

ORIGINAL ARTICLE

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Distribution of boron in wood treated with aqueous and methanolic boric acid solutions

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Abstract The distributions of boron in Japanese cedar (*Cryptomeria japonica* D. Don) sapwood blocks treated with aqueous or methanolic boric acid [B(OH)₃] solutions were explored through Raman spectroscopy and prompt gamma-ray analysis (PGA). B(OH)₃ was the sole boron species observed in Raman spectra of the wood blocks treated with either solution. Plots of weight gain of the treated wood blocks versus boron concentration in treatment solutions were found to be linear. The results indicated that the methanolic solution makes it possible to impregnate wood with much larger amounts of boron than the aqueous solution. PGA confirmed that B(OH)₃ was highly enriched near the end grains of the treated wood blocks. Raman measurements suggested that boron content in the bulk of the wood block is not as large as expected from the weight gain of the treated wood blocks when an ordinary air-drying method is used. It was concluded that the aqueous solution impregnates the cell walls of wood with boron more easily than the methanolic solution.

Key words Boric acid · Methanol · Prompt gamma-ray analysis · Raman spectroscopy · Wood preservative

Introduction

In recent years, many countries have prohibited the use of wood preservatives containing arsenic and/or chromium. Boric acid [B(OH)₃] and borates have been regarded as a substitute preservative for a long time because of their lower toxicity.^{1,2} However, such preservatives have not been commercially available in Japan because they are easily eluted from wood by rainwater. Although the mechanism of elution from timber has been investigated,^{3,4} and several processes of boron fixation have been proposed,^{5–10} no satisfactory method for fixing boron in wood has yet been established. Boric acid will have some negative effects on the environment if it is eluted in large amounts, although boric acid is much less toxic than arsenic or chromium compounds. Therefore, in order to put wood treated with boric acid to practical application, it is essential to develop techniques for fixing and removing boron.

We have tried several approaches to the problem of preventing the easy elution of boron compounds from wood. To explore the physicochemical state of boron species in wood, we have studied Japanese cedar (*Cryptomeria japonica* D. Don) wood treated with aqueous and methanolic boric acid solutions by Raman spectroscopy^{11–13} and prompt gamma-ray analysis (PGA).¹⁴

Boron treatment of woody materials is usually performed by using aqueous boric acid and/or borate solutions, although the vapor-phase application of trimethyl borate has been attempted recently.^{15,16} Boric acid is used most frequently because it is the most common and lowest-cost boron compound. However, the solubility of boric acid in water is relatively low at ambient temperature, making it difficult to impregnate wood sufficiently with boron. Thus, borax (Na₂B₄O₇·10H₂O) has been adopted to raise boron concentration in the treatment solution even though the

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amount of borax used cannot be large because borax increases the pH of the solution.

The use of organic solvents for boric acid can be employed for the purpose of increasing boron concentration in the solution. Boric acid is highly soluble in such hydrophilic organic solvents as methanol, ethanol, dioxane, and ethylene glycol. Methanol will be the most suitable organic solvent for boron treatment, because the solubility of boric acid in methanol is much greater than in water and it can be obtained at lower cost compared with other organic solvents. Moreover, it is expected that methanol can be easily removed from woody materials owing to its low boiling point.

In aqueous solution, most dissolved boric acid exists in the chemical form of $B(OH)_3$, while boric acid reacts with methanol molecules to yield boron esters in methanolic solution. Hence, the chemical species of boron in methanolic solutions should be entirely different from those in aqueous solutions.

Accordingly, it is essential to obtain information on the boron species and their distribution in treated wood in order to properly evaluate boron treatment using methanolic solutions. The analytical methods for boron in the solid state are confined to a few techniques. Previously, there has been only an electron probe microanalysis (EPMA) study¹⁷ of boron in timber in addition to our studies using Raman spectroscopy.^{11–14} Raman spectroscopy is a promising technique for the identification of boron species in solids because characteristic Raman bands can be found for boric acid and borates, and it enables us to obtain information on relative changes in boron content from the Raman scattering intensity. However, ordinary Raman spectroscopy is not sensitive enough to detect small quantities of boron species in wood and it is difficult to determine absolute boron content only from Raman measurements.

