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# The color change analysis of historic wooden remains after fire-suppression by fluorinated chemical gases

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## Abstract

Many wooden Chinese historic buildings are destroyed due to the ravages of frequent fire disasters. The fire risk of historic buildings are highly enlarged since a long-time weathered wooden structures in the natural environment. The clean fire-extinguishing technology using fluorinated chemical gases to put out a historic building fire rapidly at the initial stage is highly recommended and widely used. However, the gaseous hydrogen fluoride (HF) yielded during the fire suppression process could be a potential method to result in secondary damage due to its corrosiveness. Nowadays, experiments were employed to clarify the effect of fire suppression on the surface of historic wooden buildings. Five traditional fluorinated chemical gases, H-37, FK-5-1-12, H-1323, H-2402, and H-1301, are used to suppress a fixed flame. The wooden samples, including a Dao Talisman board, a painting paper, and wooden chips, are placed in a chamber. Wooden chips consist of traditional and weathered samples (acting as the Chinese historic buildings). The concentration of gaseous products yielded from fire suppression are monitored by a gas-FTIR from ABB, and the surface analysis is conducted by a Quanta FEG SEM–EDX from FEI. It is observed that flame enhancement happens at the early stage of fire suppression and varies with fire agents. The amount of F-deposited on the wooden surface is positively correlated with a total amount of gaseous HF. The color change mechanism of the wooden surface is comprehensive, although the amount of HF is a leading factor. The influence of HF on color change depends on the amount of both gaseous H<sub>2</sub>O and HF. It is concluded that the value of L\* of the traditional chip is much easier to be reduced comparing with weathered samples with the same wood grain. The reduction of b\* value of weathered samples is much larger than the traditional ones. It suggests the weathered chips show a color shift toward blue because of fire suppression. The present study hopes to provide a basic acknowledgment for the comprehensive understanding of secondary damage caused by fire suppression.

**Keywords:** Wooden culture heritage, Fire suppression, Hydrogen fluoride, Corrosiveness, Color change

## Introduction

Historic buildings are an important cultural heritage since the potential historical and cultural values are precious and non-renewable [1]. However, a great many historic buildings in the world, unfortunately, had been

destroyed because of the ravages of fire disasters [2–5], for example, the Gothic spire of the Notre Dame Cathedral [6], the National Museum of Brazil [7], the SHURI Castle World Heritage site [8] and so on. The fire protection of historic buildings has been a big challenge in the world. It is a fact that China has retained many historic buildings in the long historical process since it is an ancient country of historical civilization [9]. In addition, a great many historic buildings are recognized recently and recorded in the Chinese official database to protect

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them. The damage of historic buildings by fire is also devastating and serious in China [10] since wooden structures characterize most Chinese historic buildings. This is different from other countries. Wooden structures are much easier to be ignited because of the severe deterioration caused by natural weathering. The fire extinguishing agents with a high-extinguish efficiency and environmental-friendly merit is highly recommended to put out a historic building fire at the early stage. The secondary damage from fire suppression to residual materials should be reduced. Although the fire-extinguishing performance of water-mist in historic buildings has been tried [11], clean chemical gas agents are needed. A water-based fire extinguishing agent is composed of water and other chemical additives. After use, it will cause secondary damage to corroded wood, and wastewater will enter surface water, soil and other environmental media, which is potentially harmful to human health and the natural environment. Fluorinated chemical gases are gas fire extinguishing agents. Although they are mainly chemical fire extinguishing agents, the gas has no residue after complete combustion, does not produce solid or liquid reactants, does not cause secondary damage to the wood, and can reduce the gas itself and The environmental pollution caused by reactants is more environmentally friendly. The fluorinated chemical gas agents have been widely used in supercomputer rooms, historic buildings, and so on due to their cleanliness [12]. Nowadays, it has been widely used in the fire protection of historic buildings [13]. However, there are still many uncertain issues available. One of them is that the color change of historic wooden buildings after fire suppression using fluorinated chemical gases because of HF. From a chemical viewpoint, wood is composed of cellulose (40–50%), hemicelluloses (20–30%), lignin (20–30%) and extractives (3–10%). These amounts vary in different wood species [14]. HF is extremely corrosive and will cause severe damage to the appearance of the wood and its internal fiber structure, thereby affecting the color change of the wood.

There have been many attempts in the literature to develop approaches that address the HF generation mechanism during fire suppression. The main emphasis of available researches are focused on HF yield amount [15] and mechanism of  $\text{CF}_3\text{H}$  [16], thermal decomposition mechanism of  $\text{CHF}_2\text{CF}_3$  [17, 18] and other Halon alternatives [19], HF production of  $\text{CF}_3\text{CHFCF}_3$  [20], thermal decomposition of  $\text{trans-CF}_3\text{CH=CHCF}_3$  [21], HF pyrolysis of  $\text{CF}_2\text{H}_2$  [22], thermal decomposition of  $\text{CF}_3\text{CBrH=CH}$  [23] and so on. Although the yield of corrosive gases has been reported to impact potential damage on the surface of materials [24], the comprehensive study of the influence of HF on the color change of

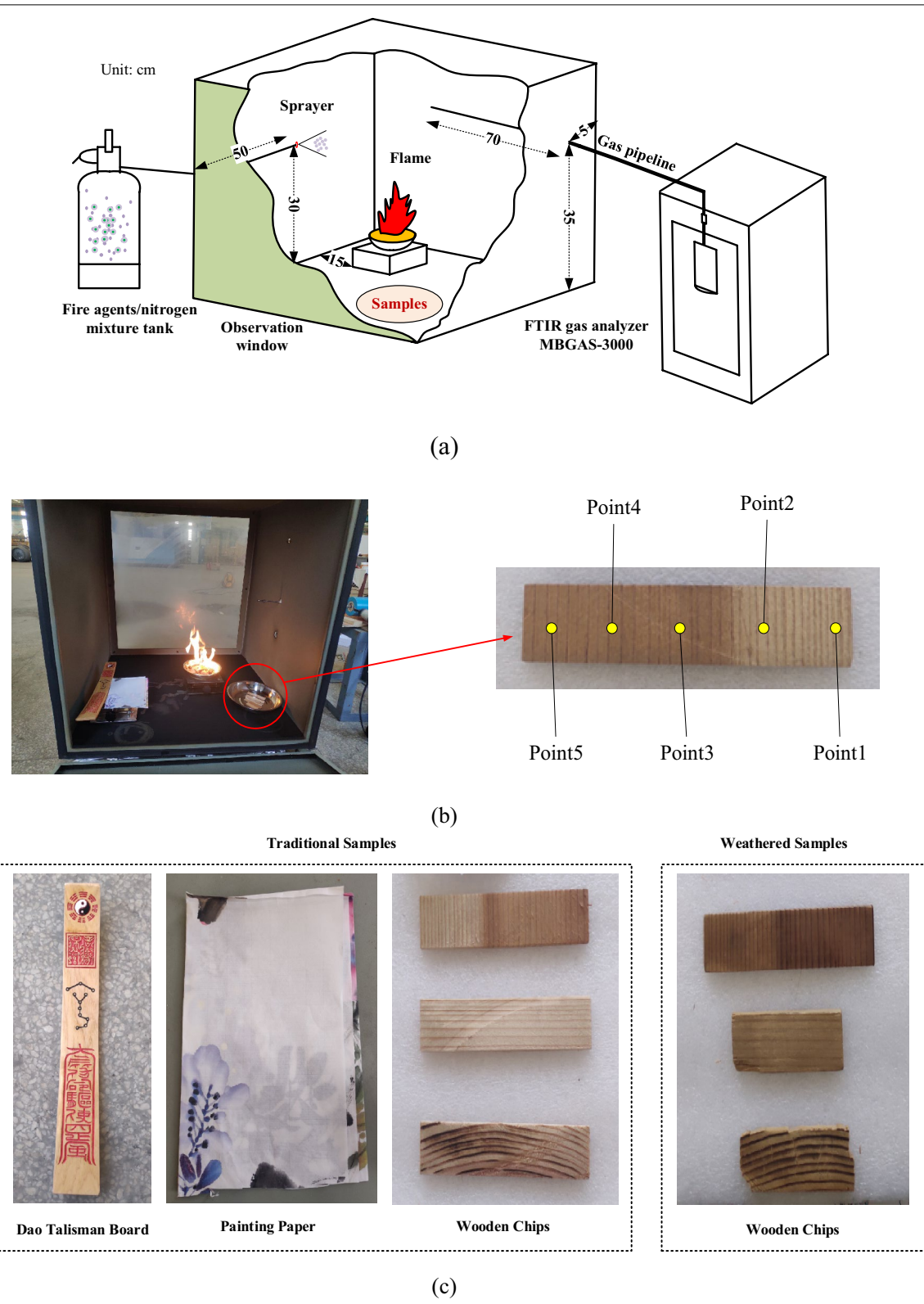
wooden materials is still unavailable. Otherwise, previous works were just focused on the mechanism of HF generation from the chemical aspects but not the influence of HF on the color change. The color of wood is that various pigments contained in wood cells penetrate into the cell wall to make the wood show different colors. The color of wood can be used as one of the characteristics of wood identification. After high temperature, the color of wood will change significantly, and the change of color is often the preliminary judgment basis for the detection and identification of building structure after fire [25]. From a chemical viewpoint, wood is composed of cellulose (40–50%), hemicelluloses (20–30%), lignin (20–30%) and extractives (3–10%). These amounts vary in different wood species [14]. HF is extremely corrosive and will cause severe damage to the appearance of the wood and its internal fiber structure, thereby affecting the color change of the wood. However, the deep understanding of the HF effect on the color change of wooden samples is of great necessity since Chinese historic buildings are characterized by a wooden structure. The basic investigation about it should be conducted before the engineer application. The color change of commonly used fluorinated chemical gas on wooden samples is mostly misunderstanding.

