Mössbauer Spectroscopic Characterization of Iron in Ashes Made from the Ancient Woods Excavated in the Foothills of Mt. Chokai

Shigeru Yamauchi,^{a,*} Yasuji Kurimoto^a and Yoichi Sakai^b

^aInstitute of Wood Technology, Akita Prefectural University, Noshiro, Akita 016-0876, Japan

^bDepartment of Chemistry, Daido University, Nagoya, Aichi 457-8530, Japan

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The chemical states of iron in ashes made from umoregi woods excavated in the foothills of Mt. Chokai in 2015, were characterized by using ⁵⁷Fe-Mössbauer spectroscopy and complementary analytical techniques. Four kinds of ancient trees, Japanese oak, Japanese chestnut, Japanese cedar, and Japanese zelkova were burned at 650-710 °C. The ashes showed brown, reddish brown, or yellowish brown colors. Elements (> Na) in the ashes were determined by X-ray fluorescence spectrometry using a compact spectrometer. ⁵⁷Fe-Mössbauer spectra of the ashes and soil from the excavation site were recorded at 293 and 78 K. Raman scattering of the ashes was measured in the 1200-900 cm⁻¹ range. It was confirmed that calcium ferrite, Ca₂Fe₂O₅, was formed in the three ashes and its formation rate depended on the Fe/Ca ratio. Mössbauer spectra suggested that CaFe₂O₄ and/or similar iron oxides were contained in the two ashes. In the case of Fe/Ca > 2, sextet components assigned to α-Fe₂O₃ were also detected in the Mössbauer spectra. It was proposed that the color tone of the ashes was affected by Fe oxides. Mössbauer spectra suggested that some parts of Ca₂Fe₂O₅ formed in the ashes were such a fine particle that superparamagnetic phenomena were observable.

1. Introduction

The Japanese terms “umoregi” and “jindai-boku” refer to ancient trees that are buried or submerged. More specifically, these terms imply that the ancient trees were buried or submerged by natural phenomena such as a landslide or ground subsidence more than several hundred years ago, after which they have not completely decomposed because they have been in anoxic conditions. However, these Japanese terms do not belong to the scientific vocabulary and possess a degree of ambiguity. Although ancient buried trees are generally classified as “umoregi” or “jindai-boku” even if it is partially decomposed with slight carbonization, we defined “umoregi wood” here as the stem of an ancient buried tree that contains neither carbonized nor petrified components.

Most umoregi woods maintain enough strength to be used as construction materials, and they exhibit dark brown or black colors depending on the chemical reactions of their components. Thus, in Japan, umoregi wood is much more expensive than ordinary wood because of its dignified hue and wood grain pattern. It is recognized that the hue is due to the compounds consisting of polyphenols and Fe accumulated in umoregi wood. It is also known that ash made from umoregi wood, showing brown, reddish brown, or deep yellow colors, is regarded as top-quality incense burner ash for the Japanese tea ceremony (Sado) since at least the 15th century.¹

Few scientific reports, however, have been available on umoregi wood until recently. In the last decade, Narita and Yatagai have published several studies focusing on the organic components contained in umoregi woods excavated in Japan.²⁻⁶ Fe is enriched, to varying degrees, in umoregi wood,⁶ but no studies are available on the chemical state of Fe in umoregi wood except for two reports using ⁵⁷Fe-Mössbauer spectroscopy.^{7,8} In addition, there is little scientific information about the ash made from umoregi wood.

The aim of our study is to obtain the sufficient information on Fe in umoregi wood ash to be able to discuss its chemical states because enrichment of Fe is a common feature in umoregi wood. In this study, we explored the ashes using ⁵⁷Fe-Mössbauer spectroscopy and complementary analytical techniques, and investigated the relevance of Fe species to physical properties such as color and particle size.

