Mössbauer and Raman characterization of ash produced by burning ancient buried Japanese cedar and investigation for its unusual color tone

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Abstract

Mössbauer and Raman spectroscopic characterization of colored ash samples made by combustion of ancient buried Japanese cedar (*Cryptomeria japonica*) was carried out, and the factors governing the color tones were investigated mainly in terms of the chemical species of Fe. The ash samples displayed various unusual colors, depending clearly on the individual ancient tree and the part of it. Some of Mössbauer spectra of the ash samples showed magnetic hyperfine splittings due to internal magnetic fields. The Mössbauer and Raman spectra suggested that the primary Fe-containing species in all the ash samples was calcium ferrite, $\text{Ca}_2\text{Fe}_2\text{O}_5$.

Keywords Mössbauer spectroscopy · Raman spectroscopy · Calcium ferrite · Ancient buried wood · Superparamagnetic effect

Abbreviations

XRD	X-ray diffraction
UWX	(X = 1–1, 1–2, and 2) is an <i>umoregi</i> -wood sample
UAX	(X = 1–1, 1–2, and 2) is an ash sample made from UWX
MA	Is an ash sample made from modern Japanese cedar wood
MBq	Megabecquerel
<i>IS</i>	Isomer shift
<i>QS</i>	Quadrupole splitting
<i>LW</i>	Line width
<i>H</i>	Internal magnetic field
<i>T</i>	Tesla
<i>O_h</i>	Octahedral
<i>T_d</i>	Tetrahedral

Introduction

As described in our previous studies [1–3], “*umoregi*” is the most common Japanese term that refer to ancient trees buried or submerged as a result of natural phenomena (e.g., landslides, debris, avalanches, and ground subsidence) over several centuries ago. This term is generally applied to the ancient trees that have not been substantially denatured in terms of their physical properties and main chemical constituents. In English, the terms, bog wood, fossil wood (or sub-fossil wood), lignite, etc. have been utilized as translations of *umoregi*; however, the meaning of these English terms is not exactly equivalent to that of the Japanese term.

Owing to its attractive color tones, *umoregi* wood is regarded as a special woody material. Furthermore, experts or advanced learners of the Japanese tea or traditional incense ceremonies rate the ash made from *umoregi* wood, which displays various unusual colors, as top-quality ash in an incense burner or a brazier. However, there have been no reports examining the ash made from *umoregi* wood other than our previous work [1]. We investigated the coloring mechanism of ash obtained from the combustion of four species of *umoregi* trees excavated from the foothills of Mt. Chokai in 2015 [1]. The Mössbauer spectra of some ash samples made from *umoregi* wood showed obvious magnetic hyperfine splittings; however, satisfactory curve-fitting analysis could not be carried out, owing to the broad and

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complicated absorption line-shapes. We revealed in our previous report [1] that the *umoregi*-wood ash samples included calcium ferrites, CaFe_2O_4 and/or $\text{Ca}_2\text{Fe}_2\text{O}_5$, from our qualitative analysis of the Mössbauer spectral line-shapes, speculating that the calcium ferrites governed the color of the *umoregi*-wood ash samples. However, it is not sufficiently confirmative to make clear the formation of calcium ferrites and to explain more comprehensively the factors affecting the color tone of *umoregi*-wood ash.

We obtained ash samples with different colors made from Japanese cedar (*Cryptomeria japonica*) *umoregi* wood excavated within the same zone of the mountain-side of Mt. Chokai, which stands on the boundary between Akita and Yamagata Prefectures, Japan, as shown in Fig. 1, and attempted to clarify the factors governing the color tones of the samples, based on the Mössbauer and Raman characterization.

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, at 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. Heavy landslides are known to have occurred over the north-west foothills of Mt. Chokai about 2500 years ago, and the *umoregi* trees were probably buried by these landslides [4].

Fig. 1 The location of Mt. Chokai in Japan

Umoregi-wood ash samples and chemicals

Ash samples were prepared by combustion of the Japanese cedar *umoregi*-wood and modern-wood in an ordinary open-type electric furnace maintained at 600 °C for 7 h. The samples obtained were submitted to analytical measurements without further grinding. The mass percentage of the ash to the wood powder dried at 105 °C was defined here as the value of the ash content. Special-grade calcium carbonate (CaCO_3) powder used as a reference substance was purchased from Fujifirm Wako Pure Chemical Corporation.

X-ray fluorescence spectrometry

The content of elements from Na to Ba present in the Japanese cedar *umoregi*-wood and modern-wood ash were determined by X-ray fluorescence (XRF) spectrometry using a compact spectrometer (JSX-1000S, Jeol, Ltd., Japan). The ash samples (0.25–0.28 g) were placed in a cylindrical 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 measurement time of 30 s. The X-ray spot on the ash samples was an oval (9 mm × 10 mm). The X-ray tube voltage was 30 kV.

