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, Ca2Fe2O5.

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 umoregi-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
IS Isomer shift
QS Quadrupole splitting
LW Line width
H Internal magnetic field
T Tesla
Oh Octahedral
Td 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
complicated absorption line-shapes. We revealed in our previous report [1] that the umoregi-wood ash samples included calcium ferrites, CaFe$_2$O$_4$ and/or Ca$_2$Fe$_2$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 mountainside 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].

**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-Kα 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 Moss-Winn 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. 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

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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

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 UWX (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. Hiramabayashi have reported that the production ratio of CaFe$_2$O$_4$/Ca$_2$Fe$_2$O$_5$ would be dependent on the Fe/Ca ratio in the synthesis from Fe$_2$O$_3$ 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, Mg, 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$_2$O | 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$_2$O$_3$ | 0.30 (2) | 0.62 (3) | 0.20 (2) | 0.23 (1) |
| SiO$_2$ | 3.87 (3) | 2.15 (2) | 2.75 (3) | – |
| P$_2$O$_5$ | 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$_2$O | 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$_2$O$_3$ | 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 800–150 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’](image-url)
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\(_2\)O\(_4\) and/or Ca\(_2\)Fe\(_2\)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\(_2\)O\(_4\). 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

| Umoregi-wood ash samples | CaFe\(_2\)O\(_4\) | Ca\(_2\)Fe\(_2\)O\(_3\) | Ca\(_2\)Fe\(_2\)O\(_5\) | MgFe\(_2\)O\(_4\) | MgFe\(_2\)O\(_4\) | α-NaFeO\(_2\) | β-NaFeO\(_2\) |
|-------------------------|----------------|-----------------|-----------------|----------------|----------------|---------------|---------------|
| Patterns A and A′       | Raman shift (cm\(^{-1}\)) |                 |                 |                 |                 |               |               |
|                         | 210            | 213             | 212             | 217            | 217            | 220           |               |
|                         | 252            | 252             | 251             | 254            |                 |               |               |
|                         | 258            | 258             | 261             | 260            |                 |               |               |
|                         | 272*           | 288             | 292             | 290            | 305            |               |               |
|                         | 315            | 315             | 313             | 312            |                 |               |               |
|                         | 324            |                 |                 | 327            | 333            | 367           | 350           |
|                         | 383            | 379             | 380             | 379            |                 |               |               |
|                         |                | 395             | 393             | 395            |                 |               |               |
|                         |                | 428             | 428             | 427            |                 |               |               |
|                         | 457            | 476             |                 | 486            | 487            |               |               |
|                         | 558            | 558             | 558             | 555            | 554            | 550           | 566           |
|                         |                | 600             | 595             | 590            |                 |               |               |
|                         |                |                 |                 | 646            | 630            |               |               |
|                         | 678            | 693             | 667\(^{sh}\)    |                |                |               |               |
|                         | 710\(^{sh}\)   | 703             | 705             | 706            | 715            | 703           |               |

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

\(sh\) shoulder
that the three ash samples contain calcium ferrites, \( \text{CaFe}_2\text{O}_4 \) and/or \( \text{Ca}_2\text{Fe}_2\text{O}_5 \), as major components, and other ferrites, \( \text{MgFe}_2\text{O}_4 \) and \( \text{NaFeO}_2 \) 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, \( \text{O}_2\text{^2−} \), 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\(^{-1}\).

It is well known that the carbonates of metals belonging to Groups 1 and 2 have a Raman-active vibrational band at ~1080 cm\(^{-1}\); moreover, \( \text{Na}_2\text{O} \) and \( \text{CaO} \) readily react with \( \text{CO}_2 \) 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 \( \text{Na}_2\text{O}, \text{MgO}, \) and \( \text{CaO} \) other than their ferrites were produced more or less by the combustion of \( \text{umoregi} \) wood. In particular, UA2 probably include considerable amounts of \( \text{Na}_2\text{O} \) and \( \text{CaO} \) when the burning of UW2 was completed; therefore, the Raman bands observed at 1085–1073 cm\(^{-1}\) would be due to stretching vibrations of \( \text{CO}_3\text{^2−} \) ion.

Figure 6 depicts Raman spectra of MA and \( \text{CaCO}_3 \) 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 \( \text{CaCO}_3 \), indicating

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

|     | 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
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 20–60° 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 Ca$_2$Fe$_2$O$_5$ (green zone) and CaFe$_2$O$_4$ (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 samples, confirming the assignment of Raman band around 1078 cm$^{-1}$.
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.

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 Rübertsch [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 Ca$_2$Fe$_2$O$_5$. Moreover, the doublet line in the spectrum would also be assigned to Ca$_2$Fe$_2$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 Ca$_2$Fe$_2$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 Ca$_2$Fe$_2$O$_5$ and CaFe$_2$O$_4$ synthesized from Fe$_2$O$_3$ 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 Ca$_2$Fe$_2$O$_5$ decreased with increasing Fe/Ca ratio in the range from 0.67 to 2. The percentage of Ca$_2$Fe$_2$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)   | Ca$_2$Fe$_2$O$_5$ (Oh site) |
|        |          | Sextet-2 D         | 0.30 (1)  | 0.60 (3)  | 46.8 [1]| 0.51 (5)  | 31 (2)   | Ca$_2$Fe$_2$O$_5$ (Td 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; Oh octahedral; Td 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 Ca$_2$Fe$_2$O$_5$ 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 Ca$_2$Fe$_2$O$_5$ was estimated to be ~80% according to Hira-bayashi’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 Ca$_2$Fe$_2$O$_5$ 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 Ca$_2$Fe$_2$O$_5$ reported previously [23], suggesting that small amounts of the other ferrites, CaFe$_2$O$_4$, $\beta$-NaFeO$_2$, and MgFe$_2$O$_4$ might be present in UA1-1.