In this contribution, a series of tests are conducted to clarify a detailed understanding of HF influence on the color change of wooden samples. Authors detail works involving the HF concentration varying types of fire agents, explore the relationship HF amount versus color change, and discuss the color change difference between traditional and weathered wooden chips.

## Experiment and method

### Fire suppression tests

The experiment method was according to Fig. 1. The fire test facility consisted of a chamber (size in  $L \times W \times H = 1.0 \text{ m} \times 1.0 \text{ m} \times 1.0 \text{ m}$ ), a window opening (size in  $L \times W = 1.0 \text{ m} \times 1.0 \text{ m}$ ), a pool plate (diameter = 0.18 m), a sample plate (diameter = 0.18 m), specimens (fresh paper paintings or weathered timber chips), a chemical gas tank (2 L) and an FTIR (Fourier Transform infrared spectroscopy) gas analyzer. A sketch model of the test was detailed in Fig. 1a. The chamber had an inner surface area of  $6.0 \text{ m}^2$ , just as shown in Fig. 1b. The fuel of pool fire was gasoline, which was used to provide a fixed fire for suppression. A little water was added in the plate before the addition of fuels to control a uniform combustion speed. A little water was also added to the chamber to avoid the influence of dust. The samples included a Dao Talisman board, a painting paper, and wooden chips (see Fig. 1c). The physical information of wooden chips could be found in a previous art [26]. Description of the



**Fig.1** Experimental apparatus description. **a** A sketch model. **b** The experimental apparatus. **c** The samples

accelerated weathering process of wooden chips had been reported previously [27]. The width of the sample was about 2 cm. Generally, the woodgrain of the column is vertical, and the woodgrain of the beam is horizontal. So the weathered wooden chips, including three wood grain orientations, were used to simulate the wooden surface of Chinese historic buildings. The gas concentration and distribution were determined by an MBGAS-3000 FT-IR Gas Analyzer bought from ABB. The sample cell made of aluminum was 1-L volume and with resistant mirrors. The spectral range was  $500\text{ cm}^{-1}$ – $4500\text{ cm}^{-1}$ . The pump exhaust speed was about 10 L/min. During the whole test, the gas sampling tube was heated to  $200\text{ }^{\circ}\text{C}$ . The smoke was firstly treated by an adsorption facility and then went through the gas cell of FTIR. Calibration of the whole test was conducted before a test. Then the pump of FTIR exhausted the air from the chamber for 2 h.

The fire extinguishing concentration (V/V %) used in the current work of H-2402, H-1323, H-1301, H-37 and FK-5-1-12 are 5.00%, 3.64%, 5.00%, 8.04% and 5.30%, respectively [28, 29]. The releasing press is 2.0 MPa. A camera (Canon Rebel T3i 1080P) is used to record the fire suppression images at 30 frames per second with a spatial resolution of 0.47 mm/pixel. All tests are performed under a hood without ventilation. Ambient temperature and moisture are  $19\text{--}24\text{ }^{\circ}\text{C}$  and  $15\text{--}36\%$ , respectively.

### Fluorinated chemical gases

In the current study, five typical chemical gases are employed. The H-2402 ( $\text{C}_2\text{F}_4\text{Br}_2$ , CAS No.124-73-2, 99.7%), H-1323 ( $\text{C}_3\text{H}_2\text{BrF}_3$ , CAS No.1514-82-5, 99.7%), H-1301 ( $\text{CBrF}_3$ , CAS No.75-63-8, 99.7%), H-37 ( $\text{C}_3\text{HF}_7$ , CAS No.431-89-0, 99.7%) were obtained from Jiujiang Middle Ship Chang'an Fire Equipment Co., Ltd. FK-5-1-12 ( $\text{C}_6\text{F}_{12}\text{O}$ , CAS No. 756-13-8, 99.7%) was phased from Sinochem Lantian Co., Ltd.

### Colorimetric measurement

Color measurements of weathered or traditional wooden specimen surfaces were recorded using a Chroma Meter according to ASTM D 2244-89 [30]. The color change  $\Delta L^*$ ,  $\Delta a^*$ , and  $\Delta b^*$  were calculated based on the color coordinates before and after fire suppression tests. Three replicates per point and five repeats per location point of samples were measured on each specimen before and after the fire suppression. The total color difference ( $\Delta E^*$ ) was determined for each treatment group as follows:

$$\Delta a^* = a_f^* - a_i^*$$

$$\Delta b^* = b_f^* - b_i^*$$

$$\Delta L^* = L_f^* - L_i^*$$

$$\Delta E^* = \left[ (\Delta a^*)^2 + (\Delta b^*)^2 + (\Delta L^*)^2 \right]^{1/2}$$

where  $\Delta a^*$ ,  $\Delta b^*$ , and  $\Delta L^*$  are the changes between the initial (before the test) and final interval values (after fire suppression) of  $a^*$ ,  $b^*$  and  $L^*$ , respectively. An increase in  $L$  believes the sample is lightening. A positive  $\Delta a$  indicates a color shift toward red, and a negative  $\Delta a$  suggests a color shift toward green. A positive  $\Delta b$  illustrates a shift toward yellow, and a negative  $\Delta b$  means a shift toward blue [31].

### Test facilities

An MBGAS-3000 FT-IR Gas Analyzer bought from ABB is used. It is sized in a dimension  $46\text{ cm (W)} \times 70\text{ cm (H)} \times 27\text{ cm (D)}$ . The sample cell made of aluminum is a 1-L volume (temperature to  $200\text{ }^{\circ}\text{C}$ ) and with resistant mirrors. It is equipped with a deuterated triglycine sulfate detector (DTGS) detector. The spectral range is  $500\text{ cm}^{-1}$ – $4500\text{ cm}^{-1}$ . The pump exhaust speed is about 10 L/min.

A Chroma Meter, called NR-200 model, is bought from Shenzhen 3NH Technology Co. Ltd. Spectrometer software CSCQ3 helps perform color difference analysis, color difference cumulative analysis, chromaticity index, color sample database management, and so on. The current study transforms spectral data into CIELAB color coordinates ( $L^*$ ,  $a^*$  and  $b^*$ ) based on a D65 light source. NR200 precision colorimeter features an 8/d viewing geometry. The diameter of the measuring aperture is 8 mm. The errors between each piece of equipment are lower than  $0.5\Delta E^*_{ab}$ . The repeatability of measurement indicates that the standard deviation is within  $0.08\Delta E^*_{ab}$ .

