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Application of TGA and EDX Analysis to Evaluate the Process of Preservative-Treated Woods

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This study investigated the use of TGA under different thermal decomposition conditions (nitrogen or air, and 5 or 40 °C/min) to evaluate preservative-treated woods and their preservatives. It also analyzed the residual elements in the char using EDX. Two types of preservative-treated woods were investigated. One impregnated with CCA–3 and the other one treated with ACQ–1 using a full-cell treatment. The results of the TGA showed that the thermal properties of CCA– or ACQ–treated wood were similar to that of untreated wood in either a nitrogen or an air atmosphere, but the pyrolysis temperature for the heating rate of 5 °C/min was lower than that of 40 °C/min. Regardless of different atmosphere or heating rate, the char of the CCA specimens and the CCA–3 was more than that of the ACQ ones and the ACQ–1. The results of the EDX analysis of both preservative-treated woods show that the main element is C (CCA: 47.96%; ACQ: 50.24%), and that the relative proportion of C (CCA: 60.42%; ACQ: 77.89%) is higher after thermal decomposition. Cr from the char of CCA–3 is a stable element, and the amount of Cr (34.99%) is obviously more than that of As (11.89%) and Cu (16.69%). The char of ACQ–1 left a high amount of inorganic metal elements, such as Cu (50.14%). This suggests that by using EDX to analyze the residual elements in char, the results can provide experimental data for referencing the disposal-end practices (char) of both preservative-treated woods.

INTRODUCTION

Wood preservatives are chemical compounds that are used worldwide in the wood industry. No timber is immune to deterioration if not protected, and wood preservatives are important in the industry for long-lasting results (Connell, 1991). Different types of water-borne salts have been used to preserve wood from insects, fungi and water damage for the past few decades. One of the more common formulations contains copper, chromium and arsenic salts and is known as chromated copper arsenate (CCA). However, environmental concerns have drastically changed the allowable active ingredients of wood preservatives, resulting in the restricted use of CCA (Sanders and Windom, 1980; Sanders and Riedel, 1987; Weis J. and Weis P. *et al.*, 1992a, 1992b, 1996, 1999; Cooper, 2001), especially since substantial amounts of CCA remain in the treated wood for many years creating a growing problem of scrap wood disposal (Solo-Gabriele *et al.*, 2003). Today, the copper-based preservative, ammoniacal copper quats (ACQ), which is comprised of a combination of copper and organic biocides, is the main wood

preservative for wood and wood products in many countries. However, the discarded ACQ-treated wood will need to be reused, recycled, or disposed of in an environmentally acceptable manner.

Discarded CCA-treated wood is extremely difficult to be recycled as a raw material, because the waste stage has a very significant impact on the life cycle assessment results (Esser, *et al.*, 2000), and on the ACQ-treated woods as well. In many cases the preservative treatment is removed by the recycling process, or destroyed by combustion when used as fuel (Jang, 1997). Therefore, for preservative-treated woods, regardless if they were treated with CCA or ACQ, it is necessary to determine the pyrolysis temperature, and the amount of char formed (residual metal) during combustion (Kercher *et al.*, 2001; Humphrey, 2002). The recent recognition of the need for abatement of air pollution has led to further interest in, and investigation of pyrolysis as a major issue when disposing of cellulose wastes and residual materials (Helsen and Bulck, 1998). Regardless of waste minimization efforts, improved disposal-end management practices will play a key role in minimizing the impacts of disposed of CCA-treated wood in the next 25 to 40 years (Cooper, 2003). To provide an understanding of the fundamental thermal behavior and the disposal-end practices of CCA- and ACQ-treated woods, this study is comprised of two categories of examination. The first is related to the study of thermal decomposition. It examines the effectiveness of the pyrolysis of both preservative-treated woods and their preservatives, using thermogravimetric analysis (TGA). The second applies energy dispersive X-ray spectrometry (EDX) to examine certain residual

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elements of the char from either preservative-treated woods or the preservatives used in this study, before/after thermal decomposition. Our goal in this research was to acquire fundamental knowledge of the thermal behavior of CCA- and ACQ-treated woods, while at the same time obtaining a disposal-end practice (residual elements) reference for the char.