Although there are few analytical techniques to determine the boron content in solids, the recent development of PGA has allowed us to gain a powerful tool for the detection of trace amounts of boron in various samples,^{18,19} and is basically in the category of neutron-activation analysis. Boron is one of the elements for which PGA has an ultimate sensitivity by using 478-keV prompt gamma-rays emitted from 7Li produced in the $^{10}B(n, \alpha)^7Li$ reaction. 7Li represents 7Li that has an atomic nucleus in an excited state. The cross section of the nuclear reaction is 3838 barn for the thermal-neutron capture. Such a huge cross section should lead to higher analytical sensitivity.

The PGA of boron provides us not only the information on boron content but also on boron states by probing the Doppler broadened line shape of 478-keV gamma-rays.^{20–23} The details on PGA and Doppler broadening are described in a previous report.¹⁴

In this study, we semimicroscopically analyzed boron species in Japanese cedar wood treated with aqueous and methanolic boric acid solutions by Raman spectroscopy. The local boron content in the wood blocks was determined absolutely from PGA measurements. We discuss the chemical behavior and distribution of boron in the wood blocks.

Materials and methods

Wood samples and chemical reagents

The sapwood blocks, 15 (T) × 15 (R) × 50 (L) mm, were cut from an 80-year-old Japanese cedar planted in Akita Prefecture, and were used as samples for boron treatment. The blocks were kept at 25°C and 60% relative humidity (RH) in an environmental chamber until their weight became constant, and these values were used as standard weights to calculate weight gains. The water content at 25°C and 60% RH was calculated from the oven-dry weight of the block. Boric acid, methanol, and trimethyl borate were purchased from Wako Pure Chemical Industries and used without further purification.

Treatment with boric acid solutions

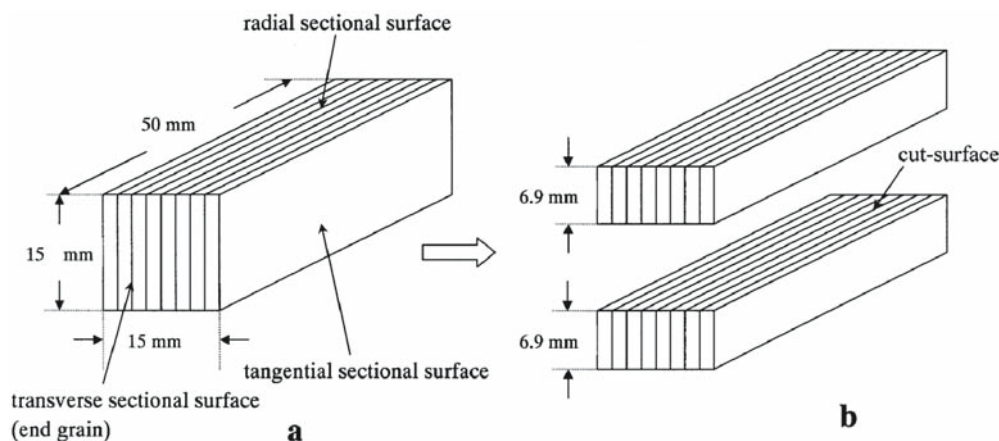
Aqueous and methanolic solutions for boron treatment were prepared in the boron concentration range of 1.9×10^{-2} to $7.3 \times 10^{-1} \text{ mol}\cdot\text{dm}^{-3}$ and 2.0×10^{-2} to $1.46 \text{ mol}\cdot\text{dm}^{-3}$, respectively. The wood blocks were completely immersed in a solution in a polypropylene beaker, and the beaker was put into a vacuum desiccator. The internal pressure was reduced with a water-jet pump until it became constant, and then returned to atmospheric pressure by opening the bulb. The desiccator was left to stand for 1 h, and then the wood samples were taken out of the solution. The surplus solution on the surface of the wood block was quickly soaked up with filter paper, and the blocks impregnated fully with boric acid solution were weighed. The wood blocks were dried at room temperature ($25^\circ \pm 2^\circ\text{C}$) in air for 2 days, and subsequently kept in the environmental chamber under the same conditions as described above. Three or four replication blocks were prepared for each treatment solution. Wood blocks treated with pure solvent were analyzed as control samples.

