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Volatile organic compounds from wood and their influences on museum artifact materials I. Differences in wood species and analyses of causal substances of deterioration

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Abstract Wood is generally used as the interior material in museum storage rooms. Recently, however, the effects of volatile organic compounds (VOCs) from wood on artifacts has become a topic of great concern. The VOCs from four species of wood (western red cedar, spruce, kiri, and sugi) and their effects on artifact materials (two types of metal, seven types of pigment) were investigated using a deterioration-accelerating test, gas chromatography-mass spectrometry, X-ray diffraction analysis, and X-ray photoelectron spectroscopy. The results suggested that the influences on artifact materials varied greatly with wood species, and depended on specific components such as hinokitiol or acetic acid rather than the amount of total volatile organic compounds (TVOCs). It is a very serious problem that of the four species of wood, western red cedar (rich in hinokitiol), which has been recommended as an interior material for museum storage rooms, showed the heaviest deterioration on metal samples, and only this type of wood discolored enpaku (white lead) and rokushou (malachite, verdigris). In such storage rooms, museum artifacts should be carefully monitored. When selecting an interior material for a storage room or studying methods of preventing deterioration, it is very important to consider fully the characteristics of wood VOCs, not only the amount of TVOC.

Key words Museum artifact material · Discoloration · Volatile organic compounds · Hinokitiol · Western red cedar

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Introduction

Recently, the influence of volatile organic compounds (VOCs) from wood on living things has attracted a great deal of public attention.[1] In the museum field, there is great concern over influences on artifacts. In these institutions, to strictly control the degradation of museum artifacts, it is essential to manage the preservation environment appropriately.

There are various environmental factors that should be managed, including temperature, humidity, light, insects, and mold. Air pollution substances such as dust, nitrogen oxide, and sulfur oxide from exhaust emissions, and formaldehyde from plywood or adhesives are also very important factors.[2–9]

In particular, the acidification of storage rooms that use wood as an interior material is becoming a serious problem (in one particular museum, an acidic condition has existed for more than 20 years).[10–12] Wood is used as an interior material for storage rooms in many museums for various reasons, one being its excellence in humidity control. Much less is known, however, about the influences of VOCs from wood on various kinds of museum artifacts. Many museums experience problems of deterioration of museum artifacts caused by VOCs from wood.

In the Tohoku History Museum, which opened in 1999, some storage rooms were initially in an acidic condition, although this condition has now improved. In our previous study, we investigated the cause of this acidic environment and methods to improve it.[13] We focused on western red

cedar (*Thuja plicata* D. Don) which had been recommended as a material for museum storage rooms, and studied its VOCs and influences on iron.[14]

In the present study, four species of wood, western red cedar, spruce (*Spruce* spp.), kiri (*Paulownia tomentosa* Steud.), and sugi (*Cryptomeria japonica* D. Don), which are generally used as interior materials for storage rooms or stock cases in museums, were used to investigate VOCs emitted and their influences on artifact materials.

This study consisted of the following:

1. Experiments on the deterioration of artifact materials (two types of metal, seven types of pigment) by VOCs from wood
2. Analysis of VOCs by gas chromatography-mass spectrometry (GC-MS)
3. Experiments on the deterioration of artifact material samples by the specific substances in their VOCs
4. Analysis of deteriorated products of artifact materials using X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS)

Materials and methods

Materials and chemicals

Four species of wood samples were used in this study, namely western red cedar (from Canada), kiri (from China), spruce (from Canada), and sugi (from Japan). Western red cedar was dried for 1 week in a chamber at 60°–70°C. The others were air-dried (kiri for 1 year, and the others for 6 months). Water contents of the samples were 14%–18%.

Metal and pigment samples were used as the artifact material samples. For the metal samples, iron (Japanese Industrial Standards, JIS: SS400) and copper (JIS: C1100P), which are specified standard samples for evaluating metal corrosivity in an air environment by the JIS, were used. For the pigment samples, special grade reagents (Kanto Chemical) used as the main ingredient of pigments were used (Table 1). The metal specimens (40 × 20 × 1 mm) were ground on both sides with emery paper (in the order of No. 400 → No. 600 → No. 800) and cleaned with ultrasonic washing (W-115 Sanpa, Honda Electronics) in acetone for 15 min, just before use. The pigments were placed directly in the hollow (20 × 15 × 0.2 mm) of a slide glass for XRD measurement.