2. Experimental

2.1. Umoregi wood and soil samples. The sample ashes were made from umoregi woods excavated from Nikaho City in Akita Prefecture, Japan, located to the north-west of Mt. Chokai (Figure 1) in 2015. Umoregi woods were the stems of trees buried by large-scale landslides from Mt. Chokai ca. 2500 years ago.^{9,10} The material umoregi woods were Japanese oak (*Quercus serrata* or *Quercus crispula*), Japanese chestnut (*Castanea crenata*), Japanese cedar (*Cryptomeria japonica*), and Japanese zelkova (*Zelkova serrata*). “Japanese” is herein-after abbreviated as “Jpn.” such as Jpn. cedar. These umoregi woods were divided into two groups based on their color. One group looked brown or dark green, and the other group showed black. The former contained Jpn. cedar and Jpn. zelkova umoregi woods, and the latter, Jpn. chestnut and Jpn. oak umoregi woods.

After removing soil and bark, the umoregi woods were dried indoors at ambient temperature for several months, and then cut into ca. 5 cm square blocks. Soil was collected at the excavation site of a Jpn. zelkova umoregi tree. The soil was ground in a mortar after air-drying.

2.2. Aqueous solution including Fe²⁺ and Fe³⁺. Aqueous Fe²⁺ and Fe³⁺ solution was prepared using Fe(NH₄)₂(SO₄)₂ · 6H₂O and FeNH₄(SO₄)₂ · 12H₂O. Fe²⁺/Fe³⁺ ratio and total Fe concentration in this solution were 3/7 and 2 w/w%, respectively. Special-grade Fe compounds were purchased from Wako Pure Chemical Industries, Ltd. and used without further purification.

*Corresponding author. E-mail: sigeru@iwt.akita-pu.ac.jp, Fax: +81-185-52-6924

Figure 1. The locations of excavation sites of the umoregi trees in this study and the summit of Mt. Chokai.

2.3. Fe-impregnated raw wood samples. Raw woods of Jpn. oak (*Quercus crispula*), Jpn. chestnut, Jpn. cedar, and Jpn. zelkova were cut into *ca.* 5 cm square blocks and dried at 105 °C for 24 hours in an electric oven. After overall immersion of the blocks in the aqueous Fe^{2+} and Fe^{3+} solution, the vessel holding the solution and blocks was placed in a vacuum desiccator. The internal pressure was reduced using a water-jet pump until it was held constant. The desiccator was sealed for 24 hours. The blocks were taken out from the solution and subsequently dried in air for more than 3 days.

2.4. Ashing method. The blocks of umoregi woods and Fe-impregnated raw woods were dried at 105 °C for 24 hours. Ashes were obtained by firing the dried blocks in an open-type electric furnace maintained at 600 °C for 24 hours. The internal temperature of the block was recorded using a thermocouple every 20 seconds until the internal temperature of the furnace reached to 50 °C. The ashes obtained by heat treatment were subjected to analytical techniques without grinding. Ash content was calculated by dividing the mass of the ash by the mass of the oven-dried wood before heat treatment.

2.5. X-ray fluorescence spectrometry. Metal elements with atomic numbers greater than 11 in the ash and soil samples were detected by X-ray fluorescence spectrometry using a spectrometer (MESA-500, Horiba, Ltd.). Ash (0.06–0.11 g) and soil (~ 2.3 g) powder were placed in a cylindrical Teflon cell with a diameter of 20 mm. A sample chamber was held in a vacuum during a measurement. X-ray irradiation was performed at ambient temperature and the total measurement time was 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 calculated using a standardless fundamental parameter method^{11, 12} from characteristic X-ray intensities.

2.6. Mössbauer spectroscopy. ^{57}Fe -Mössbauer measurements were performed in a conventional transmission mode on a Mössbauer spectrometer (Topologic System Inc. Model-222) with a $^{57}\text{Co}(\text{Rh})$ source (925 MBq). Measurement temperatures were 78 and 293 K regulated using an Oxford cryostat DN-1726 with a temperature controller ITC-601. Curve fitting of the Mössbauer spectra was performed by a nonlinear least-squares method using the MossWinn 4.0Pre program, assuming that all spectra were composed of Lorentzian-shaped peaks. The isomer shift and Doppler velocity scale were calibrated with respect to the sextet of $\alpha\text{-Fe}$ at room temperature.

The sample thicknesses of the umoregi ashes, the ash of Fe-impregnated Jpn. cedar wood and soil powder were *ca.* 15 mg/cm^2 , *ca.* 15 mg/cm^2 , and *ca.* 30 mg/cm^2 , respectively.