MATERIALS AND METHODS

Wood preservatives

The commercial wood preservatives used were provided by Kunnyih Co. Ltd., Taiwan. The basic details of these preservatives are as follows:

- a. Chromated Copper Arsenate (CCA): the type 3 of CCA (CCA-3) is employed in this study, and is produced by Tanalith C Corp., England. CCA-3 oxide is light yellow in color and contains a mixture of 28.90 wt % of chromium trioxide (CrO_3), 10.60 wt % of cupric oxide (CuO), and 16.70 wt % of arsenic pentoxide (As_2O_5).
- b. Ammonical Copper Quats (ACQ): the type 1 of ACQ (ACQ-1) was used in this study, and it was obtained from Koshi Corp., Japan. ACQ-1 oxide is deep green in color, and includes CuO with 9.00 wt %, as well as 7.20 wt % of N-alkyl benzyl dimethyl ammonium chloride (BKC).

To clarify the residual elements of discarded ACQ-treated woods after thermal decomposition, the main ingredients of CuO and BKC (Shimakyu's pure chemicals, Japan) were also prepared as experimental materials.

Preparations of the preservative-treated woods

Cryptomeria japonica D. Don (Japanese cedar) was used as a control specimen (untreated wood). Tangential sections of clear specimens measuring $285 \times 75 \times 10$ mm (L $\times$ W $\times$ T) were prepared. The specimens had a moisture content of less than 15.0% after being air-dried at ambient temperatures. They were then impregnated with CCA-3 or ACQ-1. Prior to the impregnating process, CCA-3 was adjusted to an oxide-based 2.5% CCA-3 solution, and its solid content was about 2.32%, specific gravity was 1.065 (28.0 °C), and the pH value was 3.6. For ACQ-1, its solid content was about 0.95%, specific gravity was 1.008 (27.8 °C), and the pH value was 10.3, after adjusting the concentration of ACQ-1 to 6.0%. The manufactured standard of the preservative-treated woods was in accordance with CNS 3000. A full-cell treatment (according to the procedure "Breant-Bethell") was applied. The vacuum was kept for 30 min at over 600 mmHg, and the wood was then impregnated with preservatives. Then the pressure was increased to 15 ± 1 kgf/cm², and maintained in this condition for 4 h. Finally, the pressure was released, and then the same as above-vacuum was applied for 20 min to prevent bleeding of preservatives from the surface of the treated wood. All specimens were placed in a conventional oven with air-circulation at a preset temperature of 30 °C for 60 min. The average amount of impregnation

for CCA-treated woods was over 6.20 kg/m³ (4.87 kg/m³ for heartwood; 7.60 kg/m³ for sapwood), and for ACQ-treated woods was over 4.80 kg/m³ (3.96 kg/m³ for heartwood; 5.70 kg/m³ for sapwood). Both them are grade k 3 at the CNS 3000 O1018 in Taiwan. The crushed wood particles, between 40 to 60 mesh, and both preservatives were dried in a convection oven at 40 ± 3 °C for 3 h to prepare them for evaluation of thermal behavior, pyrolysis temperature, and char using thermogravimetric analysis (TGA), as well as energy dispersive X-ray spectrometry (EDX).

Thermogravimetric analysis (TGA)

TGA is a common technique for measuring the weight change of a material as a function of temperature (Cornfield *et al.*, 1993; Pasek and McIntyre 1993; Pasek, 1995; Helsen *et al.*, 1997; Hsu *et al.*, 2000). Throughout this research project, TGA was carried out using a Perkin-Elmer TGA 1, fully supported by computer-controlled software options, from Perkin-Elmer Thermal Analysis Systems, for control and data handling. Each sample, approximately 5–10 mg in weight, was placed into an open experimental sample pan, suspended from a sensitive microbalance. A furnace surrounded the sample to provide accurate heating from 50 to 850 °C, while the measurement was taking place. In order to isolate the pyrolysis step, a nitrogen atmosphere was selected for the TGA (Hsu *et al.*, 2000), but for combustion an air atmosphere was used. All runs were purged in either an air or a nitrogen atmosphere, at a flow rate of 50 mL/min, with 2 kinds of heating rate, at 5 or 40 °C/min. That is to say, as a slow-heating or a fast-heating regime, in order to compare the differences in their thermal properties and their char for the CCA- and ACQ-treated wood, the CCA-3 and the ACQ-1.