Special grade volatile reagents (Kanto Chemical) of hinokitiol and acetic acid were used to investigate the independent effects of individual substances of wood VOCs on artifact materials.

Methods

Influences of VOCs from wood on metals and pigments

The wood samples (5 × 4 × 1 cm, eight pieces), the material samples (metals and pigments), and a small glass container (10 cm^3) containing distilled water (3.0 g) were placed in a desiccator (3 dm^3) equipped with a thermohygrometer sensor (SK-L200TH , Sato Keiryoki). They were then placed in an incubator (MIR-251, Sanyo) set at 30°C for 33 days. A control experiment was conducted without wood samples, that is, with only distilled water. The material samples were observed by visual inspection and a metallurgical microscope (BHSM, Olympus). The color difference (CIEΔE^*_{ab}) in deteriorated samples was measured with a visible and ultraviolet spectrophotometer (U-4000, Hitachi).

GC-MS analyses of the VOCs from wood

The VOCs from wood were analyzed by GC-MS (HP-6890/HP5973, Hewlett-Packard; heating desorption apparatus: JTD-505, Japan Analytical Industry).

The wood samples (5 × 2 × 1 cm) were placed in a sampling vessel (0.2 dm^3) under high purity helium gas ventilation (0.2 $dm^3\,min^{-1}$), and their VOCs were collected in an absorbent tube (Tenax-GR) at 80°C for 120 min. The heating desorptions were performed under the following conditions: trap temperature −60°C, desorption temperature 270°C, and desorption time 5 min. The GC was equipped with a capillary column (Neutra Bond-1, 0.5 mm × 60 m, film thickness 0.4 μm, GL Sciences) that was maintained at 40°C for 5 min and then raised from 40°C to 280°C at 10°C min^{-1}; the temperature was maintained at 280°C for 11 min. Helium was used as the carrier gas (flow rate 1 $cm^3\,min^{-1}$). For mass analysis detection, an electron multiplier (EM) was used.

Individual influences of the specific substances in VOCs from wood on metals and pigments

The material samples and a small glass container (10 cm^3) containing the volatile reagents were placed in a sealed

Table 1. Details of pigment samples

Pigment sample[a]	Color	Chemical formula
Mitsudasou (litharge)	Yellow	PbO
Enpaku (white lead)	White	$2PbCO_3 \cdot Pb(OH)_2$
Rokushou (malachite, verdigris)	Moderate green	$CuCO_3 \cdot Cu(OH)_2$
Gofun (powdered calcium carbonate)	White	$CaCO_3$
Entan (red lead)	Strong reddish orange	Pb_3O_4
Shu (vermilion)	Vivid reddish orange	HgS
Bengara (red iron oxide)	Dark red	Fe_2O_3

[a] Special grade reagents (Kanto Chemical) equivalent to principal ingredient of pigments

vessel (0.5 dm^3) and then set in an incubator at 40°C. After 28 days, discoloration of the material samples was observed by visual inspection. The color difference (CIEΔE^*_{ab}) of discolored samples was measured with a visible and ultraviolet spectrophotometer. Hinokitiol (about 1 mmol) and acetic acid (5 mmol) were used as the volatile reagents. For comparison, the same experiments were conducted with distilled water (15 mmol) and no reagent (control).

Analyses of the deteriorated products

To investigate substances causing the deterioration in artifact materials, the deteriorated products (corrosion or discoloration) were analyzed by XRD (JDX-3500, JEOL) and XPS (ESCA5400MC, ULVAC-PHI).

In XRD analyses, a copper target X-ray tube was used. The tube voltage was 40 kV and the tube current was 370 mA. The divergence slit and scatter slit were set to 1 degree, and a 0.2 mm receiving slit was used.

In XPS analyses, monochromatic Al K_α radiation was used and the output was 14 kV and 350 W, the measurement diameter was 1.1 mm, base pressure was about 10^{-7} Pa, and the take-off angle was 75 degrees.

Results and discussion

Influences of VOCs from wood on metals and pigments

In the desiccators containing the wood samples, the temperature was maintained at about 30°C, but humidity gradually increased to 70%–75% (final) from 55%–60% (initial). From the results of preliminary experiments, the humidity of the control experiment was presumed to be about 85%–90%.

Changes (corrosion or discoloration) in the material samples are shown in Table 2.