Raman measurements

Two Raman spectrometers were used in this study. Raman spectra of methanolic solutions were obtained at room temperature using a Renishaw Raman Imaging Microscope System 1000 equipped with an air-cooled CCD detector. A He–Ne laser (632.8 nm) was employed as the excitation source. Backscattered Raman signals were collected through a microscope and holographic notch filters in the range of $600\text{--}1000 \text{ cm}^{-1}$ with a spectral resolution of 2 cm^{-1} . The laser power was kept at about 20 mW. A quartz cell was utilized in all the Raman measurements of solution samples. The wavenumber was calibrated using the 520 cm^{-1} line of a silicon wafer and the 1332 cm^{-1} line of diamond.

Fourier transform (FT)-Raman spectra of wood samples were recorded with a Jeol JIR 7000W spectrometer connected to an RS-RSU-200 Raman module with backscattering geometry. Excitation (1064.1 nm) was provided by an

Fig. 1a, b. Cutting of sample blocks for Raman measurements to explore boron distribution. **a** Wood block before cutting, **b** wood block after cutting



Nd³⁺: YAG laser; the incident laser power was 200 mW, which was low enough to prevent irreversible thermal damage to the wood. The beam was focused to a diameter of ca. 0.5 mm on the sample surface. To obtain good-quality spectra, more than 1000 scans were required at about 2 cm⁻¹ intervals (spectral resolution, ca. 4 cm⁻¹). The wavenumber was calibrated using the 460 cm⁻¹ line of CCl₄ and the 1332 cm⁻¹ line of diamond.

The Raman measurements of wood blocks were made only on earlywood. The treated wood block was cut parallel to its radial section into two equal parts as shown in Fig. 1. Raman maps of boron distribution were made on the cut surface. The peak height of the Raman band at 879 cm⁻¹ due to B(OH)₃ was determined by a difference-spectrum method.¹²

PGA measurements

Samples for PGA were cut as a disk, 5–10 mm in diameter and about 1 mm in thickness, from the center or end grain part of the treated wood block. These disk samples did not contain any part within 1 mm from the surfaces of the wood blocks because microcrystalline boric acid was deposited on the surfaces.^{12,13}

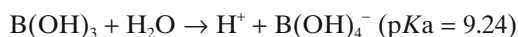
PGA of the wood samples was performed using the prompt gamma-ray analyzing system installed at the thermal-neutron beam guide of JRR-3 at the Japan Atomic Energy Research Institute.^{18,19} The thermal neutron flux was 6.5 × 10⁷ cm⁻²·s⁻¹. Measuring time varied from 10 min to 2 h depending on the boron content of the wood samples. Boron content and degradation constant (*D*) were determined from our line shape analysis procedure.²¹

To determine boron contents, a PGA measurement of the reference standard was carried out under conditions that were identical to those used for the wood samples. The reference sample was prepared by adding aqueous solution containing a known amount of boron to a piece of filter paper. For the comparison of *D* values, solid boric acid and an aqueous solution of boric acid (0.8 mol·dm⁻³) were also submitted to PGA measurement.

Results and discussion

Raman spectra of methanolic boric acid solution

In aqueous solution, an extremely small proportion of boric acid dissociates into H⁺ and B(OH)₄⁻ via



while most boron is present as B(OH)₃. We have reported that wood treated with aqueous boric acid solution was observed to contain B(OH)₃ as the only boron species according to Raman spectroscopy.^{11,12} Although a number of NMR and/or Raman studies^{24–29} on boron species in various aqueous borate solutions have been published, there is no report on boron compounds in alcoholic solutions as far as we know. However, it is well known that condensation reactions readily occur between boric acid and alcohol, and hence the following consecutive reactions are expected in methanolic boric acid solution;

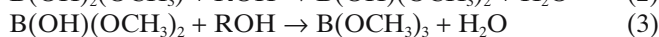
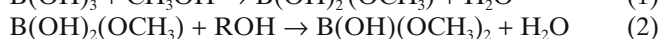
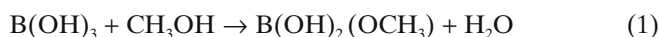