Energy Dispersive X-ray Spectrometer (EDX)

The scanning electron microscope combined with the energy dispersive X-ray spectrometer (SEM-EDX) analysis can be applied directly to a material, and determines the amount of all the elements in a single image analysis. It is a powerful tool for studying the mineral distribution and more precisely the effect of the elements on this distribution (Kotz *et al.*, 1990). In these experiments, to simulate the char obtained from the end of the TGA tests, all specimens and preservatives were individually put into a crucible and then were burned using a burner (DF-303, Deng Ying Co. Ltd.). The temperature was managed the same as for the TGA test, from room temperature to 850 °C. The residual char was analyzed using a SEM-EDX (E HONG Instrument Co. Ltd., a Hitachi general agent in Taiwan, from Hitachi High-Technologies Corporation, Japan). SEM pictures were taken using a Hitachi S-3400N scanning electron microscope. For all the investigations in this study the beam energy was 10 nm at 15.0 kV with a distance of 10.0 mm to the specimen, in order to obtain the excitation of all the elements. Analysis of the elements was carried out by EDX analysis using a Horiba EDX 7021 H system. To determine their distribution, Smart

Map acquisition was used, which performs the simultaneous acquisition of the X-ray data from each pixel on the image area with 2.00 k SE of magnification. The results of the residual elements in the char for all specimens were analyzed.

RESULTS AND DISCUSSION

Thermal properties of the preservative-treated woods

TGA is an established technique, used in the quantification of weight changes within a material, as a function of temperature or time. To comprehend the thermal behavior (pyrolysis, thermal decomposition, and char) of the preservative-treated wood specimens and the preservatives themselves were measured by TGA. Decomposition profiles were obtained while heating at a rate of 5 °C/min in either nitrogen or air, between 50 °C (initial temperature) and 850 °C (end temperature). The relationships between temperature and weight loss, and the derivative weight for Japanese cedar, CCA specimen and ACQ specimen in the TGA and DTG curves are shown in Fig. 1.

In a nitrogen atmosphere (the left side of Fig. 1), the thermogram resulting from the analysis of the

Japanese cedar (solid line), the CCA specimen (dot line) and the ACQ specimen (dash line), shows that there are two subtle changes (shoulders) at the temperature from 50 to about 300 °C, indicating that three of them had almost identical initial (the first sharp step) and secondary decomposition temperatures. These results were all supported by the derivative (DTG) curve, which shows two peaks at temperatures of 66.89 and 344.89 °C for Japanese cedar, at temperatures of 60.12 and 348.04 °C for the CCA specimen, and at temperatures of 60.06 and 343.02 °C for the ACQ specimen. The amount of char for these three samples was, at a temperature of 850 °C, Japanese cedar: 21.74 wt %, the CCA specimen: 21.50 wt %, and the ACQ specimen: 21.22 wt %.

Helsen *et al.* (1999) reported that at temperatures below 100 °C drying takes place with a corresponding peak in the DTG curve, representing the release of water vapor. The peaks observed at higher temperatures can be attributed to the pyrolysis process. Furthermore, due to the fact that the cellulose in wood compositions is one of the main portions, Shafizadeh (1984) reported that while the pyrolysis temperature is close to about 300 °C, depolymerization takes place in most of the cellulose, and thermal-degrading turns it into a combustible material (1,6-anhydro- -D-glucopy-

Fig. 1. TGA and DTG curves for Japanese cedar, CCA specimen, ACQ specimen with 5 °C/min of heating rate in either a nitrogen (left) or an air (right) atmosphere.

Symbols: — : Japanese cedar, ····· : CCA specimen, - - - : ACQ specimen.

Notes: CCA specimen: Japanese cedar treated with chromated copper arsenate;

ACQ specimen: Japanese cedar treated with ammoniacal copper quats.

ranose, levoglucosan). Then the wood continues its progress of thermal-degradation as the temperature is increased. The char is formed, and its amount depends on the highest temperature obtained in the process. In addition, since the wood is treated with different water-based preservatives, there is a difference in maximum weight loss value as shown in the TGA curve, and the temperature range is from 327.18 to 364.50 °C (Helsen *et al.*, 1999; Kercher *et al.*, 2001; Lee *et al.*, 2005), which agrees with the results of this part of the study.

