

NOTE

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Iron speciation in iron-rich wood by Mössbauer spectroscopy

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Abstract Several iron-rich wood samples were investigated using Mössbauer spectroscopy to obtain information on the chemical state of the iron species contained in them. The Mössbauer spectrum of Japanese cedar (*Cryptomeria japonica* D. Don) wood containing iron species that originated from rusted nails exhibited a symmetrical doublet from a high-spin Fe(III) species, which is expected to be γ -FeOOH (lepidocrocite). Mössbauer absorption attributable to high-spin Fe(III) was observed for ancient buried wood samples of both Japanese cedar and Japanese cypress (*Chamaecyparis obtusa* Endlicher). Moreover, Mössbauer measurement indicated that the ancient buried Japanese cedar also possessed high-spin Fe(II) species.

Key words Speciation · Mössbauer spectroscopy · Iron · Ancient buried wood · Rust

Introduction

In general, metal elements contained in wood have little or no effect on the physical properties of the wood because the amounts of metals in untreated wood are very small. Thus, researchers of wood and wood-based materials have not shown much interest in heavy metal elements in wood. Heavy metals in wood have seldom been chemically analyzed unless the wood has been treated by a preservative or paint containing metals. Almost all chemical analyses of metals in wood are determinations of metal concentration. Analytical methods using an electron microscope are often adopted to examine metal elements in wood, and these microscopic analytical procedures for determination of the

distribution of metals through wood cell walls also constitute quantitative analysis.

In contrast, “speciation analysis” can investigate the physical or chemical state of components in a substance. However, there have been few speciation analytical studies of metal elements in wood. Although untreated wood contains only very small quantities of metal elements, these metal concentrations often greatly increase in response to some treatment or environmental influence. For example, the iron concentration in wood in the immediate vicinity of junctures would rapidly increase upon the development of corrosion of the iron connectors such as nails and bolts. Moreover, ancient wood (Umoregi), buried in the ground for a long period, often contains iron and other metals at much higher concentrations.¹ A number of studies have demonstrated that there are obvious differences in organic constituents between ancient buried wood and raw wood,^{1–6} whereas no report on the chemical state of metal components in ancient buried wood has been published. It should be possible to explain in more detail the mechanisms of chemical changes of organic components in ancient buried wood if we can obtain further insights into the chemical state of heavy metal ions, especially iron, because an iron ion has two stable oxidation states [Fe(II) and Fe(III)] and frequently plays an important role in redox reactions.

Mössbauer spectroscopy is of fundamental importance in that it provides information on the chemical state of Mössbauer elements, ⁵⁷Fe, ¹¹⁹Sn, and ¹⁵¹Eu, among others. Above all, ⁵⁷Fe is the most popular Mössbauer isotope, and ⁵⁷Fe Mössbauer spectroscopy is widely used in various fields of science. The effect is observable only in the solid state, but the Mössbauer parameters of chemical isomer shift (IS) and electric quadrupole splitting (QS) give us characteristics of iron such as oxidation number, spin state, and coordination number. Recoilless fraction is an important factor determining Mössbauer absorption intensity, depending upon the physical state of the matrix including Mössbauer elements. If there is little difference in recoilless fraction between two chemical species of a Mössbauer element, the concentration ratio of the species is equivalent to their Mössbauer absorption intensity ratio. In addition, magnetic

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hyperfine splitting is observed in a Mössbauer spectrum when the iron atom exists in magnetic material.

Thus, Mössbauer spectroscopy is a powerful technique for deriving chemical information concerning the surroundings of iron atoms. However, this technique has never been utilized for characterizing iron compounds in wood, although a few environmental studies on the iron-containing fine particles deposited on the bark of trees have been published.^{7,8}

The present article attempts to demonstrate that ⁵⁷Fe Mössbauer spectroscopy is a useful tool for iron speciation in iron-rich wood. We measured the Mössbauer spectra of iron-rich wood samples, namely, Japanese cedar (*Cryptomeria japonica* D. Don) wood containing iron from rusted nails and two kinds of ancient buried wood. Here we discuss the chemical state of iron species on the basis of the Mössbauer parameters.