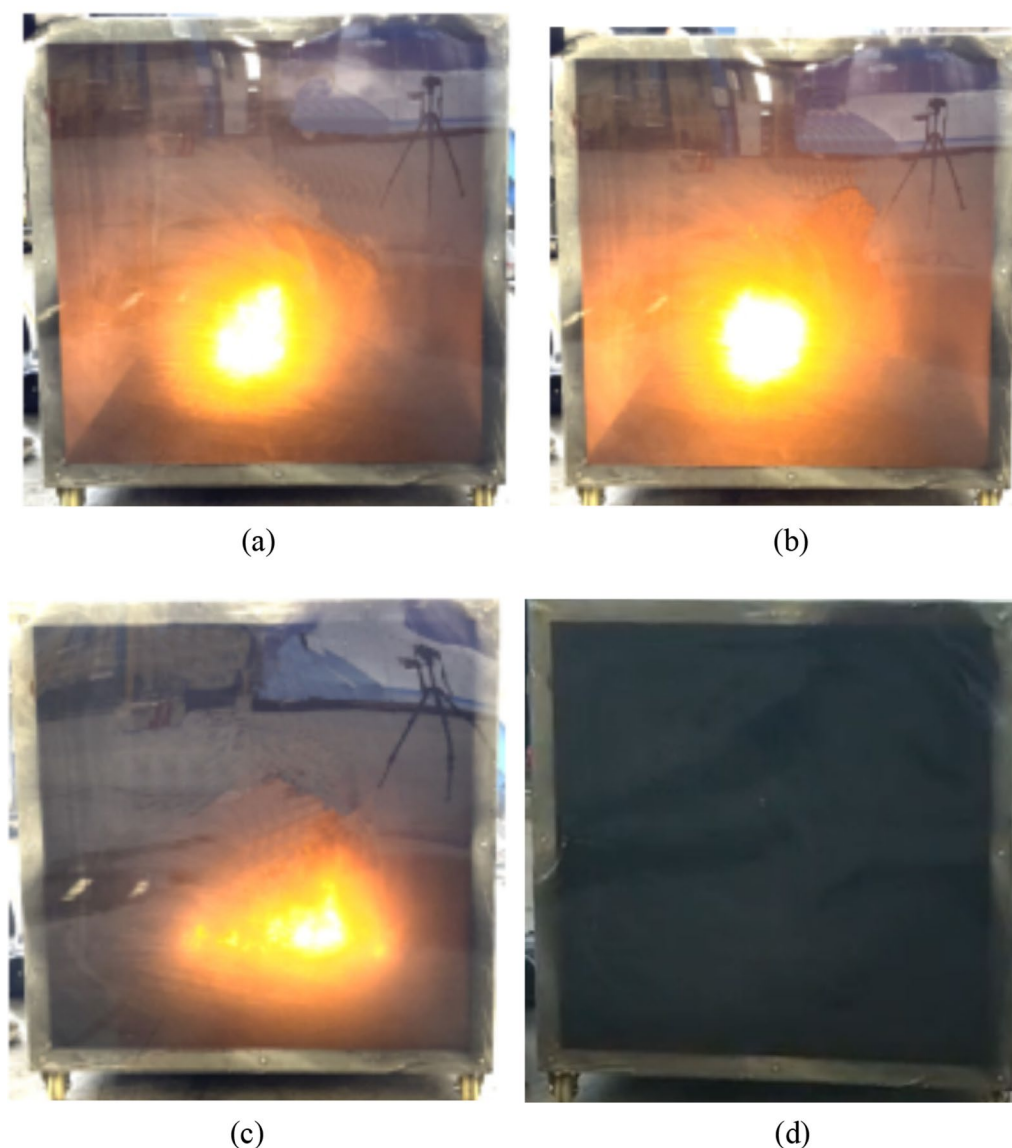
The surface morphology of the weathered timber was observed with a Quanta 650 FEG SEM at 30 kV from FEI. The EDX analysis is also conducted on it.

## Results and discussion

### The results of fire suppression using fluorinated chemical gases

In the current work, five typical fluorinated chemical gases are employed to inhibit a fixed fire. Chemical gases are comprised of H-2402, H-1323, H-1301, H-37, and FK-5-1-12. It was observed that the fire suppression time of the above chemical gases is 9 s, 9 s, 9 s, 12 s, and 9 s, respectively. The description of fire suppression performed by FK-5-1-12 is shown in Fig. 2. After keeping a pool fire for 10 s (shown in Fig. 2a), FK-5-1-12 is injected from the sprayer. The flame was observed to be enlarged at the early stage (Fig. 2b). This is inferred to





**Fig.2** The description of fire suppression using FK-5-1-12 **a**  $t=0\text{ s}$  **b**  $t=3\text{ s}$  **c**  $t=6\text{ s}$  **d**  $t=9\text{ s}$

be consistent with a combustion promotion phenomenon reported previously [32]. The process of the action of fire extinguishing agent and flame can be divided into two parts: First, the fire extinguishing agent is decomposed into small molecules containing fluorine by heat, and then these inhibitory groups react with active free radicals. Taking H-37 as an example, first half or less of H-37 is decomposed by HF elimination reaction, and the remaining H-37 is decomposed by free radical induced reaction or homolytic reaction. Although fluorinated olefins account for a relatively small amount of fluorine-containing radical pools generated by decomposition, they are very important intermediates in the decomposition

process of H-37. Due to the existence of double bonds in fluorinated olefins, the energy barriers for addition reactions with  $\cdot\text{H}$ ,  $\cdot\text{O}$ ,  $\cdot\text{OH}$ , and  $\text{O}_2$  are very low, and fluorinated olefins can be decomposed very quickly through radical addition reactions. Obviously, the fluorine-containing radical pool generated by the thermal decomposition of hydrofluoroolefins accounts for a high proportion of small fluorine-containing olefin molecules. Therefore, in a flame where  $\cdot\text{H}$ ,  $\cdot\text{O}$ , and  $\cdot\text{OH}$  radicals exist in large quantities, the radical addition reaction will be greatly affected. Accelerate the decomposition of hydrofluoroolefins. Since most of the reactions between fluorine-containing small molecules and active free radicals are

