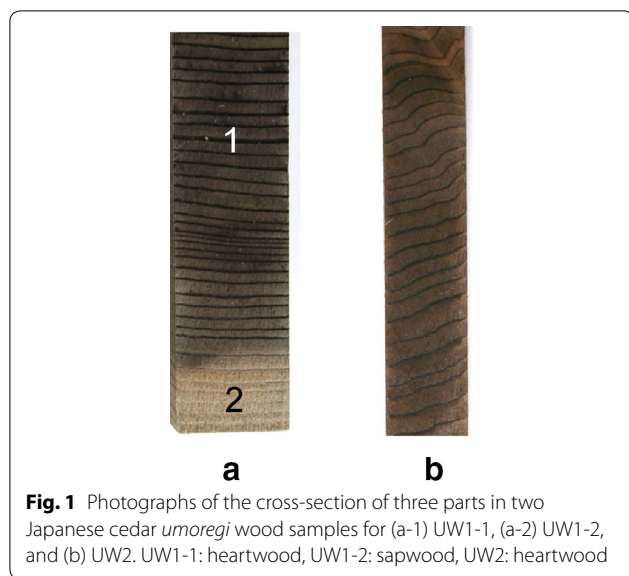
Kurimoto *et al. J Wood Sci*   (2020) 66:24

Page 3 of 6

Fig. 1 Photographs of the cross-section of three parts in two Japanese cedar *umoregi* wood samples for (a-1) UW1-1, (a-2) UW1-2, and (b) UW2. UW1-1: heartwood, UW1-2: sapwood, UW2: heartwood

(*umoregi* wood 1: UW1) contains both heartwood and sapwood parts, which, much like modern wood, are distinguishable from each other by entirely different color tones. The heartwood and sapwood sections of this sample are abbreviated as UW1-1 and UW1-2, respectively. Although the sample b (*umoregi* wood 2: UW2) most likely contains only heartwood, UW2 displays a slightly lighter and reddish-brown color as compared with UW1-1.

Figure 2 demonstrates the changes of the color tone resulting from oxalic acid treatment. The three parts (a1,
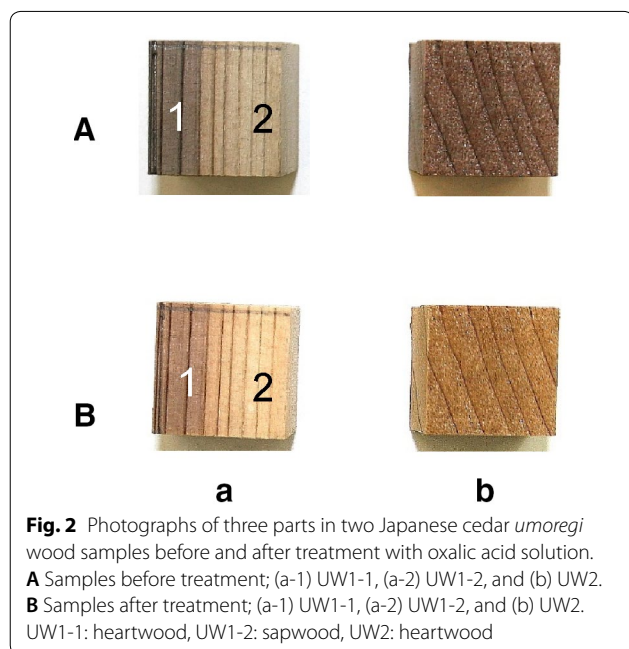
a2 and b) in the two samples before the treatment in the top row (A) of the figure show their original dark tones. As is evident from the photos in the bottom row (B) after the treatment, the three *umoregi* wood parts have the appearance of modern wood, as a result of the loss of their characteristic colors following the immersion into oxalic acid solution and subsequent drying. Thus, most of Fe in the *umoregi* wood are probably treated by oxalic acid chemically.