Materials and methods

Wood samples

Iron nails were driven into heartwood blocks taken from a 70-year-old Japanese cedar planted in Akita Prefecture. The blocks were kept at 25°C and 90% relative humidity for more than 30 months in an environmental chamber. The parts of the wood block close to the rusted nails, which had turned dark brown, were reduced to powder after a week of air-drying. The wood powder was molded into a small disk, taking care that the disk sample did not contain any part within 1.5 mm from the rusted nails to avoid direct contamination by rust powder from the nails. The Mössbauer measurements were carried out on this disk. Reference powder samples were prepared from iron and Japanese cedar wood for X-ray fluorescence analysis.

Two kinds of ancient buried wood were characterized using the Mössbauer technique. The first was ancient buried Japanese cedar that was exposed in the foothills of Mt. Chokai in the south of Akita Prefecture. This ancient Japanese cedar wood is considered to have been buried in volcanic ash about 2,500 years ago.^{9,10} The sapwood of the ancient Japanese cedar was reduced to powder and made into a disk. The other wood sample was ancient buried Japanese cypress (*Chamaecyparis obtusa* Endlicher) wood that was found on the Izu Peninsula in Shizuoka Prefecture. This wood was estimated to have remained in the ground for about 3,000 years.¹¹

Measurements and curve-fitting of Mössbauer spectra

The ⁵⁷Fe Mössbauer spectra were measured at room temperature in transmission mode using a Topologic Systems MD-222B Mössbauer spectrometer against 370 MBq ⁵⁷Co in rhodium (Rh). Curve-fitting of the Mössbauer spectra was performed by a nonlinear least squares method using the MossWinn 3.0i program, assuming that all spectra were composed of Lorentzian-shaped peaks. The Mössbauer

parameters of IS, QS, and line width (LW) were calibrated with respect to the sextet of α -Fe at room temperature.

Sample thicknesses of the Japanese cedar wood discolored by corrosion of iron nails, the ancient buried Japanese cedar, and the buried cypress were 194, 168, and 143 mg cm⁻², respectively.

X-ray fluorescence analysis

X-ray fluorescence spectra of the ancient wood and reference sample powders were recorded under vacuum using a Horiba MESA-500 spectrometer.

Results and discussion

Japanese cedar wood containing iron from rusted nails

Figure 1 depicts the Mössbauer spectrum at room temperature of the Japanese cedar heartwood discolored by iron rust. The spectrum shows only a symmetrical doublet and no magnetic hyperfine splitting. The IS and QS of the doublet were 0.377 ± 0.005 mm s⁻¹ and 0.715 ± 0.008 mm s⁻¹, respectively, indicating that iron in the Japanese cedar wood exists as high-spin Fe(III) cations. Because the iron species is likely to be a component of iron rust, it would be expected to be an iron oxide or iron oxyhydroxide such as Fe₃O₄ (magnetite), γ -Fe₂O₃ (maghemite), α -FeOOH (goethite), β -FeOOH (akaganeite), or γ -FeOOH (lepidocrocite).¹² Although the resulting values of IS and QS indicate that the iron species is β -FeOOH or γ -FeOOH,¹³ β -FeOOH should not be produced if no fluoride or chloride ion exists.^{13,14} It