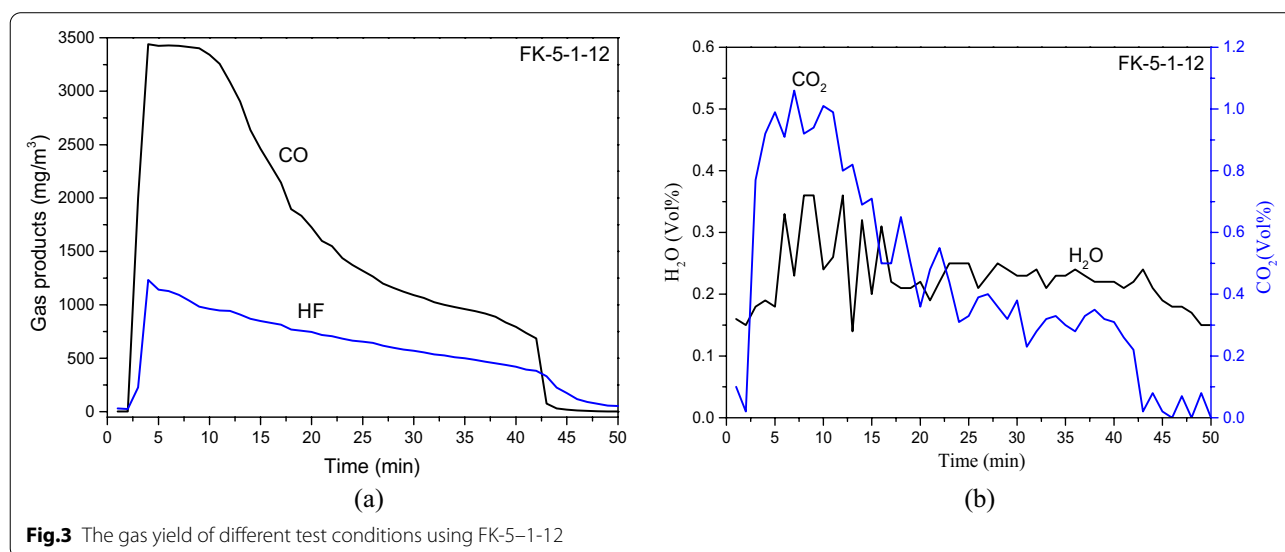
exothermic reactions, the overall heat release rate is accelerated. When the concentration of the extinguishing agent is insufficient, the amount of active free radicals captured by the inhibitor group has little effect on the combustion system, but it accelerates the release of heat, which leads to the strengthening of the overall combustion reaction. This is the combustion-promoting effect of hydrofluoroolefins main reason. Then the FK-5-1-12 diffused in the chamber surrounding the fixed flame, as shown in Fig. 2c. Finally, it is suppressed after flame fluctuation due to the inhibition of radical chain reaction. It is reported previously that most halogenated extinguishing agents added at sub-suppressing concentration result in a combustion enhancement and lead to an increase in both flame size and fluctuation. It is mainly because of the highly exothermic reactions between fluorine-containing groups and  $\cdot\text{H}$ ,  $\cdot\text{OH}$  radicals [33]. High fire-extinguishing efficiency is able to provide good fire protection of historical items from fire. Therefore, the fire-extinguishing time is one of the critical indexes when the fluorinated chemical gas is used in the fire protection of the historic building.

In addition, a variety of gaseous products are yielded. It includes HF, CO,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and so on. The description of main gas products varying test times is illustrated in Fig. 3. The composition of gas products is observed to vary greatly from fluorinated chemical gases. One of the corrosive gas products is HF. The peak of CO in gas products of fire suppression test using H-37, H-2402, FK-5-1-12, H-1323 and H-1301 is 3034.08  $\text{mg}/\text{m}^3$ , 442.49  $\text{mg}/\text{m}^3$ , 3439.43  $\text{mg}/\text{m}^3$ , 4312.6  $\text{mg}/\text{m}^3$  and 6199.47  $\text{mg}/\text{m}^3$ , respectively. The peak of  $\text{CO}_2$  yield in gas products of fire suppression test using H-37, H-2402, FK-5-1-12, H-1323, and H-1301 is 1.2 vol %, 0.8 vol %, 1.1 vol %, 0.4 vol %, and 0.5 vol %, respectively. The total amount of  $\text{CO}_2$  during 50 min fire suppression test using H-37, H-2402, FK-5-1-12, H-1323 and H-1301 is 27.5 vol %, 12.6 vol %, 21.9 vol %, 4.0 vol % and 9.4 vol %, respectively. The low yield of  $\text{CO}_2$  is obtained when H-1323 is used.

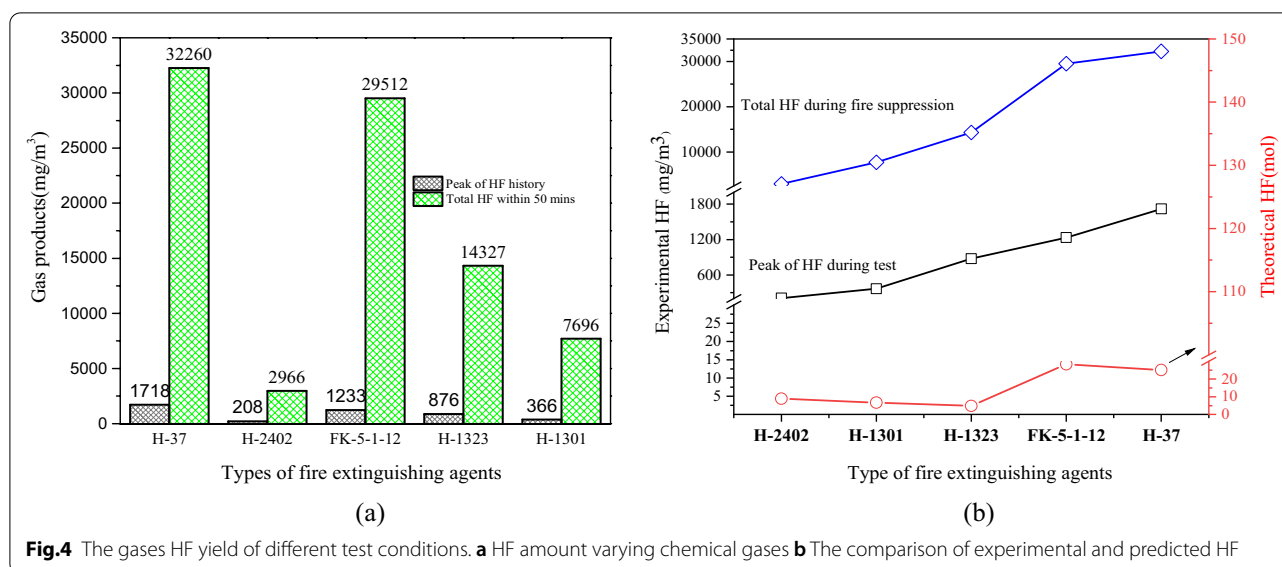
It is a fact that when HF gas is mixed with gaseous  $\text{H}_2\text{O}$ , its corrosiveness is highly improved [34, 35]. Reduction of gaseous  $\text{H}_2\text{O}$  is a potential method to lower the hazard impacted to the surrounding environment during fire suppression. Therefore, the  $\text{H}_2\text{O}$  concentration is also under discussion of current work. The peak of  $\text{H}_2\text{O}$  yield in gas products of fire suppression test using H-37, H-2402, FK-5-1-12, H-1323 and H-1301 is 0.22 vol %, 0.60 vol %, 0.35 vol %, 0.44 vol % and 0.49 vol %, respectively. The total amount of  $\text{H}_2\text{O}$  during 50 min fire suppression tests using H-37, H-2402, FK-5-1-12, H-1323, and H-1301 is 10.2 vol %, 9.4 vol %, 11.2 vol %, 8.5 vol %, and 13.8 vol %, respectively. The amount of  $\text{H}_2\text{O}$  varies from 8.5 vol % to 11.2 vol %.

#### a CO and HF b $\text{CO}_2$ and $\text{H}_2\text{O}$ .

It is reported that after pretreatment by HF, some morphological changes of wood were observed, indicating partial damage in biomasses structure although, their main framework was unchanged [36]. In addition, HF contribute to Si diminution [36, 37]. The reduction of HF is a continuous goal for various researches which lasts for many years. The HF history is summarized in Fig. 4a. The peak of HF yield in gas products of fire suppression test using H-37, H-2402, FK-5-1-12, H-1323, and H-1301 are 1718.9  $\text{mg}/\text{m}^3$ , 208.4  $\text{mg}/\text{m}^3$ , 1233.8  $\text{mg}/\text{m}^3$ , 876.8  $\text{mg}/\text{m}^3$ , and 366.5  $\text{mg}/\text{m}^3$ , respectively. The total amount of HF during 50 min fire suppression test using H-37, H-2402, FK-5-1-12, H-1323 and H-1301 are 32,260.4  $\text{mg}/\text{m}^3$ , 2966.0  $\text{mg}/\text{m}^3$ , 29,512.9  $\text{mg}/\text{m}^3$ , 14,327.9  $\text{mg}/\text{m}^3$  and



**Fig. 3** The gas yield of different test conditions using FK-5-1-12



7696.8 mg/m<sup>3</sup>, respectively. It is clarified that the yield of HF is low when H-1301 and H-2402 are used. The final product of fluorinated chemical gases decomposed at high temperature contains HF. The concentration of HF generated is proportional to the weight of F in the molecular of the gases. Therefore, HF-37 and FK-5-1-12 have the most HF production. To avoid a high yield of HF, the H-37 is not recommended. It is believed that the experimental trend of HF amount differing from kinds of fire agents is consistent with theoretical value (Fig. 4b).