2.7. Raman spectroscopy. Raman scattering by umoregi wood ashes was recorded at room temperature using a Renishaw Raman Imaging Microscope System 1000 connected to an air-cooled CCD detector. A He-Ne laser (632.8 nm) was used as an excitation source at a power of *ca.* 20 mW. Back-scattered Raman signals were collected through a microscope and edge filters in the range of 1200–900 cm^{-1} with a spectral resolution of about 2 cm^{-1} . The sample powder was spread thinly on a slide glass. The Raman measurements were repeated at more than ten points for each sample. Wavenumber calibration was carried out using the 520 cm^{-1} line of a silicon wafer and the 1332 cm^{-1} line of diamond.

3. Results and Discussion

3.1. Ashing of the ancient woods. Figure 2 shows photographs of the ashes made from four kinds of umoregi wood and Fe-impregnated Jpn. cedar wood. Fe-impregnated Jpn. cedar wood ash exhibits a vivid red color. Its appearance allows us to predict that it contains substantial amounts of $\alpha\text{-Fe}_2\text{O}_3$. Other three ashes prepared from Jpn. oak, Jpn. chestnut, and Jpn. zelkova wood impregnated with Fe also showed a red color, although their shades were subtly different to one another. On the contrary, the umoregi wood ashes show yellowish brown or brown tones although Jpn. oak umoregi wood ash has a faintly reddish tone.

A plot of internal temperature of Jpn. zelkova umoregi wood against time during the heat treatment is demonstrated in Fig. 3. It is known that the ignition temperature range of wood is relatively wide (350–490 °C), and the ignition temperatures of four umoregi wood species are within the range of 430–480 °C.¹³ Thus, the temperature curve indicates that the internal temperature of Jpn. zelkova umoregi wood exceeded 600 °C and reached ~ 700 °C by combustion of itself. Similar

Figure 2. Four kinds of umoregi wood ashes and Fe-impregnated Jpn. cedar wood ash. a: Jpn. oak umoregi wood ash, b: Jpn. chestnut umoregi wood ash, c: Jpn. cedar umoregi wood ash, d: Jpn. zelkova umoregi wood ash, e: Fe-impregnated Jpn. cedar wood ash.

Figure 3. Internal temperature curve of a Jpn. zelkova wood block.

temperature curves were obtained with respect to the other umoregi woods. The maximum temperatures during the heat treatment of Jpn. oak, Jpn. chestnut, Jpn. cedar, and Jpn. zelkova were 707 °C, 653 °C, 676 °C, and 697 °C, respectively.

As listed in Table 1, the ash content in the umoregi woods were in the range from 0.6% to 2.8%. This indicates that the organic components of umoregi wood were decomposed completely and the chemical states of Fe changed drastically by ashing.

3.2. Elements in ashes and ash contents. Table 1 contains a summary of the relative mass percentages of Mg to Fe in umoregi wood ashes, Fe-impregnated Jpn. cedar wood ash, and the soil. Several elements heavier than Fe such as Ni, Cu, Zn, and Sr, were detected in a few samples, but their mass percentages were lower than 0.2%. The molar ratio of Fe/Ca and ash content are listed in Table 1 together.

For all the umoregi wood ashes, the primary and secondary elements were Fe and Ca, respectively, and the total mass percentages of them were over 80%. Other major elements included Mg and Si. It should be noted that the amount of sulfur in Jpn. oak umoregi wood ash was much larger than that of other umoregi wood ashes. Japanese raw wood contains Ca and K as major inorganic elements regardless of tree species, whereas Fe is a trace element and its amount is less than those of Mn and Cu.¹⁴ Therefore, it appears that the elemental composition of umoregi wood ashes was predominantly due to the

Figure 4. Mössbauer spectrum at 293 K of soil collected at the excavation site of a Jpn. zelkova umoregi tree. Blue and red doublet curves indicate Fe²⁺ and Fe³⁺ components, respectively.

elemental compositions of the soil at the excavation point and the raw wood before burial around 2500 years ago. In addition, the molar ratios Fe/K and Fe/Al in umoregi wood ashes were much larger than those in the soil whereas molar ratios Fe/Si with umoregi wood ashes were significantly smaller compared with the soil, suggesting that inorganic elements exhibit different behaviors in their transfer from the soil to the wood and vice versa.