As described above, it was claimed from our Mössbauer results that the primary iron-species might be Ca$_2$Fe$_2$O$_5$ 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 Ca$_2$Fe$_2$O$_5$ 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.

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

| Ferrites   | Chemical state of iron | Type of splitting | Temp. (K) | $IS$ (mm/s) | $QS$ (mm/s) | $H$ (T) | Ref. |
|------------|------------------------|-------------------|-----------|-------------|-------------|---------|-----|
| $\alpha$-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] |
| $\beta$-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$^{3+}$ (O$_h$)      | Sextet            | 300       | 0.38        | 0.01        | 44.1    | [20] |
|             | Fe$^{3+}$ (T$_d$)      | Sextet            | 300       | 0.22        | 0.05        | 41.3    | [20] |
|             | Fe$^{3+}$ (O$_d$)      | Sextet-1          | 300       | 0.32        | –0.01       | 49.5    | [21] |
|             | Fe$^{3+}$ (O$_d$)      | Sextet-2          | 300       | 0.03        | 0.36        | 49.9    | [21] |
|             | Fe$^{3+}$ (T$_d$)      | Sextet            | 300       | 0.26        | –0.01       | 44.7    | [21] |
|             | Fe$^{3+}$ (O$_d$)      | Sextet-1          | 78        | 0.48        | 0.025       | 54.3    | [21] |
|             | Fe$^{3+}$ (O$_d$)      | Sextet-2          | 78        | 0.44        | –0.064      | 53.9    | [21] |
|             | Fe$^{3+}$ (T$_d$)      | Sextet            | 78        | 0.36        | 0.004       | 51.7    | [21] |
| CaFe$_2$O$_4$ | Fe$^{3+}$              | Sextet            | 78        | 0.48        | –0.031      | 46.2    | [5]  |
|             | Fe$^{3+}$              | Doublet           | 293       | 0.37        | 0.52        | –       | [5]  |
|             | 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] |
| Ca$_2$Fe$_2$O$_5$ | Fe$^{3+}$ (O$_d$)      | Sextet            | 77        | 0.46        | –0.52       | 54.0    | [23] |
|             | Fe$^{3+}$ (T$_d$)      | Sextet            | 77        | 0.27        | 0.71        | 47.5    | [23] |
|             | Fe$^{3+}$ (O$_d$)      | Sextet            | 300       | 0.37        | –0.52       | 50.4    | [23] |
|             | Fe$^{3+}$ (T$_d$)      | Sextet            | 300       | 0.18        | 0.72        | 42.9    | [23] |
|             | Fe$^{3+}$ (O$_d$)      | Sextet            | 293       | 0.35        | –0.52       | 50.7    | [5]  |
|             | Fe$^{3+}$ (T$_d$)      | Sextet            | 293       | 0.18        | 0.72        | 43.2    | [5]  |
|             | Fe$^{3+}$ (O$_d$)      | Sextet-1          | RT        | 0.36        | –0.54       | 51.5    | [24] |
|             | Fe$^{3+}$ (T$_d$)      | Sextet-1          | 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
As for UA2, the Fe/Ca molar ratio is estimated to be 0.372, suggesting that the primary Fe-containing species might be also Ca$_2$Fe$_2$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 ($O_1$ and $T_2$) in Ca$_2$Fe$_2$O$_5$. No observation of magnetic hyperfine splitting even at 78 K indicate that the powder including whole Ca$_2$Fe$_2$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 β-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 β-NaFeO$_2$ is also included in powder finer than ~5 nm as well as Ca$_2$Fe$_2$O$_5$. Mössbauer absorption due to β-NaFeO$_2$ should appear to be a singlet because of its very small $QS$; however, the absorption is expected not to be revolved from the primary doublet lines because of its weak intensity.

Mössbauer characterization suggests that the primary Fe-containing species is a calcium ferrite, Ca$_2$Fe$_2$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 Ca$_2$Fe$_2$O$_5$ is the primary Fe-containing species in the three umoregi-wood ash samples. The mineral name of Ca$_2$Fe$_2$O$_5$ is brownmillerite, the several studies on which have reported that synthesized Ca$_2$Fe$_2$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 Ca$_2$Fe$_2$O$_5$. It was reported that powder products of Ca$_2$Fe$_2$O$_5$ [27–29], MgFe$_2$O$_4$ [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 Ca$_2$Fe$_2$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 Ca$_2$Fe$_2$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$_4$S$_3$, P$_2$S$_5$, and P$_4$S$_7$, 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 Ca$_2$Fe$_2$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, Ca$_2$Fe$_2$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, Ca$_2$Fe$_2$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$_2$O$_4$, also presumably has a considerable effect on the color of umoregi-wood ash. However, CaFe$_2$O$_4$ appears as a brownish or blackish color as well as Ca$_2$Fe$_2$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 Ca$_2$Fe$_2$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 Ca$_2$Fe$_2$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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