Figure 2 depicts Raman spectra at room temperature of trimethyl borate [B(OCH₃)₃] and methanolic boric acid solutions. Initial concentrations of boric acid were expressed as a molar ratio of B(OH)₃/CH₃OH. The boron concentrations in methanolic solution of molar ratio 1/60 and 1/10 were equivalent to 4.1 × 10⁻¹ mol·dm⁻³ and 2.7 mol·dm⁻³, respectively. Methanol molecules show no Raman band in the region from 700 to 900 cm⁻¹. All the Raman spectra of the solutions exhibit a band at about 730 cm⁻¹ corresponding to trimethyl borate.³⁰ As shown in Fig. 2, the spectra of the solutions with higher boric acid concentration (traces a–c) demonstrate a symmetric stretching band at about 877 cm⁻¹ due to the BO₃ unit in B(OH)₃.³¹ Two other bands were observed in the range from 750 to 850 cm⁻¹. It can be presumed that the Raman bands at 773 and 814 cm⁻¹ are due to B(OH)(OCH₃)₂ and B(OH)₂(OCH₃), respectively, because the intensity of these bands increases relative to the band at 730 cm⁻¹ with increasing initial concentration of boric acid.

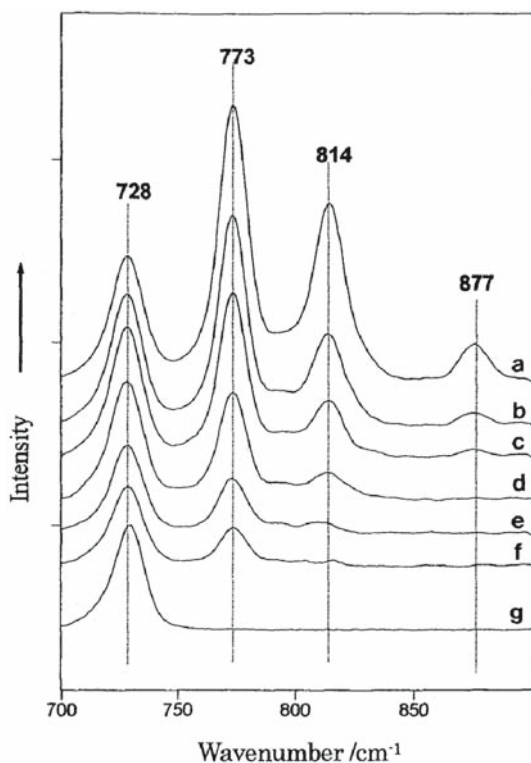


Fig. 2. Raman spectra of methanolic boric acid solutions and trimethyl borate. *a*, Initial molar ratio of boric acid/methanol: 1/10; *b*, 1/15; *c*, 1/20; *d*, 1/30; *e*, 1/45; *f*, 1/60; *g*, trimethyl borate

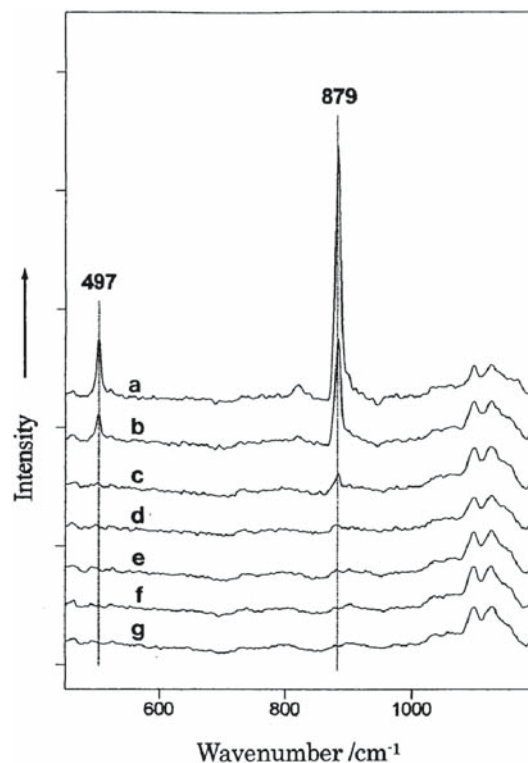


Fig. 3. Line map of Raman spectra in the longitudinal direction of the cut surface of the wood sample treated with $1.1 \text{ mol}\cdot\text{dm}^{-3}$ methanolic boric acid solution recorded at distance from the end grain: *a*, 0.5 mm; *b*, 1 mm; *c*, 2 mm; *d*, 3 mm; *e*, 5 mm; *f*, 10 mm; *g*, 25 mm

The Raman spectra revealed that boron species in methanolic solution are entirely different from those in aqueous solution, and thus it is necessary to identify the boron species in wood treated with the methanolic solution to estimate the boron content by weight gain.