IR-PA spectra of Japanese cedar *umoregi* wood

Figure 3 depicts IR-PA spectra over a 2000–800 cm^{-1} range, where the top spectrum (a) is for the modern wood and the other three ones (b, c and d) are for *umoregi* wood samples. The three IR-PA spectral line-shapes of *umoregi* wood samples are extremely similar to one another as seen in Fig. 3b–d. No significant differences were observed between the *umoregi* and modern wood with respect to the vibrational bands attributed to phenyl groups of lignin (~ 1590 cm^{-1} and ~ 1500 cm^{-1}) [16, 17] and to saturated cyclic groups of cellulose or hemicellulose (1450–1320 cm^{-1} and 1180–1000 cm^{-1}) [16]. A remarkable difference between the spectra of the modern and *umoregi* wood samples is found around 1740 cm^{-1}; the relative intensity of the band for *umoregi* wood is much weaker than that of the modern wood. This band is attributed mainly to C=O stretching vibrations in carboxy [16] and/or unconjugated carbonyl [18] groups. In
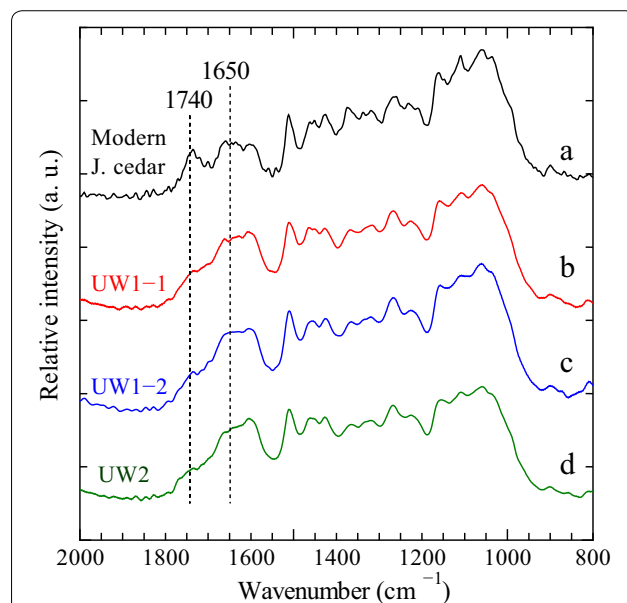

Fig. 2 Photographs of three parts in two Japanese cedar *umoregi* wood samples before and after treatment with oxalic acid solution. **A** Samples before treatment; (a-1) UW1-1, (a-2) UW1-2, and (b) UW2. **B** Samples after treatment; (a-1) UW1-1, (a-2) UW1-2, and (b) UW2. UW1-1: heartwood, UW1-2: sapwood, UW2: heartwood

Fig. 3 Infrared photoacoustic spectra in the 2000–800 cm^{-1} region for (a) modern Japanese cedar (heartwood, *black solid line*), (b) UW1-1 (heartwood, *red solid line*), (c) UW1-2 (sapwood, *blue solid line*), and (d) UW2 (heartwood, *green solid line*)

Kurimoto *et al. J Wood Sci*   (2020) 66:24

Page 4 of 6

addition, the stretching vibrations in conjugated C=O groups generate a band at ~ 1650 cm^{-1} [18], and the band intensity seems to be somewhat weaker for the *umoregi* wood than for the modern wood. Thus, the IR-PA spectra of the *umoregi* wood samples indicate that some chemical changes have occurred in the carboxy and/or carbonyl groups during the 2500-year burial. It is, however, likely that the overall chemical degradation rate had been substantially decreased for the Japanese cedar *umoregi* wood investigated here.

Elements in *umoregi* wood

Table 1 summarizes the relative mass percentage of elements from Mg to Sr in the *umoregi* wood samples determined here by XRF spectrometry.

Tsuchiya et al. measured the minor element contents in the wood and bark of many kinds of modern tree species including Japanese cedar using inductively coupled plasma emission spectrometry [19]. They reported that Ca was a primary or secondary element among metals, exceeding 800 mg/kg in the modern Japanese cedar wood samples, while Fe was undetectable or a trace element (< 10 mg/kg) and less abundant than Al.