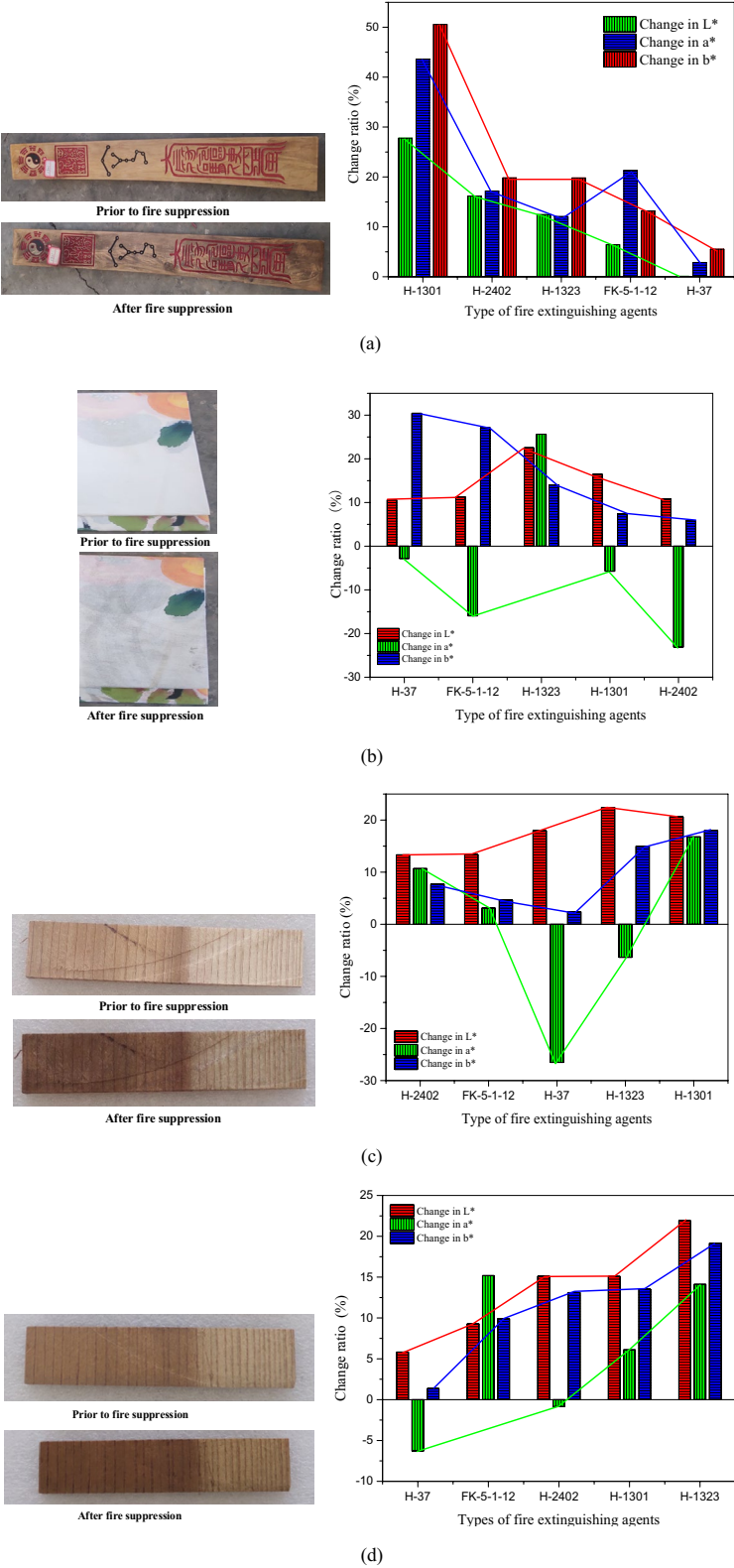
#### The colorimetric change analysis of samples after fire suppression

After the samples exposed to a fire suppression environment, the surface of the wooden samples had a dark color. The outlooks of the sample before and after fire suppression are illustrated in Fig. 5. The comparison of the colorimetric change in color coordinates ( $L^*$ ,  $a^*$ ,  $b^*$ ) is also shown in it. Regarding the Dao Talisman board, the averaged  $L^*$ ,  $a^*$ , and  $b^*$  are reduced by 12.6%, 19.4%, 21.8% after fire suppression using five fluorinated chemical gases, respectively. The fire suppression shows a significant impact on the value of  $b^*$  (just as shown in Fig. 5a). It indicates that the surface becomes darkish, greenish, and bluish. Concerning painting papers, the averaged  $L^*$  and  $b^*$  are reduced by 14.3% and 17.0%, the averaged  $a^*$  is increased by 4.4%. The fire suppression impacts a little on the value of  $a^*$  and makes the surface turn darkish, reddish, and bluish (just as shown in Fig. 5b). For the traditional wooden chips (woodgrain is vertical), the averaged  $L^*$  and  $b^*$  are reduced by 17.6% and 9.6%, the averaged  $a^*$  is increased by 0.5%. However, the averaged  $L^*$ ,  $a^*$ , and  $b^*$  of weathered wooden chips are reduced by 13.5%, 5.7%,

11.4% after fire suppression using five fluorinated chemical gases, respectively. The surface of wooden chips is darkish and bluish. The difference found in the value of  $a^*$  is due to the color change of green. After weathering, the sample exposed to a fire suppression seems much easier to be greenish. The final product of fluorinated chemical gases decomposed at high temperature contains HF. The concentration of HF generated is proportional to the content of F atoms in the gas. The difference in HF concentration results in different colors of samples in different tests. High temperatures during thermal modification cause the degradation of hemicelluloses and lignin, resulting in the production of water, carbon dioxide, formic acid, acetic acid, and other substances that can be involved in condensation reactions, and chromophore groups are formed [38]. Different test samples have different types of wood, and their internal wood fiber structure is also different. Therefore, their color changes under high temperature treatment are also different.