Raman spectra of wood blocks treated with methanolic boric acid solution

A line map of Raman spectra in the longitudinal direction on the cut surface of wood blocks treated with $1.1 \text{ mol}\cdot\text{dm}^{-3}$ methanolic boric acid solution is shown in Fig. 3. Two sharp bands due to $\text{B}(\text{OH})_3$ appear at 497 and 879 cm^{-1} in the spectrum at a distance of 0.5 mm from an end grain (spectrum *a*) and these band intensities exponentially decrease with increasing distance from an end grain, suggesting that boron is enriched near end grains as microcrystalline boric acid. Thus, it seemed that methanol included in the wood block diffused mainly through end grains into the air during air drying.

Another important point shown in Fig. 3 is that no boron species was observable except for $\text{B}(\text{OH})_3$. This will be due to the fact that all of the boron esters, $\text{B}(\text{OH})_2(\text{OCH}_3)$, $\text{B}(\text{OH})(\text{OCH}_3)_2$, and $\text{B}(\text{OCH}_3)_3$, quickly returned to $\text{B}(\text{OH})_3$ by hydrolysis during air drying.

Weight gain of wood blocks treated with boric acid solutions

For every treatment solution, the weight gains of three replications after environmental-chamber drying were approximately constant and the standard deviation was less than 3% of the average weight gain. Immediately after the vacuum-impregnation treatment, several samples were quickly cut in the longitudinal direction to observe how the solutions penetrate into the wood samples, and the observation confirmed that boric acid solutions permeated the blocks completely and uniformly.

Figure 4 shows plots of the weight gain of the wood blocks against boron concentration in treatment solutions. We have previously reported that the weight gain of a sapwood block was proportional to boron concentration in aqueous treatment solution.¹² Figure 4 shows linearity of the weight gain against boron concentration in both the aqueous and methanolic treatment solutions, and the rate of weight gain of the blocks treated with aqueous solution in this study was in good agreement with that of the previous work.¹² Thus, it seems likely that the treatment solutions filled almost all the lumens and intercellular spaces and permeated sufficiently into the cell wall during the impregnation treatment. The reason for the slightly smaller weight gain of the blocks treated with methanolic solution is discussed below.

For the wood blocks treated with methanolic solutions, the plot gives a straight line far beyond $8.8 \times 10^{-1} \text{ mol}\cdot\text{dm}^{-3}$ of the solubility of boric acid in water at 25°C . As described above, most boron in the wood treated with the methanolic solution was in the form of $\text{B}(\text{OH})_3$ after drying. The solubility of boric acid in water at 30°C is $1.1 \text{ mol}\cdot\text{dm}^{-3}$ and that in methanol at 29°C is $3.7 \text{ mol}\cdot\text{dm}^{-3}$, that is, the latter is 3.4 times greater than the former. Therefore, it is likely that treatment with the methanolic solution enables us to provide wood impregnated with a considerably larger amount of boron than the treatment with aqueous solution.

The weight gain of wood blocks treated with the methanolic solution is slightly smaller than that treated with the aqueous solution. This can be explained in terms of the evaporation of trimethyl borate. As shown in Fig. 2, a part of boric acid is transformed into trimethyl borate, which is a volatile compound, in methanolic solution, and hence a small portion of boron is likely to have emanated into the air as trimethyl borate from the wood block during air drying. In addition, two other boron esters, $\text{B}(\text{OH})_2(\text{OCH}_3)$

and $\text{B}(\text{OH})(\text{OCH}_3)_2$, may be also volatile. Such emanations would cause a slightly lower weight gain in wood blocks treated with the methanolic solution.

PGA of boron in the treated wood

All the spectral line shapes of 478-keV prompt gamma-rays from wood samples treated with boric acid solutions were trapezoidal due to Doppler broadening as we reported previously.¹⁴ Table 1 summarizes the local boron contents and D values of the wood blocks treated with the boric acid solutions. D is known as the degradation constant, and primarily depends on the elemental constituent and density around the boron atom. For the sample treated with $7.3 \times 10^{-1} \text{ mol}\cdot\text{dm}^{-3}$ methanolic boric acid solution, the boron content near the end grain was approximately ten times larger than that at the center of the wood block. The PGA measurements provided evidence that confirmed the enrichment of boron near the end grains, suggesting that the boron content at the center of the treated wood blocks was not as large as expected from the weight gain shown in Fig. 4.