The *umoregi* wood has not severely deteriorated as mentioned above, and therefore C, O, and H should be major elements as well as the wood of modern tree. However, as is evident from Table 1, Fe is a primary

or secondary element in all the Japanese cedar *umoregi* wood samples. The large Fe contents suggest that Fe was slowly transferred from the soil to the *umoregi* wood during the prolonged burial period. Other transition metals, Cr, Mn, Ni, and Cu, that have the potential to change color of *umoregi* wood were also detected, and however, their relative mass percentages are much lower than those of Fe. Hence, the effects of these elements on the color tone of the *umoregi* wood are very likely to be negligible.

The main three elements of modern wood are C, O, and H, and the sum of them is about 99% of the mass of modern wood. These elements and N are not detectable by ordinary XRF methods. Thus, the relative mass percentages listed in Table 1 should be estimated much larger than the true mass percentages, because the Japanese cedar *umoregi* wood samples have scarcely degraded as mentioned above. A simple calculation process was applied to approximate evaluation of the true mass percentage of Fe in the *umoregi* wood. In specific, the tentative true mass percentages of Fe were calculated using Eq. (1), on the assumption that C, O, H, and N were completely emitted from wood into the air by burning, although trace amounts of O remain as various oxides in the ash

$$TM_{Fe} = RM_{Fe} \times C_{ash} \times 1/100 \tag{1}$$

where TM_{Fe} and RM_{Fe} are the tentative true and relative mass percentages of Fe, respectively, and C_{ash} the ash content of *umoregi* wood. As listed in Table 1, the C_{ash} of UW1-1, UW1-2, and UW2 was 0.57%, 0.76%, and 0.91%, respectively. Thus, the TM_{Fe} calculated from Eq. (1) is in the order: UW1-2 (0.41%) > UW1-1 (0.33%) > UW2 (0.25%). Meanwhile, the color depth of *umoregi* wood seems to be in the order: UW1-1 ≥ UW2 > UW1-2, as shown in Fig. 1. Accordingly, the elemental analysis using XRF spectrometry leads to the conclusion that the color depth of *umoregi* wood does not necessarily increase with the Fe content, although it has been believed that the color depth might be dependent mainly upon Fe content.

Mössbauer spectra of *umoregi* wood

Figure 4 shows Mössbauer spectra of the *umoregi* wood samples recorded at 78 K. A curve-fitting procedure was carried out, assuming that all the spectra were composed of only a set of Lorentzian doublet. Table 2 summarizes the Mössbauer parameters for the spectra at 78 K of the three samples of *umoregi* wood.

As listed in the table, the *IS* and quadrupole splitting (*QS*) values of UW1-1 and UW1-2 were quite close to those we reported previously for the *umoregi* wood of various kinds of tree [9], whereas both the parameter

Table 1 Relative mass percentages of elements, tentative true mass percentages of Fe, and ash contents in Japanese cedar *umoregi* wood samples

Sample	UW1-1	UW1-2	UW2
C_{ash}%	0.57	0.76	0.91
TM_{Fe}	0.33	0.41	0.26
Mg	1.9	3.5	1.3
Al	1.7	1.5	2.1
Si	7.8	6.2	8.1
S	1.3	8.2	0.8
K	0.9	0.9	1.6
Ca	27.1	24.5	56.7
Ti	0.3	0.3	0.4
Cr	0.1	0.1	0.1
Mn	0.7	0.6	0.1
Fe	57.5	53.6	28.0
Ni	0.3	0.3	0.4
Cu	0.1	0.1	0.0
As	0.1		0.1
Sr	0.2	0.1	0.2

Blank space implies "not detected"