Raman spectroscopy

Raman spectra were obtained using a Raman spectrometer (inVia Raman Microscope, Renishaw PLC, UK) with 532 nm laser excitation (0.75–1.5 mW). Back-scattered Raman signals were collected through a microscope (50× objective lens) with a spectral resolution of 3 cm^{-1} , and the exposure time was 50 s. The ash samples were thinly and evenly spread on a glass plate. The diameter of the laser spot on the sample surface was ~2 μm . Since such a measurement-scope is much smaller relative to the homogeneity-scale of sample, Raman measurements were repeated at more than 30 different points for each ash sample in the present work. The calibration of Raman shifts was carried out using the 520 and 1332 cm^{-1} for a silicon wafer and diamond, respectively.

Powder X-ray diffractometry

X-ray diffraction (XRD) analysis was performed using a Shimadzu XRD-7000 X-ray diffractometer (Shimadzu

Corp., Japan) equipped with a Cu-K α radiation source (wavelength: 1.5406 Å). Diffraction patterns were acquired at 30 kV and 30 mA in a line focus mode. Scan rates were set at 4°/min.

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. The γ -ray transmission diameter of the ash samples was approximately 8 mm. 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. Two kinds of curve-fitting were carried out in the numerical analysis of the Mössbauer spectra by using of a commercially available computing-program named MossWinn 4.0i. Firstly, the Mössbauer spectra measured in this study were curve-fitted using an ordinary method, assuming that they consist only of Lorentzian-shaped lines. If this method failed to obtain the reasonable values of Mössbauer parameters, the second method was applied to the curve-fitting procedure with a distribution of Mössbauer parameters. The isomer shift (IS) values and Doppler velocity scale were calibrated with respect to α -Fe at room temperature.

The Fe-thicknesses of *umoregi*-wood ash samples were in the 7.4–9.6 mg/cm 2 ranges, which allowed us to discuss a Mössbauer absorption intensity proportional to its iron-species concentration approximately.

Results and discussion

Color tone of Japanese cedar *umoregi* wood

Figure 2 shows photos of two Japanese cedar *umoregi*-wood specimens obtained from different individual trees.

Fig. 2 Photographs of cross sections of three parts of two Japanese cedar *umoregi* wood specimens for (1–1) UW1–1: heartwood, (1–2) UW1–2: sapwood, and (2) UW2: heartwood

As shown in the figure, from specimen 1 (*umoregi* wood 1: UW1) two parts were sampled as heartwood (UW1-1) and sapwood (UW1-2). It should be noted that UW1-1 and UW1-2 are distinguishable by their entirely different color tones, like modern wood. Specimen 2 (*umoregi* wood 2: UW2) is most likely composed of only heartwood. It looks that the color tone of UW1-1 is somewhat different from that of UW2.

Color tone of *umoregi*-wood ash

Figure 3 shows photographs of three ash samples made from the two specimens of Japanese cedar *umoregi* wood. The

Fig. 3 Photographs of ash samples made from Japanese cedar *umoregi* wood and modern Japanese cedar wood for (1–1) UA1–1, (1–2) UA1–2, (2) UA2, and (3) MA UAX and MA were made from UW X (X = 1–1, 1–2, and 2) and modern Japanese cedar wood, respectively

ash made from UWX ($X=1-1$, $1-2$, and 2) is abbreviated as UAX. The photo of modern Japanese cedar wood ash (MA), of which the color turns completely white, is shown as a reference. The three UA samples show characteristic colors and they are quite different from one another. The colors of UA1-1 and UA1-2 are dark brown and orange-colored, respectively. In contrast, that of UA2 is grayish-yellow. Interestingly, the color tone of ash made from sapwood (UA1-2) is clearly different from that of ash made from heartwood (UA1-1), despite the fact that both UA1-1 and UA1-2 were obtained from the same Japanese cedar *umoregi* tree.

Elements in ash samples

The molar percentages of elements from Na to Ba in UAX ($X=1-1$, $1-2$, and 2) and MA determined using XRF spectrometry are listed in Table 1. The elements for which the molar percentage is less than 0.10% are omitted from the table. As is expected from the previous study [1], Fe was concentrated considerably in the three *umoregi*-wood ash samples compared with MA. The XRF elemental-analysis results could provide two important pieces of information about the Fe-containing species.

The first information is on the Fe/Ca molar ratio. Hirabayashi have reported that the production ratio of $\text{CaFe}_2\text{O}_4/\text{Ca}_2\text{Fe}_2\text{O}_5$ would be dependent on the Fe/Ca ratio in the synthesis from Fe_2O_3 and CaO [5]. As shown in Table 1, Fe and

Ca are primary elements in all the ash samples; therefore, the chemical species containing Fe and/or Ca would substantially influence the color tone of the ash samples.