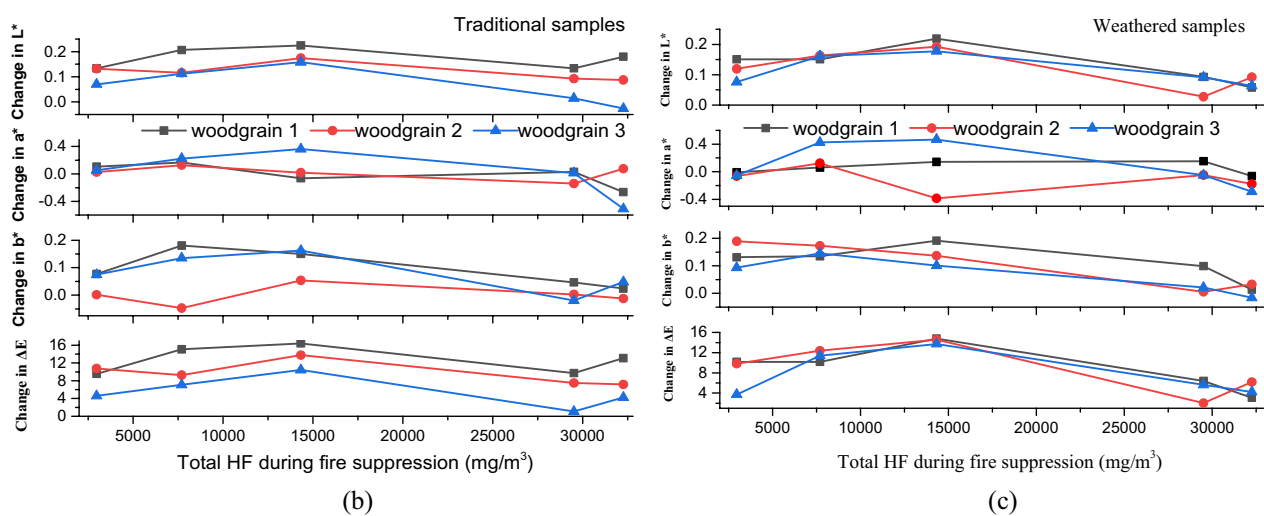
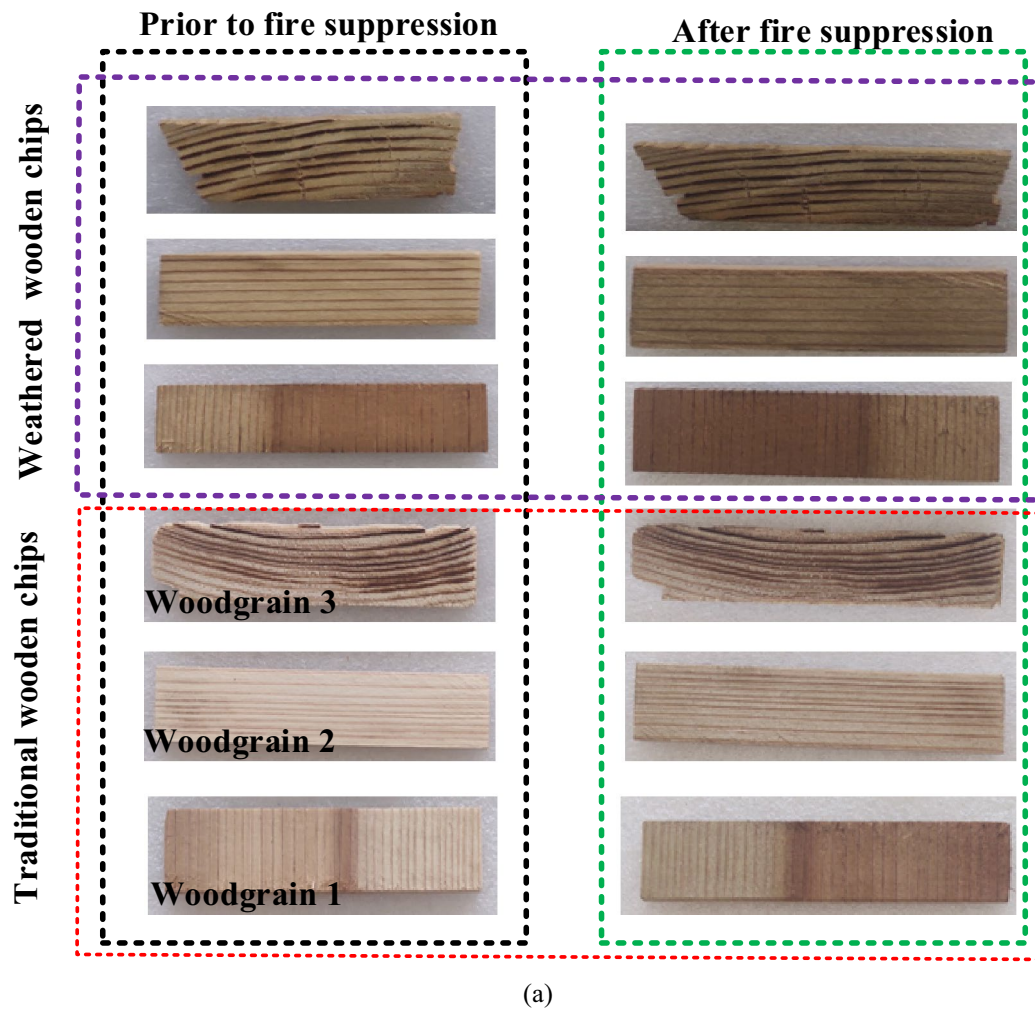
#### Influence of HF amount on the change of surface color

It is reported that HF plays an essential role in the color change of materials due to its corrosion [39]. Here, the color change of wooden chips differing the peak of HF history and total HF during fire suppression are detailed, respectively. Both traditional and weathered wooden samples, including three kinds of woodgrain styles, are tested. The description of samples is listed in Fig. 6a. The section of the wooden column is woodgrain 1 and the beam is woodgrain 2, which is used widely in Chinese historic buildings. To discuss the influence of HF on the color change of weathered wooden chips could provide a deep understanding of fire suppression impacting



**Fig.5** Color parameters change of samples before and after the fire suppression. **a** Dao Talisman board **b** painting paper **c** traditional wooden chips **d** weathered wooden chips





**Fig.6** Color parameters change varying HF amount during fire suppression. **a** The outlook before and after the fire suppression **b** color change versus total HF of traditional chips **c** color change versus total HF regarding weathered chips

the historic buildings. It is observed in Fig. 6b that the color change of wooden chips differing woodgrain styles. In general, the fire suppression impacting on the color change of wooden chips is ranked as woodgrain 2 > woodgrain 1 > woodgrain 3. However, a slight difference shows in each coordinate of the color value of  $L^*$ ,  $a^*$ , and  $b^*$  concerning both traditional and weathered wooden chips. After fire suppression using fluorinated chemical gases, the total color difference ( $\Delta E^*$ ) of traditional chips is found to be sensitive to the peak of HF history and total HF. The HF amount shows a predominant influence on the color difference varying woodgrain styles. The total color difference of traditional samples after fire suppression is ranked as woodgrain 1 > woodgrain 2 > woodgrain 3.

When the weathered wooden chips are exposed to the fire suppression environment, the total color difference of samples before and after the fire suppression is smaller than the traditional samples (see Fig. 6c). In addition, both high yields of  $H_2O$  and HF would result in a significant color difference, which is consistent with the results of H-37 and FK-5-1-12. Although the gaseous HF is highly yielded when the two above chemical gases are employed, the low concentration of  $H_2O$  results in a slight color change. The reduction of  $H_2O$  during fire suppression could be a good method to decrease the effects of acid gas on the color change of historic wooden buildings.

#### Influence of weathering process on color change of wooden chips

The observation of Fig. 6a shows that the color of weathered samples is much easier changed due to fire suppression. Regarding the traditional wooden chips, the averaged coordinate parameters  $L^*$ ,  $a^*$ , and  $b^*$  of samples with woodgrain 2 are reduced by 12.6%, 2.1%, 0.1% after fire suppression using five fluorinated chemical gases, respectively. It is described in Fig. 7a. The averaged  $L^*$ ,  $a^*$ , and  $b^*$  of samples with woodgrain 1 are reduced by 17.6%, 0.5%, 9.6%, respectively. The averaged  $L^*$ ,  $a^*$ , and  $b^*$  of samples with woodgrain 3 are reduced by 6.6%, 2.8%, 8.0%, respectively. The color change of traditional wooden chips with woodgrain 1, woodgrain 2, and woodgrain 3 are 12.8, 9.7, and 5.5, respectively.