In an air atmosphere (the right side of Fig. 1) with a heating rate of 5 °C/min, there are three shoulders at temperatures varying between 50 to about 480 °C for Japanese cedar and the CCA specimen, and two subtle changes for the ACQ specimen. The results show three peaks at temperatures of 61.11, 271.43 and 424.34 °C for Japanese cedar, at temperature of 275.11, 377.76 and 470.35 °C for the CCA specimen, and at temperatures of 260.56 and 396.33 °C for the ACQ specimen. The amount of char at a temperature of 850 °C was, Japanese cedar: 0.41 wt %, CCA specimen: 3.14 wt % and ACQ specimen: 0.91 wt %. The results from adding either CCA-3 or ACQ-1 to wood were as follows. The pyrolysis of the treated woods shows different onset temperatures with a different weight loss as compared to the

untreated wood. This is because both treated woods contain residual metal from the preservatives, Cr (chromium) and Cu (copper) elements from the CCA specimen (Osawa, 1988), and Cu from the ACQ specimen. Moreover, the char from the CCA specimen is higher because the residual metal (Cr or Cu) is unable to combust, except for the C in the char (Kercher *et al.*, 2001; Lee *et al.*, 2005). When comparing the differences between an air or a nitrogen atmosphere, the results show that the thermal properties of CCA- or ACQ-treated wood specimen are similar to that of the untreated one (Japanese cedar), but in a nitrogen the pyrolysis temperature is slower and the char is higher than in air, and both treated specimens also have a lower pyrolysis temperature compared to the control. These results agree with those in the literature (Helsen *et al.*, 1999; Kercher *et al.*, 2001; Lee *et al.*, 2005).

To obtain a better understanding of the thermal properties of CCA- or ACQ-treated wood with a different heating regime in either an air or a nitrogen atmosphere, the relationships between temperature and weight loss, and the derivative weight for CCA and ACQ specimens, of the TGA and DTG curves, are shown in Fig. 2. As expected, the two types of specimens show a typical gradual weight loss. Regardless of the different

Fig. 2. TGA and DTG curves for CCA specimen, ACQ specimen in a nitrogen and an air atmosphere with either 5 (left) or 40 (right) °C/min of heating rate.

Symbols: — : CCA specimen (nitrogen), - - - - : ACQ specimen (nitrogen),
 : CCA specimen (air), - . - . : ACQ specimen (air).

Notes: Abbreviations of CCA specimen and ACQ specimen are the same as Figure 1.
 (nitrogen): in a nitrogen atmosphere; (air): in an air atmosphere.

atmospheres, the pyrolysis and the decomposition of both specimens at a 5 °C/min of heating rate are all slower than with 40 °C/min. At 40 °C/min of heating rate there is a shift of the DTG peak to higher temperatures for both treated specimens. The char, regardless of the difference in heating rate, is higher in the nitrogen atmosphere than in air. Shafizadeh (1984) and Lee *et al.* (2004) reported that wood and their components (such as cellulose) combusting in an air atmosphere, whether reacted or not, underwent rapid weight loss by evaporation of their pyrolysis products, and that this rapid weight loss was superimposed upon and followed by a continuous weight loss as a result of the oxidation of the charred residues. Therefore, the char of both specimens in an air atmosphere are all lower than those in a nitrogen atmosphere. It is evident that the atmosphere has a significant influence on the thermal properties of the specimens, especially the temperature at the onset of pyrolysis, where the maximum rate of decomposition occurs and the final char is yielded (including the metals).

Thermal properties of the preservatives

To elucidate the comprehension of the thermal properties of CCA-3 and ACQ-1, a comparison is made

between the slow-heating regime and the fast-heating regime in both a nitrogen and an air atmosphere for both preservatives. The results are shown in Fig. 3. Regardless of the atmosphere, the CCA-3 weight loss at either 5 °C/min (solid line) or 40 °C/min (dash line) heating rate is significantly less than that of ACQ-1 at 5 °C/min (dot line) or 40 °C/min (dash-dot-dash line) heating rate. The results of CCA-3 show that the weight loss gradually decreases in air or nitrogen at 40 °C/min, but it shows a great weight loss around 270 °C in air or nitrogen at 5 °C/min and then decreases gradually. The onset of weight loss for 40 °C/min in a nitrogen atmosphere is observed at temperatures of 72.40, 166.62, 334.48 and 495.96 °C, and in an air atmosphere at temperatures of 65.89, 161.59, 320.29 and 477.41 °C. For 5 °C/min under a nitrogen atmosphere the weight loss is evident at temperatures of 142.16, 162.14, 285.37 and 455.51 °C, and under air at temperatures of 138.12, 155.46, 169.85, 192.51, 280.96 and 468.09 °C. These findings are supported by the derivative (DTG) curve. As to the amount of char, at a temperature of 850 °C, for CCA-3 it was 67.89 wt % in air at 5 °C/min and 77.17 wt % at 40 °C/min. In a nitrogen atmosphere, for CCA-3 it was 62.17 wt % at 5 °C/min and 67.91 wt % at 40 °C/min. These numbers are higher than the ACQ-1 in an air or in a nitrogen

Fig. 3. TGA and DTG curves for CCA-3 and ACQ-1 with 5 and 40 °C/min of heating rate in either a nitrogen (left) or an air (right) atmosphere.