3.3. Mössbauer spectra. Figure 4 depicts a ⁵⁷Fe-Mössbauer spectrum at 293 K of the soil collected at the excavation site of Jpn. zelkova umoregi tree. The gray soil was a clay-like substance and included a considerable amount of water when it was sampled, but its viscosity disappeared completely upon drying in air. The spectrum was only composed of two symmetrical doublets, and their Mössbauer parameters are summarized in Table 2. It was concluded that doublets 1 (blue curve) and 2 (red curve) were assigned to high-spin Fe²⁺ and high-spin Fe³⁺, respectively. The area ratio of Fe²⁺/Fe³⁺ was approximately 3/7. The IS value of doublet 1 indicated that the atoms in the primary coordination sphere of Fe²⁺ formed an octahedron, whereas it was difficult to determine based on the IS and QS values of doublet 2 whether Fe³⁺ was placed at the center of tetrahedral or octahedral structures. However, it was reported that Fe³⁺ in silicate or aluminate glass species forms a

TABLE 1: Relative mass percentage of elements in ashes and soil

Sample	Element wt%									Molar ratio, Fe/Ca	Ash content, %
	Mg	Al	Si	P	S	K	Ca	Mn	Fe		
Jpn. oak umoregi wood ash	3.6	1.1	1.8	-	8.0	0.4	19.5	2.0	63.3	2.3	1.31
Jpn. chestnut umoregi wood ash	5.3	0.3	3.5	-	0.2	1.2	30.9	0.4	57.5	1.3	2.73
Jpn. cedar umoregi wood ash	8.9	0.6	1.7	-	0.4	1.0	44.5	1.2	41.6	0.7	0.62
Jpn. zelkova umoregi wood ash	9.9	1.6	4.8	0.1	0.8	0.8	46.0	0.3	35.6	0.6	1.38
Fe-impregnated Jpn. cedar wood ash	-	0.7	0.4	0.1	3.2	1.5	2.9	-	91.1	15	3.24
Soil*	2.2	11.6	61.5	-	1.2	4.5	4.2	0.2	13.3	2.3	-

*gray soil at the excavation point of Jpn. zelkova umoregi

TABLE 2: Mössbauer parameters of soil sampled at excavation point of Jpn. zelkova umoregi tree

	IS, mm s ⁻¹	QS, mm s ⁻¹	LW, mm s ⁻¹
Doublet 1	1.13(1)	2.59(1)	0.41(2)
Doublet 2	0.34(1)	0.63(1)	0.51(2)

Figure 5. Mössbauer spectrum at 293 K of Fe-impregnated Jpn. cedar wood ash.

tetrahedral structure.^{15, 16} The soil contained Al and Si as major elements as shown in Table 1. Therefore, Fe³⁺ in the soil was likely to be located at the center of tetrahedral structures.

The Mössbauer spectrum at 293 K of Fe-impregnated Jpn. cedar wood ash is displayed in Figure 5 and was composed of a sextet (IS: 0.372(1) mm/s, QS: -0.207(1) mm/s, H: 51.535(3) T, LW: 0.292(1) mm/s). These parameters were completely identical with those of α -Fe₂O₃.¹⁷ If Mg or Ca included in Fe-impregnated woods is comparable to Fe, it can be expected that the Mössbauer absorptions attributed to magnesium ferrites or calcium ferrites are observed. However, such ferrites were not observable in the Mössbauer spectrum because Mg was negligible and Fe/Ca ratio was substantially large. The Mössbauer spectra at 293 K of the other three Fe-impregnated wood ashes also showed only a sextet whose parameters had no significant differences from those of α -Fe₂O₃. Thus, almost all of the Fe species produced by ashing of Fe-impregnated woods were found to be α -Fe₂O₃, which exhibits no characteristics of nanoparticles. This suggested that Fe compounds precipitated as microcrystals in the woods by drying.

Figure 6 illustrates the Mössbauer spectra at 293 K of umoregi wood ashes. All the spectra showed an apparent doublet whose center was placed in the range of 0.3–0.4 mm/s. Except for Jpn. cedar umoregi wood ash, the Mössbauer spectra of other umoregi wood ashes exhibited obvious magnetic hyperfine structures. One and two sextets were observed in the spectra of Jpn. oak and Jpn. zelkova umoregi wood ashes, respectively and their Mössbauer parameters were determined based on curve-fitting analysis.