The second is the contents of Na and Mg that can form ferrites. Na and Mg are secondary elements in UA1-1 and UA1-2, and their molar percentages are so large that they cannot be ignored. As for UA2, Na is one of primary elements as well as Ca and Fe. Hence, all the *umoregi*-wood ash samples may comprise multiple species of ferrite. Furthermore, it is expected that Na, Mg, and Ca were partly formed as their oxides in the ash samples, especially UA2, because the total molar percentages of Na, Ma, and Ca are excessively large compared with those of Fe in the ash samples. This will be discussed in detail later.

In addition, UA1-2 contains a considerable amount of S and P, compared with other samples. The abundance of S and P might exert some influence on the color of the ash samples. Transition metals, Ti and Mn, which have the potential to affect the color tone of *umoregi*-wood ash were also present; however, their molar percentages are much lower than those of Fe. Accordingly, the effects of these elements on the color tone will be negligible.

Table 1 Molar percentages of elements as an ordinary-type oxide in ash samples

Ash samples	UA1-1	UA1-2	UA2	MA
C_{ash} (wt%)	0.57	0.76	0.91	0.24
Na_2O	5.04 (19)	3.23 (16)	23.47 (30)	1.23 (11)
MgO	13.82 (11)	12.67 (11)	7.83 (9)	5.81 (6)
Al_2O_3	0.30 (2)	0.62 (3)	0.20 (2)	0.23 (1)
SiO_2	3.87 (3)	2.15 (2)	2.75 (3)	—
P_2O_5	0.20 (1)	3.10 (3)	0.36 (1)	0.95 (1)
SO_3	1.88 (1)	16.74 (4)	0.99 (1)	1.24 (1)
K_2O	1.00 (1)	0.80 (1)	1.14 (1)	13.34 (4)
CaO	48.73 (6)	42.23 (6)	53.80 (7)	76.44 (7)
TiO_2	—	0.17 (1)	—	—
MnO	0.66 (1)	0.55 (1)	0.19*	0.21*
Fe_2O_3	24.19 (5)	17.52 (4)	8.99 (3)	0.10*
SrO	—	—	0.11*	0.20*
BaO	0.16 (1)	0.11 (1)	0.18 (1)	0.16 (1)

UAX was ash made from UWX ($X=1-1$, $1-2$, and 2)

MA was ash made from modern Japanese cedar wood

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

— indicates “not detected” or “less than 0.10”

*Standard deviation is less than 0.01

Fig. 4 Raman spectra in the range $800\text{--}150\text{ cm}^{-1}$ of ash samples for **a** and **b** UA1-1 (black solid line), **c** and **d** UA1-2 (red solid line), **e** and **f** UA2 (blue solid line) UAX was made from UWX ($X=1-1$, $1-2$, and 2). Spectra **a**, **c** and **e** belong to pattern A. Spectra **b** and **d** belong to pattern B. Spectrum **f** belongs to pattern A'

Raman spectra of ash samples

Figure 4 illustrates two kinds of typical Raman spectrum of each *umoregi*-wood ash sample in the range from 800 cm^{-1} to 150 cm^{-1} . Almost all the Raman spectra of UA1-1 and UA1-2 were roughly classified into two patterns, A and B, showing spectral line-shapes different from each other. The Raman spectra shown in Figs. 4a, c corresponds to the spectral pattern A, and those shown in Figs. 4b, d belong to the pattern B. In contrast, almost the Raman spectra of UA2 showed pattern A; however, a Raman band was observed at 272 cm^{-1} in a few spectra. This spectral pattern is referred to A'.

In Table 2 are summarized the Raman band frequencies of the ash samples in this work, where those of calcium [6–8], magnesium [9, 10], and sodium [11] ferrites reported previously are also presented for a comparison. It is evidently exhibited in the table that all the ash samples contain CaFe_2O_4 and/or $\text{Ca}_2\text{Fe}_2\text{O}_5$; however, it is difficult to distinguish the two calcium ferrites based only on the Raman

bands detected in this region because of no significant differences in Raman bands between the two ferrites [6–8].

Observations of the Raman bands at 324 and 476 cm^{-1} in the spectral pattern B might suggest that UA1-1 and UA1-2 comprise small amounts of magnesium ferrite, MgFe_2O_4 . The crystal structure of sodium ferrite, NaFeO_2 , is a rock salt (α) or zinc blend (β) type. A number of studies on the compounds with the same structure as NaFeO_2 have been reported; nevertheless, there have been few Raman spectroscopic studies on NaFeO_2 in itself. The Raman band frequencies of α - and β - NaFeO_2 listed in Table 2 were estimated from the spectra illustrated in the literature [11]. As can be seen in Fig. 4, the Raman band at 457 cm^{-1} observed in the spectra of A and A' patterns may indicate the presence of β - NaFeO_2 . This assignment of the band at 457 cm^{-1} is probably supported by the fact that UA2 is the most Na-rich ash sample, and the relative intensities of the band in the spectra of UA2 are obviously stronger than those of UA1-1 and UA1-2. Finally, the results obtained from Raman measurements in the 800–150 cm^{-1} region suggest