Assuming that the boron species in the treated wood is $\text{B}(\text{OH})_3$ alone, total boron content in the wood block can be calculated from the weight gain. The boron contents of the blocks treated with 2.0×10^{-1} and $7.3 \times 10^{-1} \text{ mol}\cdot\text{dm}^{-3}$ aqueous solutions were 0.70% and 1.77%, respectively, but the boron contents at the center measured by PGA were 0.422% and 1.029%, as shown in Table 1. For the methanolic solutions, total boron contents in the blocks treated with 1.8×10^{-1} , 7.3×10^{-1} , and $1.46 \text{ mol}\cdot\text{dm}^{-3}$ methanolic solutions were calculated to be 0.45%, 1.21%, and 2.78%, respectively, whereas the boron contents measured at the center were 0.161%, 0.854%, and 1.31%, respectively.

There was little difference in boron content at the center between the wood blocks treated with $1.9 \times 10^{-2} \text{ mol}\cdot\text{dm}^{-3}$ aqueous and $2.0 \times 10^{-2} \text{ mol}\cdot\text{dm}^{-3}$ methanolic boric acid solutions. However, for more concentrated solutions, significant differences in the boron content were observed between the blocks treated with aqueous and methanolic solutions. The PGA measurements revealed the interesting result that the boron content at the center of the wood block treated with