The influences of wood-based VOCs on the artifact material deteriorations differed greatly with wood species. Although humidity was lower than the control, the metal samples were discolored (corroded) by VOCs from all wood species, particularly from western red cedar and spruce. Iron samples changed to yellowish red and yielded brown speckles with western red cedar, yielded dark brown deposits with spruce, and were slightly tarnished with kiri and sugi. In the case of copper, the samples were discolored to yellowish orange and yielded brown speckles with western red cedar, and were discolored to reddish brown and yielded brown speckles with the others.

Regarding the pigments, mitsudasou deteriorated very easily in this experimental condition. The samples were discolored yellow to white, all over with spruce, and partially (at the edges) with kiri. With western red cedar, the sample was discolored to yellowish gray. With sugi, discoloration was not observed. Enpaku was discolored from white to yellow only with western red cedar. Rokushou was discolored moderate green to yellowish green only with western red cedar. By visual inspection, discoloration was not observed in gofun, entan, shu, and bengara.

GC-MS analyses of VOCs from wood

With the influence on artifact materials changing with wood species, the VOCs of each wood were analyzed by GC-MS (Fig. 1). In this study, the total volatile organic compounds (TVOC), acetic acid,[15] and hinokitiol were selected as targets for investigation from among the various VOCs. Museums have so far been concerned with the effects of acetic acid from adhesives, etc. on artifacts; on the other hand, the influences of hinokitiol have not been studied, but it is known to react readily with iron, copper, and basic compounds.[16–19] Because it is necessary to consider urgent countermeasures for acidic conditions at present, this study focused on these ingredients. The deterioration effects of

Table 2. Changes in artifact materials by volatile compounds from wood

Species	Metal		Pigment[a]		
	Iron	Copper	Mitsudasou	Enpaku	Rokushou
Western red cedar	+++ Yellowish red with brown speckles over part of the surface	+++ Yellowish orange and some dark brown speckles	Yellowish gray [17.0]	Yellow [16.0]	Yellowish green [6.3]
Spruce	++ Dark brown deposit	++ Reddish brown and some dark brown speckles	White [28.3]	NC	NC
Kiri	± Slight tarnish	+ Reddish brown and some dark brown speckles	White (edges) [14.7]	NC	NC
Sugi	± Slight tarnish	+ Reddish brown and some dark brown speckles	NC	NC	NC
Control	NC	NC	NC	NC	NC

Extent of metal discoloration expressed by four grades from +++ (remarkable) to ± (very slight). Figures in square brackets show color difference (CIEΔ*ab) from control
NC, no change (visual inspection)
[a] Gofun, entan, shu, and bengara: no change (visual inspection)

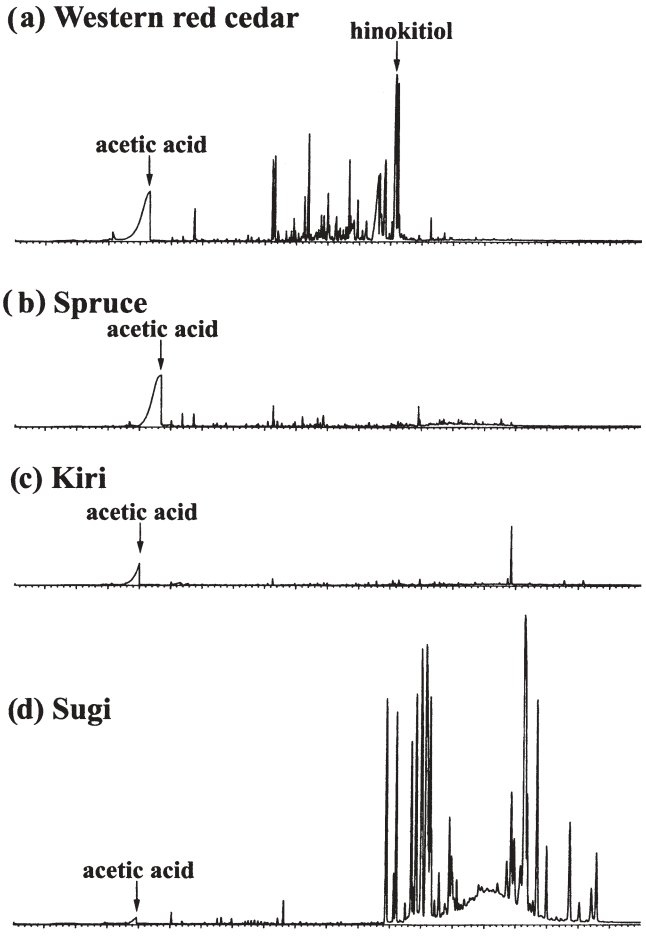

Fig. 1a–d. Gas chromatography-mass spectrometry spectra of volatile organic compounds from wood. **a** Western red cedar, **b** spruce, **c** kiri, and **d** sugi

compounds other than acetic acid and hinokitiol will be studied in a future study.