Table 2 Raman band frequencies of ash samples and calcium, magnesium, and sodium ferrites reported in the previous works

Umorigi-wood ash samples		CaFe_2O_4	$\text{Ca}_2\text{Fe}_2\text{O}_5$	$\text{Ca}_2\text{Fe}_2\text{O}_5$	MgFe_2O_4	MgFe_2O_4	α - NaFeO_2	β - NaFeO_2
Patterns A and A'	Pattern B							
Raman shift (cm^{-1})								
	210	213		212				
					217	217	220	
252		252	251	254				
		258	261					260
272*								
		288	292	290				305
		315	313	312				
	324					327		
					333			
							350	
						367		
383		379	380	379				
		395	393	395				415
		428	428	427				
457								455
	476				486	487		
558		558	558	555	554	550	566	
		600	595			590		600
					646	630		
678				667 ^{sh}				
	693							
710*, ^{sh}		703	705	706	715	703		
This study	Ref. [6]	Ref. [7]	Ref. [8]	Ref. [9]	Ref. [10]	Ref. [11]	Ref. [11]	

*The band was observed only in the pattern A' spectra

sh shoulder

Fig. 5 Raman spectra in the range 1200–950 cm^{-1} of ash samples for **a** UA1-1 (black solid line), **b–e** UA1-2 (red solid line), **f, g,** and **(h)** UA2 (blue solid line) UAX was made from UWX (X=1–1, 1–2, and 2)

that the three ash samples contain calcium ferrites, CaFe_2O_4 and/or $\text{Ca}_2\text{Fe}_2\text{O}_5$, as major components, and other ferrites, MgFe_2O_4 and NaFeO_2 may be slightly present in the ash samples.

Figure 5 depicts typical Raman spectra of the three ash samples in the range 1200–950 cm^{-1} . As for UA1-1, a Raman band was only observed at 1078 cm^{-1} in nearly half of measurement points, and no bands were detected at the other points. Conversely, multi-Raman peaks appeared in almost all of the UA1-2 spectra. It is interesting to note that all the spectra of UA2 exhibited the strong Raman bands at around 1078 cm^{-1} .

In general, Raman bands appearing in this frequency region are due to a stretching vibration of the superoxide anion, O_2^- , with respect to substances comprising mainly oxides such as UA samples. The vibrational bands of this anion in a number of compounds have been reported, and they were detected over a relatively wide frequency-range [12–16]. Accordingly, Raman bands shown in Fig. 5 are likely to be assigned to the vibrational mode of superoxide anions, excluding those appearing at around 1078 cm^{-1} .

Table 3 Molar ratios of Fe/Ca, Fe/(Na + Mg + Ca), Na/Ca, and Mg/Ca

Umoregi-wood ash samples	Molar ratio			
	Fe/Ca	Fe/(Na + Mg + Ca)	Na/Ca	Mg/Ca
UA1-1	0.993 (2)	0.666 (4)	0.207 (4)	0.284 (2)
UA1-2	0.830 (2)	0.571 (4)	0.153 (4)	0.300 (3)
UA2	0.334 (1)	0.166 (1)	0.872 (7)	0.146 (1)

Error ranges were estimated from the standard deviations shown in Table 1

It is well known that the carbonates of metals belonging to Groups 1 and 2 have a Raman-active vibrational band at $\sim 1080 \text{ cm}^{-1}$; moreover, Na_2O and CaO readily react with CO_2 in air and change to their carbonates. As shown in Tables 1 and 3, the total molar percentage of Na, Mg, and Ca is much larger than that of Fe in UA samples, especially in UA2. Thus, it is likely that Na_2O , MgO , and CaO other than their ferrites were produced more or less by the combustion of *umoregi* wood. In particular, UA2 probably include considerable amounts of Na_2O and CaO when the burning of UW2 was completed; therefore, the Raman bands observed at 1085–1073 cm^{-1} would be due to stretching vibrations of CO_3^{2-} ion.

Figure 6 depicts Raman spectra of MA and CaCO_3 in the range 1200–150 cm^{-1} . The line-shapes of all observed Raman spectra of MA were nearly independent of the measurement points in a sample. The Raman spectral shape of MA is the same as that of neat CaCO_3 , indicating

Fig. 6 Raman spectra in the range 1200–150 cm^{-1} of ash samples for **a** MA (black solid line) and **b** CaCO_3 (red solid line) MA was made from modern Japanese cedar wood

Fig. 7 XRD patterns of ash samples for **a** UA1-1 (black solid line), **b** UA1-2 (red solid line), **c** UA2 (blue solid line), and MA (gray solid line) Red full circles and blue full circles show the peaks due to calcite-type and aragonite-type CaCO_3 , respectively. Green and orange zones are 2-theta ranges in which characteristic XRD peaks due to $\text{Ca}_2\text{Fe}_2\text{O}_5$ and CaFe_2O_4 , respectively, appear

that the bands at around 1078 cm^{-1} are assigned to stretching vibrational modes of the CO_3^{2-} ion.