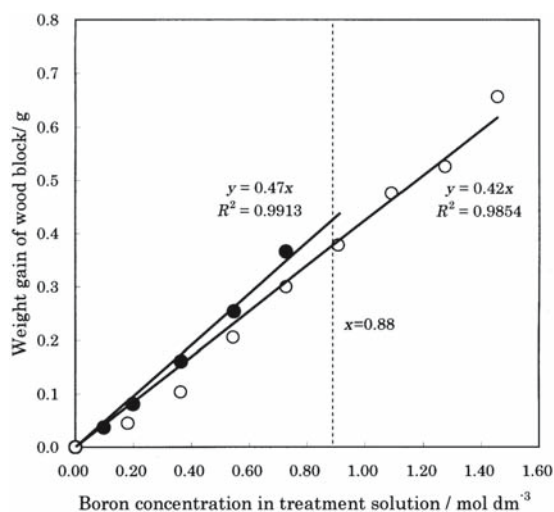


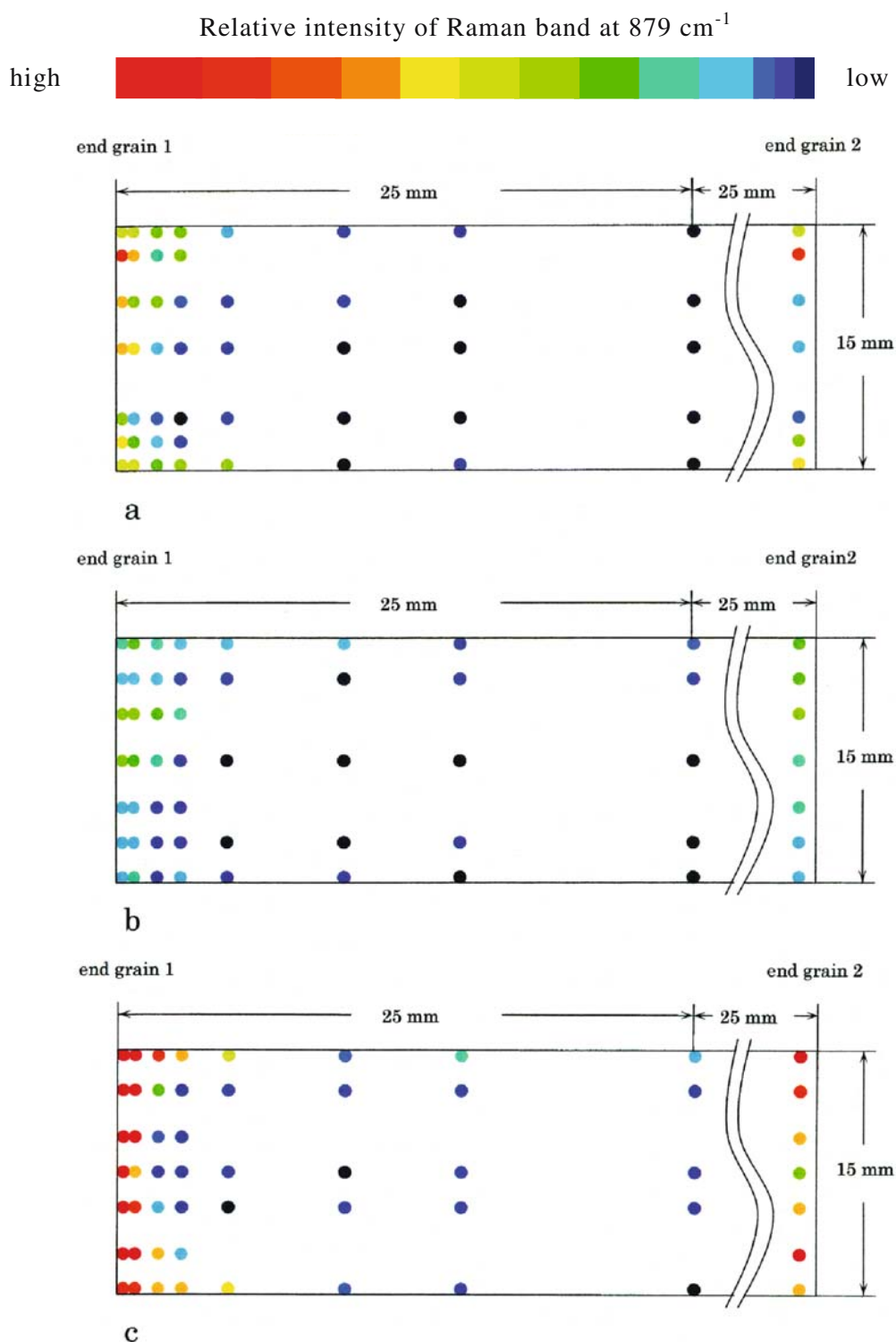
Fig. 4. Relationships between weight gain and boron concentration of treatment solution. *Open circles*, wood block treated with methanolic boric acid solution; *filled circles*, wood block treated with aqueous boric acid solution

Table 1. Boron content and degradation constant of wood samples treated with boric acid solutions

Location of Japanese cedar sample in wood block	Initial boric acid concentration in treatment solution ($\text{mol}\cdot\text{dm}^{-3}$)	Solvent	Boron content ^a (% , w/w)	Degradation constant ^a (10^{12} s^{-1})
Center of block	No treatment		0.0098 ± 0.0006	1.37 ± 0.03
Center of block	0.019	Water	0.0261 ± 0.001	1.33 ± 0.01
Center of block	0.20	Water	0.422 ± 0.002	1.36 ± 0.02
Center of block	0.73	Water	1.029 ± 0.009	1.33 ± 0.02
Center of block	0.020	Methanol	0.0245 ± 0.004	1.35 ± 0.05
Center of block	0.18	Methanol	0.161 ± 0.001	1.32 ± 0.02
Center of block	0.73	Methanol	0.854 ± 0.009	1.40 ± 0.02
Vicinity of end grain	0.73	Methanol	9.19 ± 0.10	1.36 ± 0.02
Center of block	1.46	Methanol	1.31 ± 0.05	1.40 ± 0.01
Solid boric acid, microcrystalline				1.39 ± 0.01
Aqueous boric acid solution (5%, w/w)				1.10 ± 0.01

^a Errors estimated from fitting results

Fig. 5a–c. Raman images of boron distribution on the cut surface of the wood block. **a** Wood block treated with $7.3 \times 10^{-1} \text{ mol}\cdot\text{dm}^{-3}$ methanolic boric acid solution, **b** wood block treated with $7.3 \times 10^{-1} \text{ mol}\cdot\text{dm}^{-3}$ aqueous boric acid solution, **c** wood block treated with $1.46 \text{ mol}\cdot\text{dm}^{-3}$ methanolic boric acid solution



aqueous solution was higher than that treated with methanolic solution when the initial boric acid concentration increased to some degree. A possible mechanism to account for the differences in the boron content would be swelling of the wood by the solvent. Although the solvent effect was not obvious in low concentration solutions, water molecules probably pull a greater amount of the boron species into the cell wall than methanol molecules in intermediate or

higher concentration solutions because water possesses a more powerful swelling property than methanol.