Symbols: — : CCA-3 (5 °C), - - - - : ACQ-1 (5 °C),

- . . . : CCA-3 (40 °C), - . - . : ACQ-1 (40 °C).

Notes: CCA-3: the type 3 of chromated copper arsenate;

ACQ-1: the type 1 of ammonical copper quats.

(5 °C): 5 °C/min of heating rate; (40 °C): 40 °C/min of heating rate.

atmosphere at 5 or 40 °C/min.

The results of ACQ-1 show that the weight loss drastically decreases in both air and nitrogen at either heating rate. The pyrolysis temperature for the heating rate of 5 °C/min is lower than that of 40 °C/min in either atmosphere. The onset of weight loss for the 5 °C/min heating rate under air was observed at temperatures of 105.76, 141.03 and 439.58 °C and under a nitrogen atmosphere at temperatures of 141.55 °C. At a 40 °C/min heating rate under air, the onset of weight loss is obtained at temperatures of 156.42 °C and under a nitrogen atmosphere at temperatures of 155.37 °C. These findings are also supported by the derivative (DTG) curve. For the amount of char in this portion of the TGA tests, ACQ-1 was 26.61 wt% in air at 5 °C/min and was 27.72 wt% at 40 °C/min. In nitrogen, it was 15.30 wt% at 5 °C/min and 18.30 wt% at 40 °C/min. Helsen *et al.* (1999) reported that the final char yield (including the metals) for CCA is higher and the rate of weight loss is much more peaked. It can be said that the CCA compounds act as promoters of the pyrolysis reactions favoring the formation of char. It is concluded that the char of the CCA-3 for the fast-heating regime is higher than that for the slow-heating regime, but for ACQ-1 either of the heating rates the amount of char remained relatively

unchanged.

Hirata *et al.* (1993) reported that Cr and Cu from the CCA preservatives were largely present in the char and that As (arsenic) was easily volatilized with the increase in temperature during combustion. Some researches (Kercher *et al.*, 2001; Cooper, 2003; Helsen and Bulck, 2005) stated that in the TGA tests, when CCA preservatives were analyzed with either air or nitrogen, As_2O_5 was formed in a gaseous state and that it disappeared at a temperature of over 600 °C. In addition, CuO produced Cu_2O when the temperature reached about 800 °C both in air or nitrogen atmosphere, CO was then further volatilized and only Cu remained. Also, Cr (III) is a stable element with an unproductive thermal decomposition. It was evident that after combustion only the Cr and Cu from the preservatives remained. In other words, it is indicated that CCA preservatives after combustion was left the element of Cr and Cu. For ACQ preservatives, a combination of copper and organic biocides, it was inferred that the main residual element was Cu, that is, the others were volatilized with the increase in temperature during combustion. Therefore, according to the different thermal decomposition conditions (nitrogen or air, and 5 or 40 °C/min) set in this study, the char of CCA preserva-

Fig. 4. TGA and DTG curves for BKC and CuO with 5 and 40 °C/min of heating rate in either a nitrogen (left) or an air (right) atmosphere.

Symbols: : BKC (5 °C), - - - - : CuO (5 °C),
- - - - : BKC (40 °C), - - - - : CuO (40 °C).

Notes: BKC: N-alkyl benzyl dimethyl ammonium chloride; CuO: copper oxide.

Abbreviations of (5 °C) and (40 °C) are the same as Figure 3.

tive-treated wood was higher than that of ACQ treated wood (Fig. 2).