Another possible reaction of the metal oxides in air is hydrolysis; however, no OH stretching vibrational bands were detected on the three ash samples by Raman spectroscopy. Hence, it is concluded that the ash samples do not contain any hydroxides and oxyhydroxides.

XRD patterns of ash samples

Figure 7 illustrates XRD patterns in the 2-theta range $20\text{--}60^\circ$ of ash powder samples. The four XRD patterns may be entirely different from one another. All three XRD patterns of *umoregi*-wood ash samples show multi-peaks in the 2-theta regions in which the characteristic XRD peaks due to $\text{Ca}_2\text{Fe}_2\text{O}_5$ (green zone) and CaFe_2O_4 (orange zone) should be observed; however, the peaks are not well-resolved. Moreover, the XRD pattern of MA also exhibits peaks in green and orange zones in the figure despite little or no calcium ferrites. Accordingly, it is likely difficult to identify the calcium ferrites in the *umoregi*-wood ash samples on the basis of the XRD data.

In contrast with the calcium ferrites, several peaks attributable to CaCO_3 are detected in the XRD patterns of all ash

Fig. 8 Mössbauer spectra 78 K of ash samples for **a** UA1-1, **b** UA1-2, and **c** UA2 Red solid curves correspond to the sum of spectral components. Orange and green solid curves correspond to O_h and T_d sites in $\text{Ca}_2\text{Fe}_2\text{O}_5$, respectively. UA2 was made from UW2 (X = 1–1, 1–2, and 2). Vertical dotted lines correspond to peak positions of two sextets and a doublet in UA1-1 spectrum

samples, confirming the assignment of Raman band around 1078 cm^{-1} .

Fig. 9 Mössbauer spectra 298 K of ash samples for **a** UA1-1, **b** UA1-2, and **c** UA2 Red solid curve corresponds to the sum of spectral components. UA2 was made from UW2 (X = 1–1, 1–2, and 2). Vertical dotted lines correspond to peak positions of a doublet in UA1-1 spectrum

Mössbauer spectra of ash samples

Figures 8 and 9 display Mössbauer spectra of *umoregi*-wood ash samples at 78 K and 298 K, respectively. With respect to Mössbauer measurements at 78 K, the complicated spectral profiles due to magnetic hyperfine splitting are observed in the spectra of UA1-1 and UA1-2, while only a quadrupole doublet is recorded in that of UA2. On the other hand, the primary absorption is a doublet line in the three spectra at 298 K, although the spectrum of UA1-1 and UA1-2 seems to possess weak absorptions on both sides of the doublet. The Mössbauer spectra of UA2 (78 K and 298 K) were successfully analyzed using the ordinary curve-fitting procedure on the assumption that they consist of a Lorentzian-shaped doublet absorption. However, we could not obtain reliable Mössbauer parameters for the UA1-1 and UA1-2 spectra using the ordinary method, owing to their broad and complicated line-shapes.

Fig. 10 Distributions of internal magnetic field (H) in Mössbauer spectra at 78 K of UA1-1 for internal magnetic field (H) of Mössbauer absorptions corresponding to two sextets

The most likely explanation for the broadening and complication in Mössbauer absorption lines might be the multi-chemical iron-bearing species, leading to the wide-range distribution of their IS , QS , and H values. Thus, the three spectra were numerically re-analyzed using by the curve-fitting procedure with a distribution of Mössbauer parameters, the principle of which was developed by Hesse and Rübarsch [17]. A typical example of the obtained distributions is shown in Fig. 10, where the hyperfine-field distribution for the UA1-1 spectrum at 78 K. Finally, the procedure provided satisfactory results with respect to the spectrum of UA1-1 at 78 K. These Mössbauer parameters of the ash samples are listed in Table 4, and Mössbauer parameters of sodium [18, 19], magnesium [20, 21], and calcium [5, 18, 22–24] ferrites reported previously are summarized in Table 5.

As shown in Fig. 8, the Mössbauer spectrum at 78 K of UA1-1 was resolved into a doublet and two sextets. By comparing the Mössbauer data reported previously [23], the Mössbauer parameters calculated on the two sextets are probably attributed to the two Fe^{3+} sites in $\text{Ca}_2\text{Fe}_2\text{O}_5$. Moreover, the doublet line in the spectrum would also be assigned to $\text{Ca}_2\text{Fe}_2\text{O}_5$ in terms of the IS and QS values. A likely explanation for the disappearance of magnetic hyperfine splitting is due to a superparamagnetic effect, namely a part of $\text{Ca}_2\text{Fe}_2\text{O}_5$ powder is less than ~ 5 nm. Because this effect increases more remarkably as temperature increases [25], the explanation is supported by the fact that the ratio of the whole sextet absorption intensity to the doublet absorption intensity at 298 K is extremely weak, as compared with that at 78 K.