The parameters of umoregi wood ashes are given in Table 3. It was expected that calcium ferrites would have formed, because umoregi wood ashes were enriched with Fe and Ca as described above. Thus, the Mössbauer parameters of CaFe₂O₄ and Ca₂Fe₂O₅ reported previously^{18, 19} are shown together for

Figure 6. Mössbauer spectra at 293 K of umoregi wood ashes, a: Jpn. oak umoregi wood ash, b: Jpn. chestnut umoregi wood ash, c: Jpn. cedar umoregi wood ash, d: Jpn. zelkova umoregi wood ash. Orange and green straight lines indicate Fe³⁺ in *Oh* and *Td* sites of Ca₂Fe₂O₅, respectively (cf. TABLE 3).

comparison. Brownmillerite type calcium ferrite, Ca₂Fe₂O₅, has a tetrahedral and octahedral site in terms of Fe³⁺.

It was concluded that the sextet observed in the spectrum of Jpn. oak umoregi wood ash was attributed to bulky particles of α -Fe₂O₃ because its Mössbauer parameters agree well with those of Fe-impregnated Jpn. cedar wood ash described above. The parameters of sextets 1 and 2 in the spectrum of Jpn. zelkova umoregi wood ash are close to those of Fe³⁺ (*Oh*) and Fe³⁺ (*Td*) in Ca₂Fe₂O₅, respectively, suggesting the formation of brownmillerite type calcium ferrite by ashing of Jpn. zelkova umoregi wood. Line widths of the two sextets were much larger than that of the sextet of Jpn. oak umoregi wood ash. This broadening was possibly caused by structural distortion due to the influence of Al, Mg, and K impurities.

The positions of the two sextets reported by Randhawa and Sweet¹⁸ are shown in Fig. 6 using colored lines, with orange and green straight lines corresponding to Fe³⁺ (*Oh*) and Fe³⁺ (*Td*), respectively. Thus, these lines indicated that the considerable yield of Fe was distributed as brownmillerite type calcium ferrite (Ca₂Fe₂O₅) in Jpn. chestnut umoregi wood ash. Furthermore, it seemed likely that weak absorptions assigned to Ca₂Fe₂O₅ appeared in the Mössbauer spectrum of Jpn. cedar umoregi wood ash.

Hirabayashi et al. reported that the yields of Ca₂Fe₂O₅ and CaFe₂O₄ depended upon the Fe/Ca ratio in synthesis using Fe₂O₃ and CaO at 1000 °C.¹⁹ According to their study, most of Fe species are Ca₂Fe₂O₅ when the Fe/Ca ratio is less than 1.0, and the two calcium ferrites have the almost same production rate when the Fe/Ca ratio is about 1.3. Moreover, more than 85 % of iron forms CaFe₂O₄ when the Fe/Ca ratio exceeds 2.0.

It was expected that the major Fe species contained in Jpn. cedar, and Jpn. zelkova umoregi wood ash would be Ca₂Fe₂O₅

TABLE 3: Mössbauer parameters of iron species in umoregi wood ashes and calcium ferrites

Sample	Chemical sate of iron	Type of line-shape	Temp., K	IS, mm s ⁻¹	QS, mm s ⁻¹	H, T	LW, mm s ⁻¹	Ref.
Jpn. oak umoregi wood ash	-	Sextet*	293	0.372(5)	-0.22(1)	51.41(4)	0.27(1)	-
Jpn. zelkova umoregi wood ash	-	Doublet	293	0.317(5)	0.798(9)	-	0.82(2)	-
	-	Sextet**	293	0.35(1)	-0.44(3)	49.5(1)	0.72(3)	-
	-	Sextet***	293	0.16(1)	0.66(2)	41.5(9)	0.72(3)	-
CaFe ₂ O ₄	Fe ³⁺	Doublet	293	0.37	0.52	-	-	19
	Fe ³⁺	Sextet	78	0.48	-0.031	46	-	19
	Fe ³⁺ (<i>O_h</i>)	Sextet	300	0.37	-0.52	50.4	-	18
Ca ₂ Fe ₂ O ₅	Fe ³⁺ (<i>T_d</i>)	Sextet	300	0.18	0.72	42.9	-	18
	Fe ³⁺ (<i>O_h</i>)	Sextet	77	0.46	-0.52	54.0	-	18
	Fe ³⁺ (<i>T_d</i>)	Sextet	77	0.27	0.71	47.5	-	18
	Fe ³⁺ (<i>O_h</i>)	Sextet	293	0.35	-0.52	50.7	-	19
	Fe ³⁺ (<i>T_d</i>)	Sextet	293	0.18	0.72	43.2	-	19