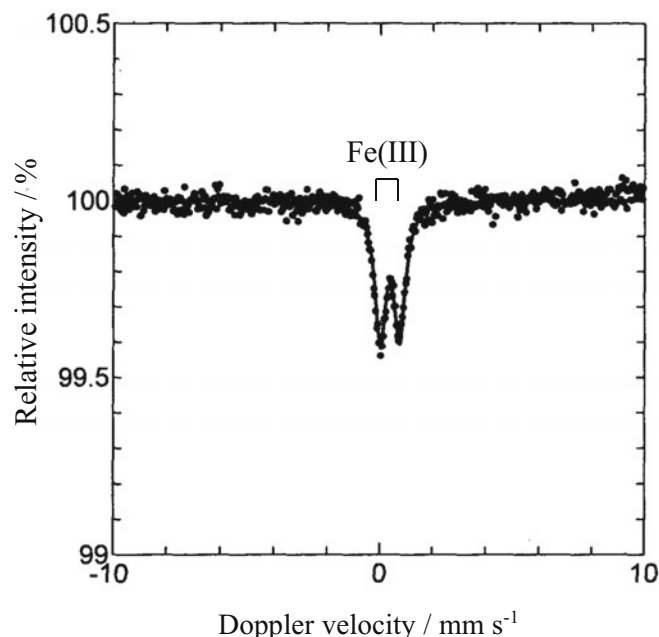


Fig. 1. Mössbauer spectrum at room temperature of Japanese cedar wood discolored by iron rust

can be, therefore, presumed that the iron species in wood is γ -FeOOH. However, Mössbauer measurements at low temperatures are essential to completely prove the absence of β -FeOOH.

The mechanisms of iron corrosion are extremely complicated, and the constituents of iron rust are greatly dependent upon the conditions of the corrosion. Although there have been reports¹³⁻¹⁶ that the iron rust produced in the atmosphere contains fine particles of α -FeOOH, Mössbauer absorption due to α -FeOOH was not observable in the spectrum shown in Fig. 1. Furthermore, it is generally considered that "green rust," which is a precursor of rust including Fe(II), is formed in the corrosion process,^{14,17} but no Fe(II) component was detected.

Ancient buried Japanese cypress

From fluorescence X-ray analysis, it was confirmed that the ancient Japanese cypress sample certainly contains iron, although the amount of iron is fairly small. It was inferred that iron content is roughly 0.02 wt% from comparison with the reference samples. For ordinary Japanese cypress, X-ray analysis showed iron was undetectable in this study. The ancient buried wood possessed a much larger content of silicon, aluminum, and sulfur than ordinary raw wood, and the X-ray analysis showed no heavy metals other than iron.

The Mössbauer spectrum of the ancient Japanese cypress wood is shown in Fig. 2. Mössbauer absorption with little QS is observed at ~ 0.5 mm s⁻¹, although curve-fitting techniques could not be applied to obtain Mössbauer parameters with satisfactory accuracy because of the weak intensity. Hence, it can be presumed that iron, which has been supplied from the soil, exists as high-spin Fe(III) species in the ancient buried wood.

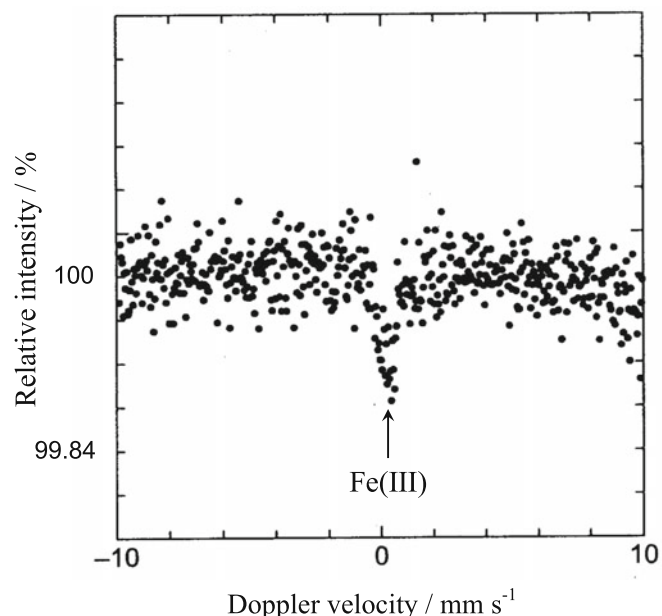


Fig. 2. Mössbauer spectrum at room temperature of ancient buried Japanese cypress wood

Ancient buried Japanese cedar

Iron signals were observed as considerably intense peaks in the fluorescence X-ray spectrum, and iron content was estimated to range from 0.4 to 0.7 wt% by comparison with the reference samples. High levels of silicon, aluminum, and sulfur were detected in the ancient Japanese cedar as well as the ancient Japanese cypress. In addition, X-ray measurement clearly revealed the presence of manganese.