Table 3 shows each ingredient's peak area, percentage of TVOC, and discolored artifact material. The results of GC-MS analysis and the relation to deterioration of artifact material are summarized below:

In western red cedar, the level of TVOC was about one third of that of sugi, and almost all ingredients appeared with a retention time (RT) of up to 25 min. Acetic acid (RT 7–9 min) and hinokitiol (RT 24.3 min) were detected in larger quantities than the other species. Metal samples were remarkably deteriorated (corroded) and mitsudasou was discolored to yellowish gray. Only this type of wood out of the four species caused discoloration of enpaku and rokushou.

In spruce, although the peak area of its TVOC was about one seventh of that of sugi, the quantity and the content ratio of acetic acid were the largest among the four species. Mitsudasou was discolored to white, and metal samples were severely deteriorated (corroded).

In kiri, although it had the least quantity of TVOC of the four species (about 1/15 of that of sugi), the content ratio of acetic acid was large. Mitsudasou was partially discolored to white.

In sugi, the peak area of its TVOC was the largest, and the percentage contents of compounds which had an RT of longer than 24 min were high. The amount of acetic acid was the smallest and hinokitiol was not detected. Discoloration in material samples was not observed (except copper).

Individual influences of the specific substances in VOCs from wood on metals and pigments

Volatile reagents vaporized completely, except hinokitiol, which vaporized about 0.1 mmol (Table 4). Table 5 shows the changes (corrosion or discoloration) in artifact materials.

For the metals, iron was discolored remarkably by acetic acid and tarnished slightly by hinokitiol. Copper was discolored to a reddish color by acetic acid and distilled water, and gray deposits were observed on the surface after exposure to hinokitiol.

For pigments, mitsudasou was discolored from yellow to white by acetic acid. Enpaku was partially discolored from white to yellow by hinokitiol. It was not discolored by acetic acid, but a sign, produced by recrystallization after deliquescence, was observed. Rokushou was discolored from moderate green to yellowish green by hinokitiol and to bluish green by acetic acid. Visually, there was no discoloration of gofun, entan, shu, and bengara.

From the comparison of the influences of wood VOCs and volatile reagents, it was presumed that hinokitiol in western red cedar participated in the discoloration of enpaku and rokushou, and acetic acid in western red cedar, spruce, and kiri participated in the discoloration of mitsudasou.

Analyses of the deterioration products

The deterioration products of iron and mitsudasou after exposure to acetic acid, in which remarkable deterioration was observed, and those of copper after exposure to hinokitiol were analyzed.

The XRD spectra of the deterioration products of iron exposed to acetic acid (I-A) and the control (I) are shown in Fig. 2. The peaks were compared with spectra of authentic library samples. The result suggested several types of deteriorated products, including FeO(OH), $Fe(OH)_2$, and others, although the other compounds could not be identified. In the XPS analysis of I-A, oxygen and carbon were detected in addition to iron (Fig. 3). In the full analyses of the chemical shift of each peak, the electronic states of Fe2p and O1s suggested FeO(OH). The electronic state of carbon was similar to that of acetic acid, but the peak intensity was weak compared with when it was left in a normal atmosphere, indicating that an acetic acid derivative was not obtained.

There was no large difference in XRD spectra between the deterioration products of copper derived by exposure to hinokitiol (C-H) and the control (C) (Fig. 2). In the XPS analysis of C-H, oxygen and carbon were detected in addition to copper (Fig. 3). The intensity of carbon peaks

Table 3. Gas chromatography-mass spectrometry analyses of total volatile organic compound (TVOC), hinokitiol, and acetic acid from wood and remarkably changed artifact materials

Species	TVOC	Hinokitiol		Acetic acid		Remarkably changed artifact materials
	Peak area $\times 10^8$	Peak area $\times 10^8$	Percentage of TVOC	Peak area $\times 10^8$	Percentage of TVOC	
Western red cedar	227 (1)	5.63 (1)	2.5 (1)	8.06 (1)	3.6 (1)	Iron, copper, mitsudasou, enpaku, rokushou
Spruce	98.4 (0.4)	ND	–	8.88 (1.1)	9.0 (2.5)	Iron, copper, mitsudasou
Kiri	45.8 (0.2)	ND	–	1.87 (0.2)	4.1 (1.1)	Mitsudasou (edges only)
Sugi	683 (3)	ND	–	0.38 (0.1)	0.1 (0.02)	–