*red curve, **orange curve (sextet 1), ***green curve (sextet 2)

assuming that the yields of Ca₂Fe₂O₅ and CaFe₂O₄ reported by Hirabayashi et al. were applicable to the umoregi wood ashes, because the Fe/Ca ratios of Jpn. cedar, and Jpn. zelkova umoregi wood ash were 0.7, and 0.6, respectively. In addition, it can be presumed that Jpn. chestnut umoregi wood ash (Fe/Ca = 1.3) contained CaFe₂O₄ as well as Ca₂Fe₂O₅, and CaFe₂O₄ was included in Jpn. oak umoregi wood ash (Fe/Ca = 2.3) as a major Fe species. Magnetic hyperfine structures will not appear in Mössbauer absorptions due to CaFe₂O₄ at 293 K because the Néel temperature of CaFe₂O₄ is around 190 K,¹⁹ and the absorptions are likely to appear as a doublet.

Figure 7 shows the Mössbauer spectra at 78 K of the four kinds of umoregi wood ashes. In the figure, the positions of a sextet assigned to CaFe₂O₄¹⁹ were marked with blue straight lines in addition to those of the sextets at 77 K of Ca₂Fe₂O₅.¹⁸ Drastic changes because of cooling down to 78 K were observed in the Mössbauer spectra of Jpn. oak and Jpn. chestnut umoregi wood ashes. For Jpn. oak umoregi wood ash, the doublet disappeared almost entirely, and the asymmetric and broad sextet absorptions appeared dramatically. Although this apparent sextet was likely to correspond to more than one Fe species, it would not substantially contain absorptions attributed to Ca₂Fe₂O₅. In addition, there was incomplete agreement between the six blue lines and sextet absorption bottom positions. However, these differences would not be negative evidence for the formation of CaFe₂O₄. The asymmetric line shape of Mössbauer absorptions allowed us to speculate that CaFe₂O₄ and the ferrites having similar structures to CaFe₂O₄, such as MgFe₂O₄ and Mg_{1-x}Ca_xFe₂O₄,²⁰ are contained in the ash, because Mg is a major element in all ashes as shown in Table 1. Besides, the magnetic hyperfine structures (red straight line) assigned to α-Fe₂O₃ were also observed obviously.

The Mössbauer spectrum of Jpn. chestnut umoregi wood ash was likely to have magnetic hyperfine structures other than those assigned to Ca₂Fe₂O₅. On the basis of the line shape of absorptions, it may be expected that the considerable amounts of CaFe₂O₄ and similar ferrites showing magnetic hyperfine structures at 78 K are included as well as Jpn. oak umoregi wood ash.

On the contrary, no sextet components other than those due to Ca₂Fe₂O₅ were confirmed in the Mössbauer spectra of Jpn. cedar and Jpn. zelkova umoregi wood ashes, although the sextets due to Ca₂Fe₂O₅ increased relative to the doublet. A possible explanation for the increase in intensity of the sextets at 78 K in the spectra of Jpn. cedar and Jpn. zelkova umoregi wood

Figure 7. Mössbauer spectra at 78 K of umoregi wood ashes. a: Jpn. oak umoregi wood ash, b: Jpn. chestnut umoregi wood ash, c: Jpn. cedar umoregi wood ash, d: Jpn. zelkova umoregi wood ash. Orange and green straight lines indicate Fe³⁺ in *O_h* and *T_d* sites of Ca₂Fe₂O₅, respectively (cf. TABLE 3). Red and blue straight lines indicate Fe³⁺ in α-Fe₂O₃ and CaFe₂O₄, respectively (cf. TABLE 3).

ashes was nanoparticles having a magnetic transition point in the temperature range from 78 K to 293 K. Moreover, Jpn. cedar umoregi wood ash maintained the high intensity doublet even at 78 K, suggesting that its particle size was significantly smaller than that of Jpn. zelkova umoregi wood ash. However, further experimental data, such as TEM imaging, will be necessary to confirm this explanation.