The line shape of the prompt gamma-ray spectrum reflects the physicochemical environments around boron.^{22,23} We can obtain information on the chemical state of boron in the sample by determining the D value depending on the spectral line shape. As described previously,¹⁴ by assuming that boron species might disperse homogeneously in the

wood sample, a D value of $0.41 \times 10^{12} \text{ s}^{-1}$ was calculated on the basis of the Lindhard-Scharff-Schiott (LSS) theory. This value was much smaller than the measured D values for the wood samples shown in Table 1, suggesting that micro air space and water in the cell wall should be taken into account for ^7Li degradation processes. The data in Table 1 indicates that D values of boron in the treated wood are equal to or slightly lower than those of solid boric acid ($1.39 \times 10^{12} \text{ s}^{-1}$). Hence, it may be expected that most $\text{B}(\text{OH})_3$ molecules in the wood are in a physicochemical state analogous to a microcrystalline state.

Images of boron distribution due to Raman scattering intensity at 879 cm^{-1}

To draw a map of boron distribution, Raman measurements were performed in two dimensions on a radial sectional cut surface of wood blocks treated with aqueous or methanolic solution. The color maps are shown in Fig. 5. Color coding in the maps was based on the band intensity at 879 cm^{-1} , because the only boron species observed was $\text{B}(\text{OH})_3$. Although the band intensity may not be precisely proportional to local boron content in wood, it can be used as an indicator of relative change in boron content.

As shown in Fig. 5, the map of the wood block treated with $7.3 \times 10^{-1} \text{ mol} \cdot \text{dm}^{-3}$ methanolic solution (Fig. 5a) exhibits strong bands at 879 cm^{-1} due to $\text{B}(\text{OH})_3$ at the points closest to an end grain, while such a strong band was not observed near the tangential sectional surfaces. The band intensities decreased rapidly with increasing distance from an end grain and were found to be very small when the distance increased beyond several millimeters. These results indicate that boron was highly enriched in the neighborhood of end grains.

A similar pattern was observed for a map of the wood block treated with $7.3 \times 10^{-1} \text{ mol} \cdot \text{dm}^{-3}$ aqueous solution (Fig. 5b). However, it was apparent that the band intensities at 879 cm^{-1} near end grains in Fig. 5b were smaller than those in Fig. 5a. This is a remarkable result, because the weight gain of the wood block treated with the aqueous solution is slightly larger than that with the methanolic solution as shown in Fig. 4. The results can be explained in terms of the dispersion state of $\text{B}(\text{OH})_3$ in the wood, although these maps seem to conflict with the results of weight gains. An aqueous solution probably disperses boron species in the cell wall more easily than a methanolic solution, because water possesses a more powerful swelling property of wood than methanol. In other words, larger amounts of microcrystalline boric acid are deposited on the surface of cell walls when methanol is used as a solvent. As a result, the Raman band at 879 cm^{-1} observed in the wood block treated with methanolic solution is stronger than that with the aqueous solution, because Raman spectrum reflects information on the neighborhood of the surface.

Figure 5c shows a map of the wood block treated with $1.46 \text{ mol} \cdot \text{dm}^{-3}$ methanolic solution. The band intensities at 879 cm^{-1} in the vicinity of end grains grow remarkably compared with Fig. 5a, but such great growth is not observed for the other parts of the wood block.

Conclusions

Raman and PGA studies have given us valuable information on the physicochemical state and distribution of boron in wood treated with aqueous and methanolic boric acid solutions. It was revealed from Raman measurements that almost all boron atoms in the wood treated with methanolic solution are present as $\text{B}(\text{OH})_3$. Although a small portion of boron will emanate from treated wood as methanol borates during the air-drying process, it is possible to impregnate wood with larger amounts of boron by using a methanolic solution rather than an aqueous solution. However, boron was enriched near the end grains of the wood, and the local boron content in the bulk of treated wood was not as high as expected from the weight gain when the ordinary air-drying method was used. In order to obtain a more homogeneous dispersion of boron in treated wood, it will be necessary to improve drying methods after impregnation with boric acid solution.

Moreover, it was concluded that the cell wall of wood treated with the aqueous solution includes $\text{B}(\text{OH})_3$ more abundantly than that treated with the methanolic solution if boron concentrations in the treatment solutions are equal.

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