C_{ash} is ash content of *umoregi* wood

TM_{Fe} is a tentative true mass percentage of Fe

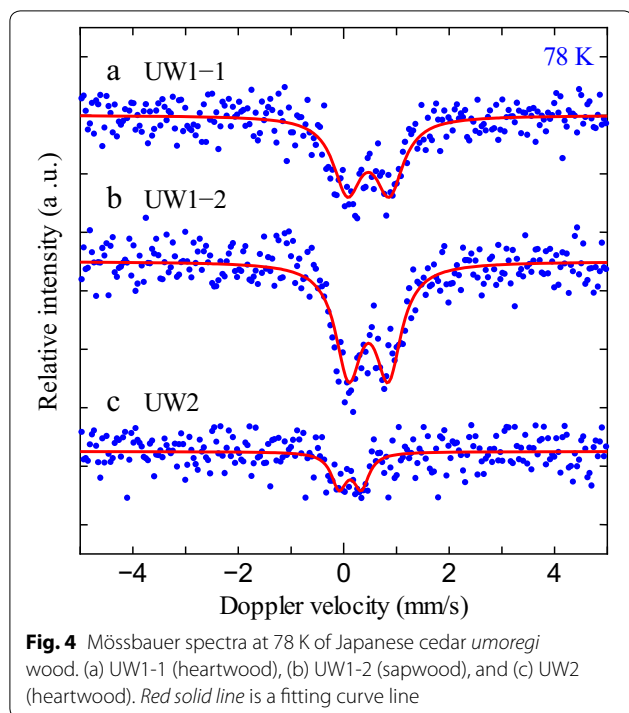Kurimoto *et al. J Wood Sci*   (2020) 66:24

Page 5 of 6

Fig. 4 Mössbauer spectra at 78 K of Japanese cedar *umoregi* wood. (a) UW1-1 (heartwood), (b) UW1-2 (sapwood), and (c) UW2 (heartwood). *Red solid line* is a fitting curve line

Table 2 Mössbauer parameters at 78 K of Japanese cedar *umoregi* wood samples

Sample	*IS* (mm/s)	*QS* (mm/s)	*LW* (mm/s)
UW1-1	0.47 (2)	0.80 (3)	0.65 (6)
UW1-2	0.47 (2)	0.75 (3)	0.59 (4)
UW2	0.12 (3)	0.42 (5)	0.35 (9)

IS isomer shift; *QS* quadrupole splitting; *LW* line width

values of UW2 were substantially smaller than those of UW1-1 and UW1-2. The Mössbauer spectra provide the following chemical information on Fe in the *umoregi* wood.

First, the *IS* and *QS* values suggested that UW1-1 and UW1-2 probably contained Fe in the form of high-spin Fe^{3+} complexes, by taking into account the Mössbauer parameters (*IS* and *QS*) previously reported [20–22]. Moreover, the ligands of the complexes are likely to be polyphenols such as tannin having pyrogallol groups. However, there have been several problems to be solved for their molecular structure, for example, the coordination number of Fe.

Second, the *IS* value at 78 K of UW2 is 0.12 mm/s, suggesting that Fe in UW2 is present in low-spin Fe^{2+} [20, 21] and has a six-coordination structure [22]. It is for the first time that low-spin Fe^{2+} was identified in *umoregi* wood. Our finding of low-spin Fe^{2+} in the *umoregi* trees excavated from the foothills of Mt. Chokai may provide a clue to clarify the transfer

mechanism of Fe from soil to *umoregi* wood since Fe probably transfers as Fe^{2+} from soil to *umoregi* wood [9]. According to the previous studies on metal-gall complexes [1–6], low-spin Fe^{2+} in UW2 presumably forms complexes with polyphenols as well as high-spin Fe^{3+}.

The factors determining the color of *umoregi* wood will be extremely complicated, and further study is required to confirm a causal relationship between the chemical state of Fe and the color tone of *umoregi* wood.

Conclusion

The present work provided an outcome that the brown color tones of Japanese cedar *umoregi* wood excavated from the foothills of Mt. Chokai are most likely due to the multinuclear complexes of Fe with polyphenol ligands having pyrogallol groups; however, the color tone depth is not necessarily proportional to the Fe concentration in *umoregi* wood. Moreover, the color tone of *umoregi* wood might be substantially dependent upon the chemical properties of Fe complexes with polyphenols.

The factors affecting the color of *umoregi* wood are very complicated. Additional studies on a wider range of *umoregi* wood samples are required to explain in detail the coloring mechanism of *umoregi* wood.

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Kurimoto *et al. J Wood Sci*   (2020) 66:24

Page 6 of 6

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