Hirabayashi and co-workers asserted that the product yields of $\text{Ca}_2\text{Fe}_2\text{O}_5$ and CaFe_2O_4 synthesized from Fe_2O_3 and CaO at 1000 °C depended upon the Fe/Ca molar ratio in the reactant [5]. They reported that Fe-containing compounds as the reaction products were only the two calcium ferrites when the Fe/Ca value is more than 0.67, and the yield of $\text{Ca}_2\text{Fe}_2\text{O}_5$ decreased with increasing Fe/Ca ratio in the range from 0.67 to 2. The percentage of $\text{Ca}_2\text{Fe}_2\text{O}_5$

Table 4 Mössbauer parameters of UA1-1, UA1-2, and UA2

Sample	Temp.(K)	Type of absorption	IS (mm/s)	QS (mm/s)	H (T)	LW (mm/s)	Area (%)	Primary Fe species
UA1-1	78	Doublet	0.45 (1)	0.62 (1)	–	0.74 (5)	42 (1)	–
		Sextet-1 D	0.47 (2)	–0.34 (4)	52.4 [2]	0.51 (5)	27 (2)	$\text{Ca}_2\text{Fe}_2\text{O}_5$ (O_h site)
		Sextet-2 D	0.30 (1)	0.60 (3)	46.8 [1]	0.51 (5)	31 (2)	$\text{Ca}_2\text{Fe}_2\text{O}_5$ (T_d site)
	298	Doublet	0.32 (2)	0.66 (2)	–	0.82 (5)	64 (1)	–
		Sextet D	0.2 (5)	0.4 (1)	43 [5]	0.8 (2)	36 (5)	–
UA1-2	78	Singlet	0.49 (5)	–	–	–	30 (4)	–
		Sextet D	0.43 (1)	0.00 (3)	49 [3]	–	70 (5)	–
UA2	78	Doublet	0.454 (3)	0.627 (4)	–	0.524 (7)	100	–
	298	Doublet	0.345 (3)	0.601 (6)	–	0.49 (1)	100	–

IS isomer shift; QS quadrupole splitting; H internal magnetic field; T tesla; LW line width; O_h octahedral; T_d tetrahedral

Table 5 Mössbauer parameters of sodium, magnesium, and calcium ferrites reported previously

Ferrites	Chemical state of iron	Type of splitting	Temp. (K)	<i>IS</i> (mm/s)	<i>QS</i> (mm/s)	<i>H</i> (T)	Ref.
α -NaFeO ₂	Fe ³⁺	Doublet	77	0.47	0.45	–	[18]
	Fe ³⁺	Doublet	295	0.36	0.48	–	[18]
	Fe ³⁺	Doublet	283	0.22	0.23	–	[19]
β -NaFeO ₂	Fe ³⁺	Sextet	295	0.17	0.05	49.0	[18]
	Fe ³⁺	Sextet	283	0.194	–0.057	49.35	[19]
MgFe ₂ O ₄	Fe ³⁺ (<i>O_h</i>)	Sextet	300	0.38	0.01	44.1	[20]
	Fe ³⁺ (<i>T_d</i>)	Sextet	300	0.22	0.05	41.3	[20]
	Fe ³⁺ (<i>O_h</i>)	Sextet-1	300	0.32	–0.01	49.5	[21]
	Fe ³⁺ (<i>O_h</i>)	Sextet-2	300	0.03	0.36	49.9	[21]
	Fe ³⁺ (<i>T_d</i>)	Sextet	300	0.26	–0.01	44.7	[21]
	Fe ³⁺ (<i>O_h</i>)	Sextet-1	78	0.48	0.025	54.3	[21]
	Fe ³⁺ (<i>O_h</i>)	Sextet-2	78	0.44	–0.064	53.9	[21]
	Fe ³⁺ (<i>T_d</i>)	Sextet	78	0.36	0.004	51.7	[21]
	Fe ³⁺	Sextet	78	0.48	–0.031	46.2	[5]
	Fe ³⁺	Doublet	293	0.37	0.52	–	[5]
CaFe ₂ O ₄	Fe ³⁺	Sextet	77	0.45	0.00	46.0	[18]
	Fe ³⁺	Doublet-1	295	0.37	0.33	–	[18]
	Fe ³⁺	Doublet-2	295	0.37	0.74	–	[18]
	Fe ³⁺	Doublet-1	295	0.37	0.30	–	[22]
	Fe ³⁺	Doublet-2	295	0.37	0.75	–	[22]
	Fe ³⁺	Doublet-2	295	0.37	0.75	–	[22]
Ca ₂ Fe ₂ O ₅	Fe ³⁺ (<i>O_h</i>)	Sextet	77	0.46	–0.52	54.0	[23]
	Fe ³⁺ (<i>T_d</i>)	Sextet	77	0.27	0.71	47.5	[23]
	Fe ³⁺ (<i>O_h</i>)	Sextet	300	0.37	–0.52	50.4	[23]
	Fe ³⁺ (<i>T_d</i>)	Sextet	300	0.18	0.72	42.9	[23]
	Fe ³⁺ (<i>O_h</i>)	Sextet	293	0.35	–0.52	50.7	[5]
	Fe ³⁺ (<i>T_d</i>)	Sextet	293	0.18	0.72	43.2	[5]
	Fe ³⁺ (<i>O_h</i>)	Sextet	RT	0.36	–0.54	51.5	[24]
	Fe ³⁺ (<i>T_d</i>)	Sextet	RT	0.18	0.72	43.9	[24]