These results indicated that the reddish tone observed over Jpn. oak umoregi wood ash was due to α - Fe_2O_3 and the yellowish brown tones of other umoregi wood ashes were mainly due to the calcium ferrite $\text{Ca}_2\text{Fe}_2\text{O}_5$. Furthermore, it is generally believed that umoregi wood ash has qualities of fineness and smoothness. The doublet observed in the Mössbauer spectra at 78 K could be scientific evidence of these characteristics of umoregi wood ash, if it corresponds to superparamagnetic components, suggesting that Fe dispersed homogeneously in the Jpn. cedar and Jpn. zelkova umoregi woods. Mössbauer measurements at lower temperatures may be required to discuss the ferrites in the umoregi wood ashes in more detail.

3.4. Raman spectra. Figure 8 shows Raman spectra of umoregi wood ashes in the range from 1200 to 900 cm^{-1} . For Jpn. oak umoregi wood ash, a Raman band was detected at 1085 cm^{-1} on some measuring points (Fig. 8a), whereas most of the spectra had a band at 1015 cm^{-1} (Fig. 8b). Typical Raman spectra of Jpn. chestnut umoregi wood ash exhibited nothing in this region but a weak band was observed rarely at 1085 cm^{-1} as shown in Fig. 8c. Raman spectra of Jpn. cedar and Jpn. zelkova umoregi wood ashes always showed a band clearly at 1085 cm^{-1} .

Hirabayashi et al. reported that the Raman spectra of calcium ferrites synthesized from Fe_2O_3 and CaO ($\text{Fe}/\text{Ca}=1$ and 2) at 1000 °C showed a band at 1093 cm^{-1} assigned to a stretching mode of a superoxide radical O_2^- and another band was found at 1022 cm^{-1} in the case of $\text{Fe}/\text{Ca}=2$.²¹ The frequency of these bands seemed to be readily variable over a relatively wide range.²²⁻²⁵ The Fe/Ca ratio is 2.3 for Jpn. oak umoregi wood ash showing the two Raman bands. Assuming that the Raman bands at 1085 and 1015 cm^{-1} correspond to those at 1093 and 1022 cm^{-1} reported by Hirabayashi,²¹ the Raman spectra were further evidence for the formation of $\text{Ca}_2\text{Fe}_2\text{O}_5$ by ashing of umoregi woods.

4. Conclusions.

In the present study of the chemical states of iron in ashes made from umoregi woods excavated in the foothills of Mt. Chokai, the important findings were obtained from Mössbauer spectroscopy and complementary analytical techniques. It was confirmed that α - Fe_2O_3 was included in Jpn. oak umoregi wood ash ($\text{Fe}/\text{Ca} = 2.3$). Moreover, it was revealed that Jpn. chestnut ($\text{Fe}/\text{Ca} = 1.3$), J. cedar ($\text{Fe}/\text{Ca} = 0.7$) and Jpn. zelkova ($\text{Fe}/\text{Ca} = 0.6$) umoregi wood ashes contained $\text{Ca}_2\text{Fe}_2\text{O}_5$. Our Mössbauer data proposed that CaFe_2O_4 and/or similar ferrites were made by ashing of Jpn. oak and Jpn. chestnut umoregi wood. The formation rate of these Fe oxides mainly depends on Fe/Ca ratio in ashes. It was proposed that the Fe oxides significantly affected the color tone of umoregi wood ash. Furthermore, the Mössbauer spectra suggested that the ashes contained some parts of $\text{Ca}_2\text{Fe}_2\text{O}_5$ as such fine particles that a superparamagnetic effect appears.

We hope that our analytical method described here is applicable to other umoregi wood ashes.

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Figure 8. Raman spectra at room temperature of umoregi wood ashes. a: Jpn. oak umoregi wood ash, b: Jpn. oak umoregi wood ash, c: Jpn. chestnut umoregi wood ash, d: Jpn. cedar umoregi wood ash, e: Jpn. zelkova umoregi wood ash.

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