In order to better understand the char of ACQ preservative-treated woods so that the findings could be used as a reference data for reusing it, recycling, or disposing it in an environmentally acceptable manner; we analyzed the basic combination of copper and organic biocides, CuO and BKC, through TGA. The results are shown in Fig. 4. The results show that CuO pyrolysis does not take place under either atmosphere or heating rate. However, BKC pyrolysis in either nitrogen/air or heating rate decreased linearly at a temperature of about 100 to 200 °C, and was almost burned out around 400 °C. The onset of weight loss for BKC at 5 °C/min under a nitrogen atmosphere was observed at temperatures of 170.59 °C, and under air at temperatures of 167.78 °C. For 40 °C/min, it was obtained from a temperature of 198.39 °C under nitrogen and at a temperature of 195.95 °C under air. These findings are supported by the derivative (DTG) curve. The amount of char at the end of the TGA tests in air was 0.76 wt % for BKC at 5 °C/min and 0.07 wt % at 40 °C/min. In nitrogen, it was 0.01 wt % at both 5 and 40 °C/min. For the char of CuO in nitrogen, it was 93.46 wt % at 5 °C/min and 100.0 wt % at 40 °C/min. In air, it was 97.02 wt % and 99.44 wt % at 40 °C/min. These indicate that the main make-up of char of either ACQ-treated wood (Fig. 2) or ACQ-1 (Fig. 3) is Cu.

EDX analysis of preservative woods and preservatives

Kotz *et al.* (1990) reported that EDX analysis is a powerful tool to study the mineral distribution in a small area, especially for metal elements. In this portion of the experiment, to analyze the char of both treated woods and the preservatives in the end of the TGA tests, all specimens were individually burned using a burner to simulate the char obtained from the end of the TGA tests. The results are shown on Table 1.

The main element of Japanese cedar (untreated specimen), both preservative woods and preservatives

was C, 57.25% for the untreated specimens, 47.96% for the CCA specimens, 50.24% for the ACQ specimens. For their preservatives, CCA-3 was 4.30%, and ACQ-1 was 3.74%. After combustion, the relative proportion of C was higher, 90.42% for the untreated specimen, 60.42% for the CCA specimens, 77.89% for the ACQ ones, and 22.13% for the ACQ-1, in addition to 2.70% for the CCA-3. The results of element O showed that it had relatively decreased for all specimens after being burned. The results also showed that the amount of Cr for the CCA specimens was 7.38%, and the CCA-3 was 34.99% after being burned. Both of them were obviously more than the amount of As (4.08% for CCA specimen, 11.89% for CCA-3) and Cu (5.18% for CCA specimen, 16.29% for CCA-3). This is because the Cr from the char of the CCA preservatives was a stable element (Hirata *et al.*, 1993; Kercher *et al.*, 2001; Cooper, 2003; Helsen and Bulck, 2005; Lee *et al.*, 2005). The char of ACQ-1, left a great amount of inorganic metal elements, Cu (50.14%). As the results indicated, the main char of the ACQ-treated wood (Fig. 2) or the ACQ-1 (Fig. 3) was Cu, which was almost unable to be combusted toward the end of the TGA tests. The above results suggest that by using EDX to analyze the residual elements in char, the results can provide experimental data for referencing the char of preservative-treated woods and the preservatives in TGA tests.

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Table 1. EDX analysis of various specimens before and after the combustion

Unit: weight (%)

Element	Orbital	Japanese cedar		CCA specimen ¹⁾		ACQ specimen ¹⁾		CCA-3 ¹⁾		ACQ-1 ¹⁾	
		before	after	before	after	before	after	before	after	before	after
C		57.25	90.42	47.96	60.42	50.24	77.89	4.30	2.70	3.74	22.13
O		42.55	7.09	49.43	20.55	49.30	7.01	59.78	33.50	29.94	26.38
Mg		—	—	—	—	—	—	—	—	—	0.36
Na		0.11	2.11	—	1.43	—	—	—	—	—	—
S	K	—	—	0.06	0.96	—	—	1.39	0.86	—	0.66
P		—	—	—	—	—	—	—	—	—	—
K		0.09	—	—	—	—	0.09	—	—	—	0.33
Si		—	—	—	—	—	0.16	—	—	—	—
Cl		—	—	—	—	—	0.14	—	—	0.55	—
Ca		—	0.32	—	—	—	0.24	—	—	—	—
Cr		—	—	0.08	7.38	—	—	7.41	34.99	—	—
Cu	L	—	—	1.75	5.18	0.45	2.67	16.29	16.69	65.76	50.14
As		—	—	0.72	4.08	—	—	10.21	11.89	—	—

¹⁾ Abbreviations of CCA specimen and ACQ specimen are the same as Figure 1, as well as CCA-3 and ACQ-1 are the same as Figure 3.

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