Concerning the weathered samples, the averaged coordinate parameters  $L^*$  and  $b^*$  of samples with woodgrain 2 are reduced by 11.9% and 10.8%,  $a^*$  of the sample with woodgrain 1 is increased by 11.1%. Figure 7b shows that the averaged  $L^*$ ,  $a^*$ , and  $b^*$  of samples with woodgrain 1 are reduced by 13.5%, 5.7%, 11.4%, respectively. The averaged  $L^*$ ,  $a^*$ , and  $b^*$  of samples with woodgrain 3 are reduced by 11.4%, 9.9%, 6.9%, respectively (see Fig. 7c). The color change of traditional wooden chips with

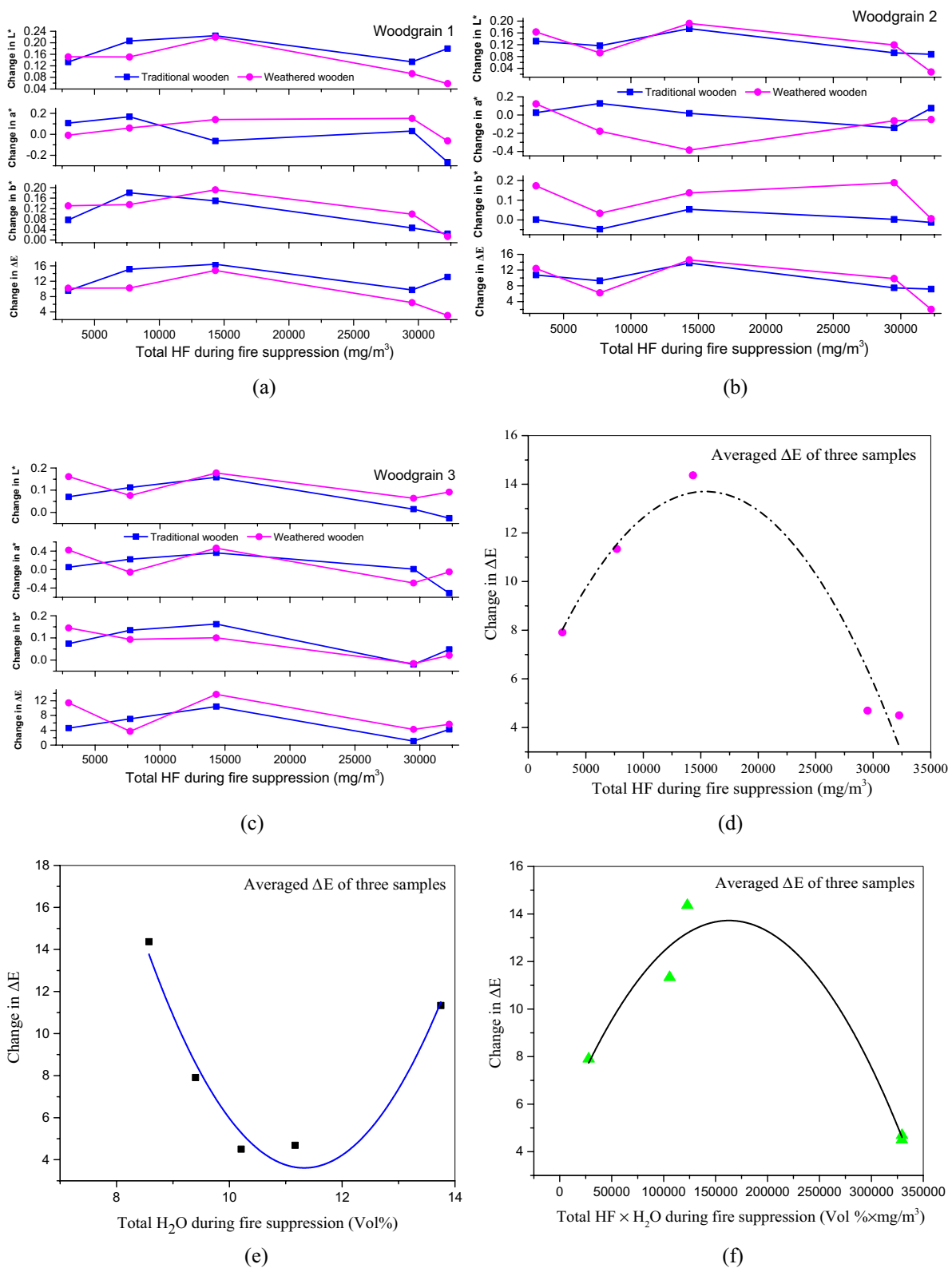
woodgrain 1, woodgrain 2, and woodgrain 3 are 8.9, 9.0, and 7.8, respectively. The color change difference varying the total HF,  $H_2O$  and total  $HF \times H_2O$  are illustrated in Fig. 7d, Fig. 7e, and Fig. 7f, respectively. The color change of samples is found to be consistent with the amount of total HF and  $HF \times H_2O$ . It is concluded that gaseous HF is playing a predominant role in the color change of wooden surfaces.

Comparing of the traditional and weathered samples with the same woodgrain style indicates that the value of  $L^*$  of the traditional chip is much easier to reduce. The apparent difference is also found in the change of  $b^*$ . The reduction of  $b^*$  value of weathered samples is much larger than that of the traditional ones. It means the weathered chip suggests a color shift toward blue because of fire suppression. This phenomenon may be related to the different moisture content in the wood.

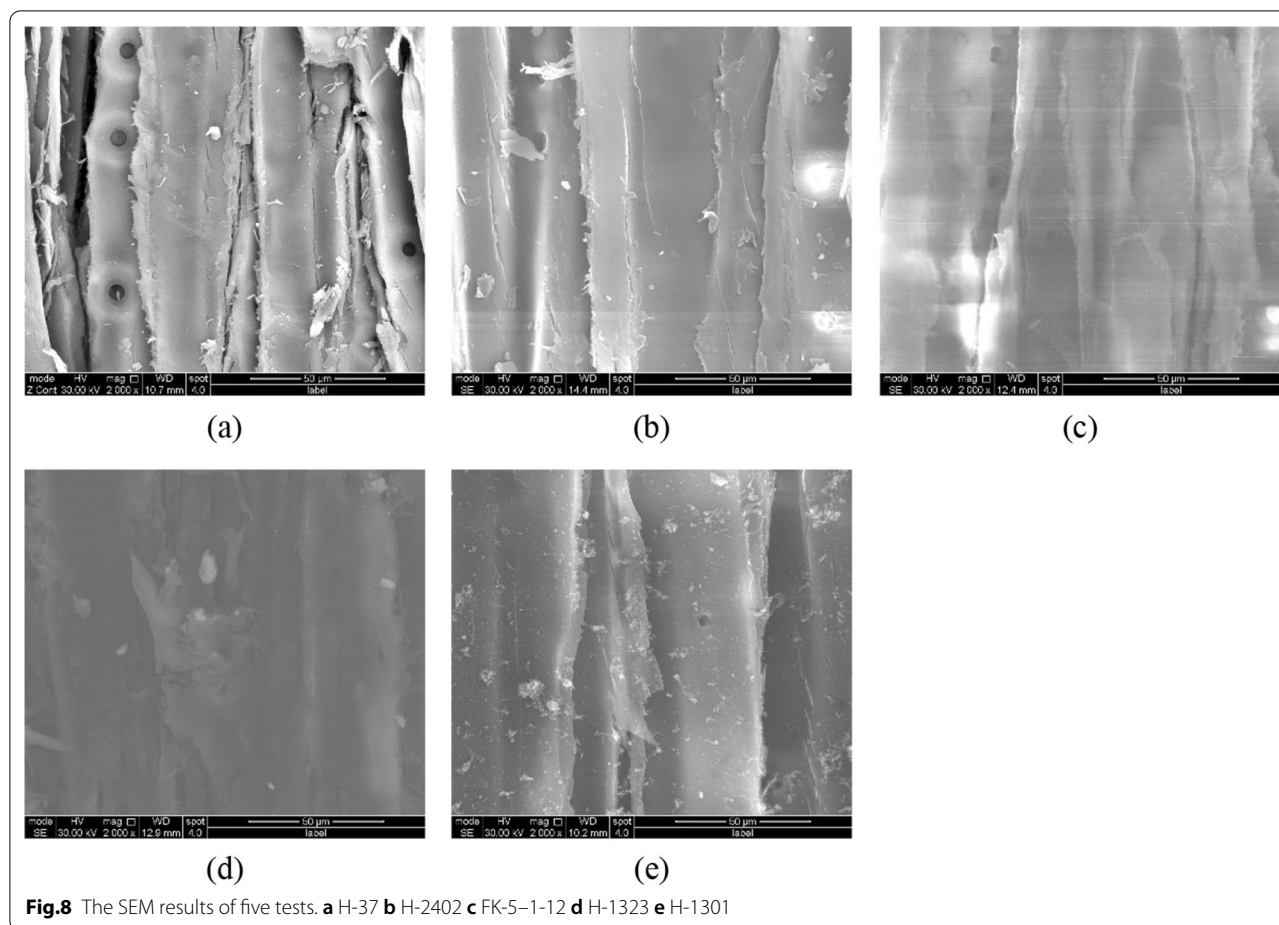
#### The surface investigation of weathered wooden chips

It is known to all that, high concentration of HF yield during fire suppression would show a danger to the surface of surrounding materials. Here, the weathered timbers are employed to be acting as the traditional Chinese historic building. Then the gaseous HF effects on the weathered samples could be clarified. During our test, the weathered timber chips are placed in the chamber during fire suppression, then the characteristic of the wooden surface is identified with the help of SEM at 50  $\mu m$ . The preliminary results are shown in Fig. 8. It is observed that the surface of the wood is full of porous cells, especially after weathering by natural condition, the surface area would be highly enlarged. Much more gases would be absorbed by weathered surfaces. It is believable when the weathered wood surfaces (acting as a Chinese historic building) are exposed to a variety of corrosive gases, the deposition of HF and  $H_2O$  would impact a significant hazard. The surfaces of materials would be corroded a little when they were treated with high concentration acid. In addition, the deposited F is hard to be removed since the wood or paper historic artwork is brittle during the repair process after fire suppression.