Figure 3 demonstrates the Mössbauer spectrum of the ancient Japanese cedar sapwood at room temperature. The spectrum consists of two symmetrical doublets from high-spin Fe(III) (IS, 0.361 ± 0.001 mm s⁻¹; QS, 0.717 ± 0.002 mm s⁻¹) and high-spin Fe(II) (IS, 1.121 ± 0.002 mm s⁻¹; QS, 2.600 ± 0.004 mm s⁻¹). It is most likely that the spectral differences between Figs. 2 and 3 result from both the amount and species of iron in the soil, including the ancient woods. The absorption area ratios of Fe(II) and Fe(III) to total iron [Fe(II) + Fe(III)] are 0.257 and 0.743, respectively. Thus, assuming that the recoilless fraction of iron in the Fe(II) state is equivalent to that in Fe(III), the ratio of Fe(III) to Fe(II) is 2.9; that is, the content of Fe(III) is 2.9 times as much as that of Fe(II). However, in the Mössbauer measurement of another sample from the same ancient Japanese cedar wood, Mössbauer absorption intensities of Fe(II) and Fe(III), especially Fe(II), were weak compared with those shown in Fig. 3, so both total iron content and the Fe(III)/Fe(II) ratio may not be consistent in ancient Japanese cedar wood.

The Mössbauer spectrum shown in Fig. 3 reveals an interesting result in that both Fe(II) and Fe(III) species exist together in the ancient buried Japanese cedar, suggesting that Mössbauer spectroscopic analysis may be one of the keys to clarifying the role of iron in redox reactions of wood constituents in buried wood.

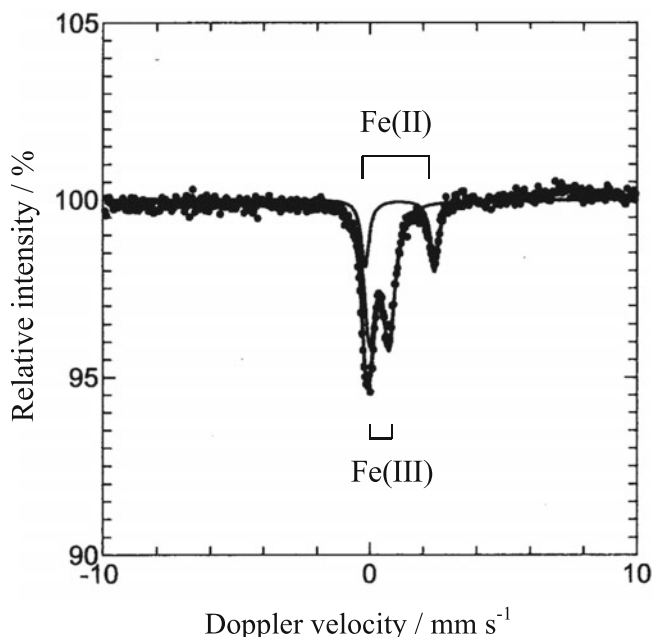


Fig. 3. Mössbauer spectrum at room temperature of ancient buried Japanese cedar wood

Conclusion

For the Japanese cedar wood block with iron nails prepared here, the present study suggested that iron species from rusted nails in wood existed as γ -FeOOH. Mössbauer spectra shown in Figs. 2 and 3 revealed that both the ancient buried Japanese cedar and the buried Japanese cypress possess high-spin Fe(III) species. Furthermore, the Mössbauer absorptions from Fe(II) allow us to conclude that iron plays an important role in redox reactions of organic wood constituents in buried wood.

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