IS isomer shift; *QS* quadrupole splitting; *H* internal magnetic field; *T* tesla; *RT* room temperature

O_h octahedral; *T_d* tetrahedral

was ~78% at a ratio of Fe/Ca of 1.0 and reached a maximum value (~96%) at 0.67. However, the yield of Ca₂Fe₂O₅ decreased with the decrease in the Fe/Ca molar ratio when the Fe/Ca value was less than 0.67, and fell to ~87% at 0.33.

On the other hand, the Fe/Ca molar ratio in UA1-1 is 0.993 as shown in Table 3; therefore, the percentage of Ca₂Fe₂O₅ was estimated to be ~80% according to Hirabayashi's study [5]. However, Fe in UA1-1 was shared with Ca, Na, and Mg, and hence, the actual Fe/Ca ratio should be considerably smaller than 0.993, because the Fe/(Ca + Na + Mg) molar ratio is 0.666. Furthermore, the Na/Ca and Mg/Ca molar ratios are calculated as 0.207 and 0.284, respectively (Table 3). Thus, it can be assumed that Ca₂Fe₂O₅ occupies most of the Fe-containing species in UA1-1. In addition, the Mössbauer parameter values at 78 K of two sextets for UA1-1 show slight differences from those for Ca₂Fe₂O₅ reported previously [23], suggesting that small amounts of the other ferrites, CaFe₂O₄, β -NaFeO₂, and MgFe₂O₄ might be present in UA1-1.

As described above, it was claimed from our Mössbauer results that the primary iron-species might be Ca₂Fe₂O₅ in UA1-1. First, we tried to analyze the Mössbauer line-shape for UA1-2 at 78 K, assuming that there could be three components (one doublet and two sextets) all with parameter distributions as well as for UA1-1. However, on such an assumption, we could not obtain any satisfactory fitting result. As results of trial and error, it is found at last that the line shape is consist of one sextet with parameter distribution and one broaden singlet, as shown in Fig. 8 and Table 4.

This curve-fitting result is provisionally explained in the followings. All the peak-tops with the sextet line (*purple solid curve*) in UA1-2 spectrum occupy intermediate positions between those with the two sextet lines (*green and orange solid curves*) in UA1-1 spectrum, suggesting that Ca₂Fe₂O₅ is also present as a primary Fe-containing species in UA1-2. In addition, small amounts of the other ferrites are also expected in UA1-2.

As for UA2, the Fe/Ca molar ratio is estimated to be 0.372, suggesting that the primary Fe-containing species might be also $\text{Ca}_2\text{Fe}_2\text{O}_5$ same as in UA1-1 and UA1-2. Apparently, both the spectra at 78 K and 298 K consist of only a doublet, and their Mössbauer parameters, IS and QS , are explained as unresolved absorptions due to two Fe^{3+} sites (O_h and T_d) in $\text{Ca}_2\text{Fe}_2\text{O}_5$. No observation of magnetic hyperfine splitting even at 78 K indicate that the powder including whole $\text{Ca}_2\text{Fe}_2\text{O}_5$ in UA2 is much finer than that in UA1-1 or UA1-2 in terms of the superparamagnetic phenomenon. The Raman measurements suggest the presence of $\beta\text{-NaFeO}_2$, the Mössbauer spectrum of which shows magnetic hyperfine splitting even at room temperature [18, 19]. Here, however, no magnetic hyperfine splitting is observed in UA2. This probably indicates that $\beta\text{-NaFeO}_2$ is also included in powder finer than ~ 5 nm as well as $\text{Ca}_2\text{Fe}_2\text{O}_5$. Mössbauer absorption due to $\beta\text{-NaFeO}_2$ should appear to be a singlet because of its very small QS ; however, the absorption is expected not to be resolved from the primary doublet lines because of its weak intensity.

Mössbauer characterization suggests that the primary Fe-containing species is a calcium ferrite, $\text{Ca}_2\text{Fe}_2\text{O}_5$, in every ash sample.

Factors governing the color tone of *umoregi*-wood ash

Here, we comprehensively discuss the chemical components affecting on the color tone of the ash samples.