Figures in parentheses show ratio (western red cedar = 1)
ND, not detected

Table 4. Amount of volatilized reagents

Reagents	Before experiment		Amount of volatilization
	mg	mmol	
Hinokitiol	139	0.8	14 mg (0.09 mmol)
Acetic acid	307	5.1	~100%
Distilled water	276	15.3	~100%

Table 5. Changes in artifact materials caused by volatile reagents

Reagents	Metals		Pigments[a]		
	Iron	Copper	Mitsudasou	Enpaku	Rokushou
Hinokitiol	+ Tarnish	++ Gray deposit	NC	Yellow [14.3]	Yellowish green [9.9]
Acetic acid	+++ Dark brown deposit	+ Reddish orange	White[b] [32.5]	No discoloration[b]	Blue [17.2]
Distilled water	NC	± Reddish brown	NC	NC	NC
Control	NC	NC	NC	NC	NC

[a] Gofun, entan, shu, and bengara: no change (visual inspection)
[b] There was a trace of deliquescence. Some reactions may have occurred

increased, and their electronic state was similar to that of hinokitiol. The results suggested that hinokitiol formed complexes with copper or adsorbed onto it.

The XRD spectrum suggested the main deterioration products of mitsudasou after exposure to acetic acid (M-A) were $3[Pb(CH_3COO)_2]\cdot PbO\cdot H_2O$ (Fig. 2).

Because the amount of deterioration products by the VOCs from wood was very small, XRD analysis was difficult. Therefore, investigation of the causal substances and the deterioration mechanism by comparing with samples that had been exposed to volatile reagents was not performed.

Conclusions

The conclusions from this study are summarized as follows:

1. The influences on artifact materials varied greatly with the type of wood, and depended on the specific components, such as hinokitiol or acetic acid, rather than the amount of TVOC.
2. Hinokitiol and acetic acid corroded metals and discolored pigments under this experimental condition. Western red cedar and spruce, which are rich in these components, deteriorated artifact materials more