When the weathered timber chips were exposed to fire suppression, the element concentration distribution of the wooden surface is evaluated by EDX analysis of SEM. The results are summarized in Fig. 9. Figure 9a indicates the ratio of the main elements after fire suppression using HF-37 gases. It is observed the deposited F on wooden surface using H-37, H-2402, FK-5-1-12, H-1323 and H-1301 are found to be 1.6%, 0.5%, 1.0%, 1.0% and 0.4%, respectively. It is consistent with the total amount of HF generated during fire suppression, as illustrated in Fig. 9b. The amount of F-deposited on the wooden surface is positively correlated with a total amount of gaseous HF.



**Fig.7** Color change varying total HF during fire suppression. **a** Woodgrain 1 **b** woodgrain 2 **c** woodgrain 3 **d** total color difference varying total HF **e** total color difference varying total H<sub>2</sub>O **f** total color difference varying total HF × H<sub>2</sub>O



The biggest amount of gaseous HF is generated by HF-37. An interesting relationship between the concentration of deposited F on the surface and total color change is found in Fig. 9c. It interferes that the color change mechanism of wooden surface is comprehensive, although the amount of HF is a leading factor. However, the long-time effects of deposited F on the surface change of historic buildings still need to be made for further analysis.

## Conclusion

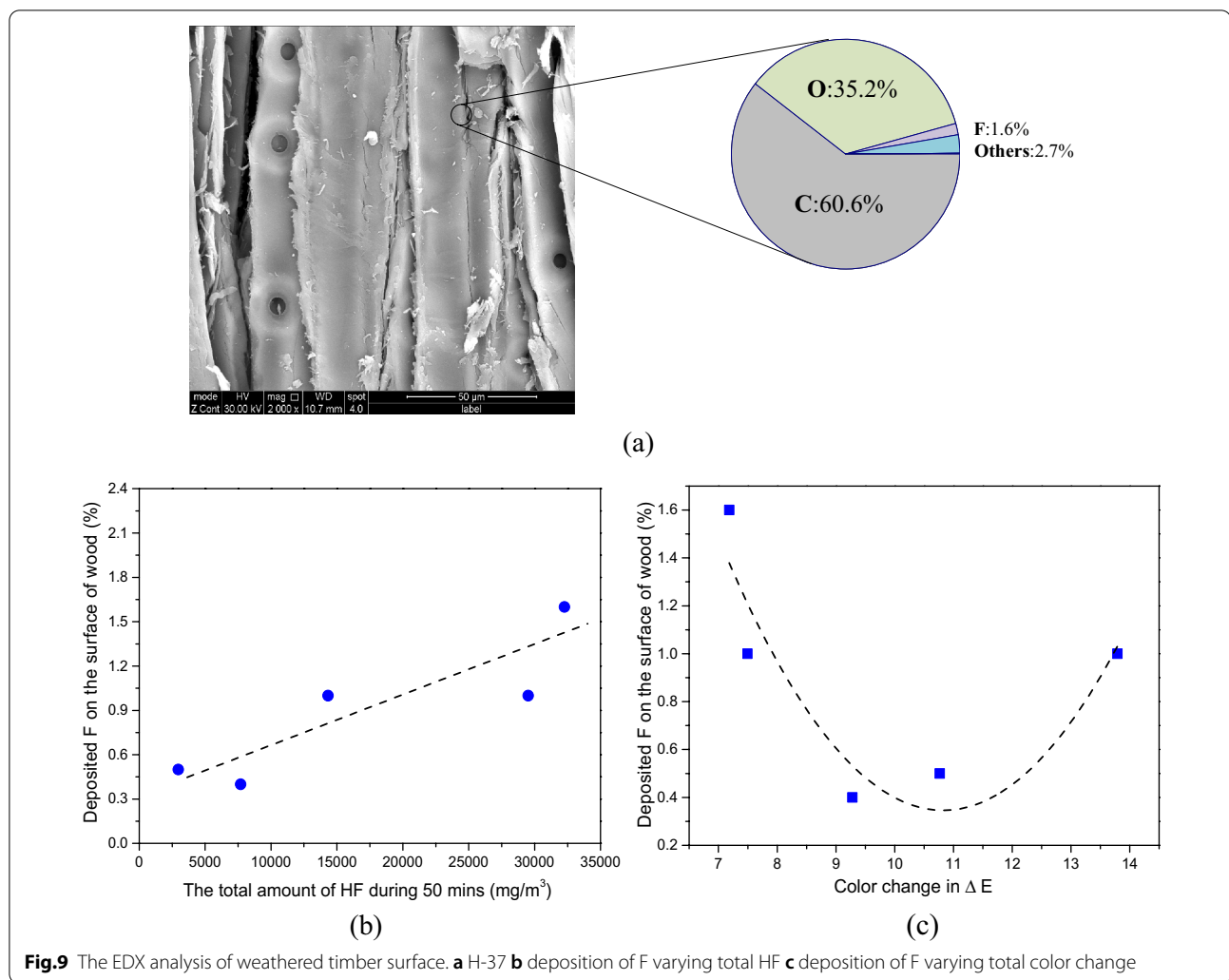
In this work, a series of fire suppression tests using fluorinated chemical gases were conducted. The concentration of HF and H<sub>2</sub>O yielded from fire suppression are monitored by an FTIR. The surface analysis is conducted by SEM–EDX. Finally, the followings were obtained based on experimental results and detailed analysis:

(1) The fluorinated chemical gas is found to be effective for flame inhibition under a fixed condition. The flame enhancement and enlargement after the injection of chemical gas are observed.

(2) The trend of experimental HF amount is consistent with the theoretical value, which is calculated according to the weight of F in the molecular of fluorinated chemical gases.

(3) The amount of F-deposited on the wooden surface is positively correlated with a total amount of gaseous HF. The amount of HF is a leading factor of color change mechanism of the wooden surface. The influence of HF on color change depends on the amount of both gaseous H<sub>2</sub>O and HF. The existence of H<sub>2</sub>O highly improves the ability to change color. The reduction of gaseous H<sub>2</sub>O could be a potential method to protect the surface from being corroded.

(4) It is concluded that the value of L\* of the traditional chip is much easier to be reduced comparing with weathered samples with the same woodgrain. It suggests the weathered chip shows a color shift toward blue because of fire suppression.



**Fig. 9** The EDX analysis of weathered timber surface. **a** H-37 **b** deposition of F varying total HF **c** deposition of F varying total color change

#### Authors' contributions

Conceptualization-WK and KW, methodology-WY, experiment-BZ and JS, validation-KW, formal analysis-WK and WY, resources-BQ and WW, writing—original draft preparation-WK, XS and MX, writing—review and editing-WK, BZ and KW, supervision-KW, project administration-QC and XW. All authors have read and approved the final manuscript.

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#### Availability of data and materials

The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request.

#### Declarations

#### Competing interests

The authors declare that they have no competing interests.

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