Based on the results obtained from Mössbauer and Raman characterization, it is confirmed that $\text{Ca}_2\text{Fe}_2\text{O}_5$ is the primary Fe-containing species in the three *umoregi*-wood ash samples. The mineral name of $\text{Ca}_2\text{Fe}_2\text{O}_5$ is brownmillerite, the several studies on which have reported that synthesized $\text{Ca}_2\text{Fe}_2\text{O}_5$ powder looked dark brown [26], brown [23], or dark red [7]. Consequently, we conclude that the dark-brown color of the UA1-1 ash sample is due mainly to $\text{Ca}_2\text{Fe}_2\text{O}_5$. It was reported that powder products of CaFe_2O_4 [27–29], MgFe_2O_4 [9, 30, 31], and NaFeO_2 [32] look reddish, brownish or blackish colors; therefore, small amounts of other ferrites, even if existing, presumably have little effect on the color of UA1-1.

As shown in Table 3, the Fe/Ca and Fe/(Na + Mg + Ca) molar ratios for UA1-2 are slightly smaller than those for UA1-1. This finding suggests that the ratio of $\text{Ca}_2\text{Fe}_2\text{O}_5$ to whole Fe-containing species for UA1-2 could be equal to or slightly larger than that for UA1-1. If so, UA1-2 should look dark brown like UA1-1; however, the color tone of UA1-2 is orange and much brighter than that of UA1-1. This indicates that the factors affecting the color tone of UA1-2 other than Fe-containing species need to be searched in terms of the whole components of the ash.

There are two important differences between the constituent elements in UA1-1 and UA1-2. Firstly, the molar percentage of Fe in UA1-2 is considerably smaller than that in UA1-1; therefore, the mass ratio of $\text{Ca}_2\text{Fe}_2\text{O}_5$ to whole ash for UA1-2 should also be smaller than that for UA1-1.

Secondly, S and P in UA1-2, especially S, are extremely abundant compared with UA1-1. Nevertheless, there is no positive evidence that iron sulfides were produced by the combustion of UW1-2. Most species of iron sulfide in powder turn black or dark gray; hence, any iron sulfides probably do not contribute to the orange color even if iron sulfides were generated in UA1-2. In contrast, all the sulfides of Na, Mg, and Ca are generally white or colorless. Furthermore, phosphorus sulfides, P_4S_3 , P_2S_5 , and P_4S_7 show light-yellow colors. Thus, phosphorus sulfides may contribute to orange color of UA1-2 if some of the sulfides are contained in the ash sample, although we have no experimental evidence that they are produced by burning UW1-2.

As described above, it is assumed that the UA2 ash sample has $\text{Ca}_2\text{Fe}_2\text{O}_5$ as the primary Fe-containing species like UA1-1 and UA1-2. However, UA2 shows a grayish-yellow color, which is entirely different from the other ash samples. Since the molar ratios of Fe to Na and Ca for UA2 are extremely small compared with those for UA1-1 and UA1-2 as shown in Table 3, oxides and/or carbonates of Na and Ca, which are white, should be present much more abundantly in UA2 than in UA1-1 and UA1-2. Accordingly, $\text{Ca}_2\text{Fe}_2\text{O}_5$ in UA2 is substantially diluted by oxides and/or carbonates of Na and Ca, so that UA2 appear to be grayish-yellow.

Calcium ferrite, $\text{Ca}_2\text{Fe}_2\text{O}_5$, plays a key role in determining the color tone of the *umoregi*-wood ash examined in this study. When an actual Fe/Ca molar ratio greatly exceeds 1.0, another calcium ferrite, CaFe_2O_4 , also presumably has a considerable effect on the color of *umoregi*-wood ash. However, CaFe_2O_4 appears as a brownish or blackish color as well as $\text{Ca}_2\text{Fe}_2\text{O}_5$, as described above. Thus, it is likely that the color of *umoregi*-wood ash is influenced by the molar percentage of Fe rather than the Fe/Ca molar ratio. The oxides and carbonates of Ca, Mg, and Na, would act to dilute the brown color due to ferrites, and the dilution effect increases in ash with a decrease in the molar percentage of Fe. Additionally, the particle size of ash also probably affects the color.

Conclusion

The present work provided positive evidence that $\text{Ca}_2\text{Fe}_2\text{O}_5$ can be produced by burning the Japanese cedar *umoregi*-wood excavated from Nikaho City in Japan, and confirmed that the brownish color tone of *umoregi*-wood ash examined in this study is due to the presence of $\text{Ca}_2\text{Fe}_2\text{O}_5$, the mineral

name of which is “brownmillerite”. It was concluded that the color tone of *umoregi*-wood ash mainly depends on the molar percentage of Fe in ash. Moreover, this characterization of Fe suggested that ash of *umoregi* wood usually contains several different kinds of ferrites.

The factors affecting the color of *umoregi*-wood ash are very complicated, and further studies on a wider range of *umoregi*-wood samples are required to classify the ash samples by their colors and to investigate the coloring mechanisms in detail.

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