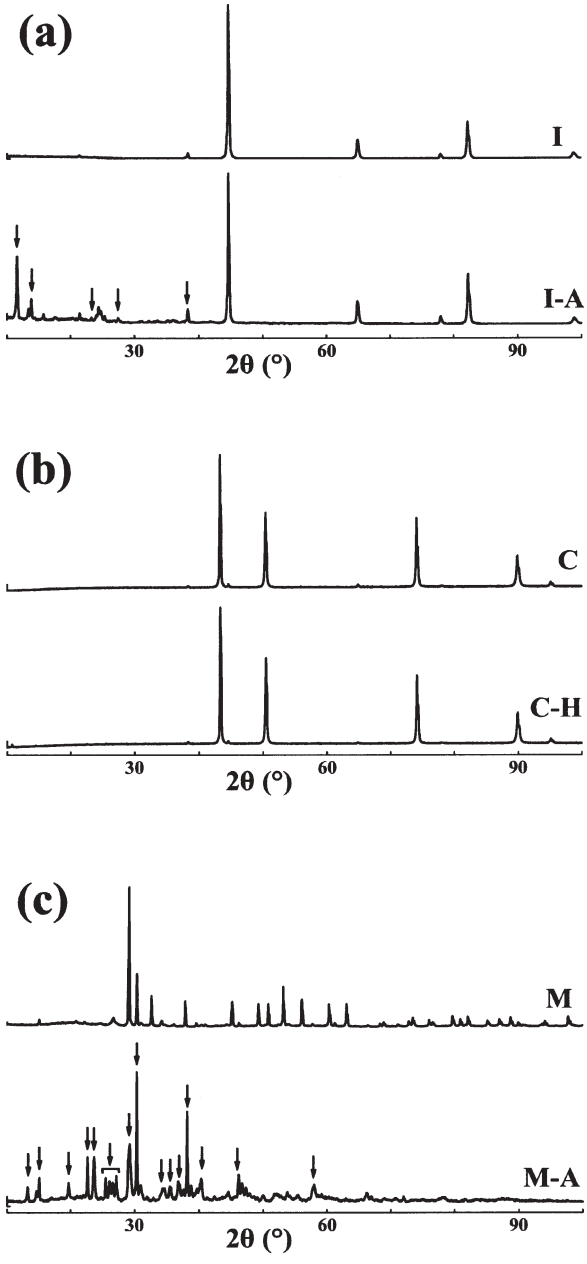

Fig. 2a–c. X-ray diffraction spectra of artifact materials. **a** Iron sample. *I*, control; *I-A*, exposed to acetic acid; *arrows*, peaks of FeO(OH) or $Fe(OH)_2$. **b** Copper sample. *C*, control; *C-H*, exposed to hinokitiol. **c** Mitsudasou sample. *M*, control; *M-A*, exposed to acetic acid; *arrows*, peaks of $3[Pb(CH_3COO)_2]\cdot PbO\cdot H_2O$

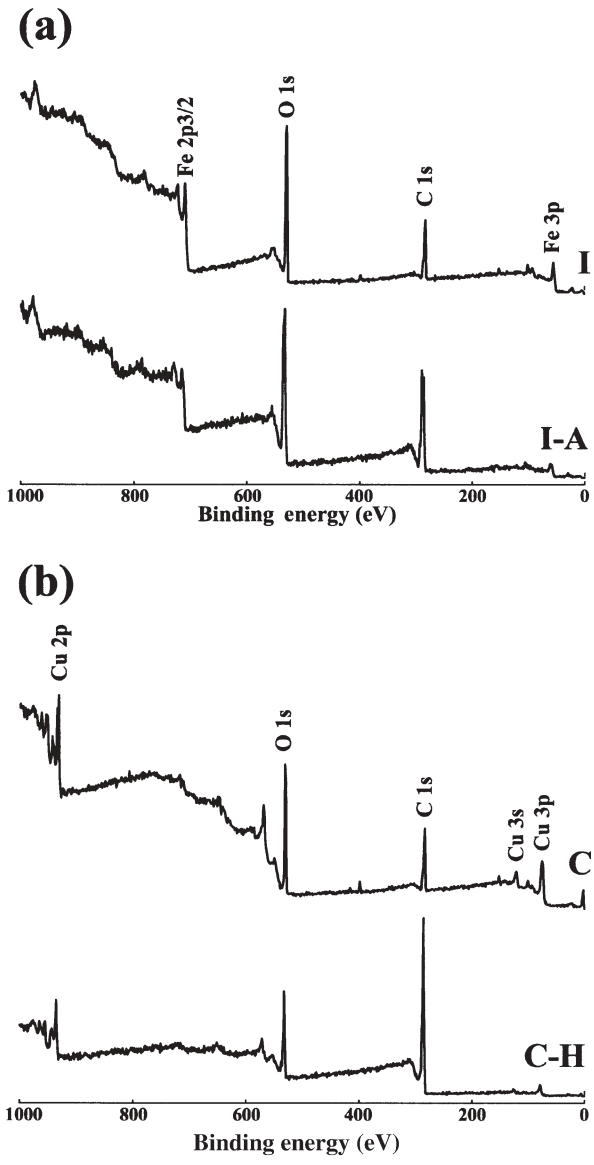

Fig. 3a,b. X-ray photoelectron spectra of artifact materials. **a** Iron sample. *I*, control; *I-A*, exposed to acetic acid. **b** Copper sample. *C*, control; *C-H*, exposed to hinokitiol

severely than sugi and kiri. Of the four types of wood, only western red cedar discolored enpaku and rokushou. It is likely that the causal substance is hinokitiol.

3. It is suggested that one of the main deterioration products caused by acetic acid was FeO(OH) in the case of iron, and $3[Pb(CH_3COO)_2]\cdot PbO\cdot H_2O$ in the case to mitsudasou.
4. The deterioration products of copper from exposure of hinokitiol were not detected by XRD analysis. XPS analysis suggested the participation of hinokitiol, but no further information was obtained.

The fact that hinokitiol, contained in western red cedar in large amounts, discolored enpaku and rokushou is a very serious problem. The influence on artifact materials will not be as extreme as in these experiments, because the concentration of wood VOCs under the practical conservation conditions is not as high as in these experiments, and pigments are used after mixing with glue and are not directly exposed. However, full consideration of VOC characteristics, not only the amount of TVOC from wood, may be very important when selecting the interior material for museum storage rooms or studying methods of preventing deterioration.

The causal substances, mechanism, specific conditions (concentration, temperature, humidity, and so forth) of the deterioration, the method of removing causal substances,

and improvement of wood interior materials will be examined in our next study.

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