



# Thermochemical chlorination of carbon indirectly driven by an unexpected sulfide of copper with inorganic chloride

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## ABSTRACT

Unintentional anthropogenic thermal chlorination of carbon is known to be a contributor to global environmental pollution of organochlorine compounds. We found unexpected, serious chlorination of carbon promoted by a “sulfide” of copper, which has been generally thought of and studied as an inactive metal catalyst. Our quantitative and X-ray spectroscopic results show that a fraction of cupric sulfide indirectly promoted thermochemical solid-phase formation of a large quantity of organochlorine compounds such as polychlorinated dibenzo-*p*-dioxins, dibenzofurans, biphenyls, and benzenes that used inactive inorganic chloride as chlorine storage, which partly caused environmental pollution by organochlorine compounds.

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## 1. Introduction

Chlorination of carbon is an essential process related to pollution and bioaccumulation of persistent and toxic organochlorine compounds on a global scale [1–3]. Although natural weathering of plants is also another possible cause of organochlorine compounds disseminating into the environment [4], old and new concerns have mainly focused on anthropogenic thermal processes [5–7]. However, we do not fully and scientifically understand the mechanism of thermochemical discharge of organochlorine compounds such as polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs), biphenyls (PCBs), benzenes (CBzs), and other unknown organics. Despite physical collection of ash to avoid atmospheric pollution, organochlorine compounds thermochemically concentrate and accumulate in the collected ash [8,9]. Eventually, a thermal solid-phase reaction in this ash is thought to contribute to serious accumulation in the environment.

In a thermal process, solid-phase trace metal chlorides and oxides promoted chemical bonding between carbon and chlorine in solid [9] and gas phases [10]. In particular, our X-ray spectroscopic studies have recently revealed that cupric and ferric

chlorides directly provide chlorine to the carbon matrix [11–14]. Cupric oxide is well known to catalyze the Deacon reaction and dimerization of organochlorine compounds in the thermal process [15]. The anthropogenic thermal-solid phase present in the fly-ash product of municipal solid-waste incineration contains many trace-metal compounds other than Cu–Cl-, Fe–Cl-, and Cu–O-bonding compounds. Characterization studies reported that “sulfide” of copper partially exists in real fly ash [16,29,34]. Nonetheless, we have only limited knowledge of other metal compounds that promote the chlorination of carbon. In this report, we present clear-cut evidence of unexpected and strong thermochemical chlorination of carbon caused by a “sulfide” of copper in solid phase.

## 2. Experimental

### 2.1. Simplified model mixture

A simplified model mixture was prepared from activated carbon (Shirasagi palm shell, 20–48 mesh (number of hole/inch); Takeda Pharmaceutical Co. Ltd., Osaka). Any organic compounds were removed by heating at 500 °C for 60 min under a stream of 100% nitrogen gas (100 mL/min). The product is referred to as “AC” in this paper. The simplified model mixture contained CuS, AC, potassium chloride (KCl), and either silicon dioxide (SiO<sub>2</sub>) or boron nitride (BN). The simplified model mixture was admixed with CuS or FeS (0.2 wt% metal) by grinding in a mortar for about 10 min in the following proportions: AC (3.0 wt%), KCl (10 wt% Cl), and

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SiO<sub>2</sub> (remainder) for use in the heating experiment with analysis of GC/MS. The percentages of carbon, metal, and chlorine in samples were determined by the procedure used in real fly ash, as described in our earlier study [9,16]. The Cu percentage used, 0.2 wt%, is that of the mean value of Cu in four types of real fly ash. A blank sample without any metal compound was prepared from a mixture of AC (3.0%), KCl (10%), and SiO<sub>2</sub> (remainder). The metal species used were CuS (99.99%, Aldrich) and FeS (99.9%, Aldrich). A simplified model sample appropriate for spectroscopic measurements was also prepared. To avoid background absorption by silicon, the base material was changed from SiO<sub>2</sub> to boron nitride (BN). The model sample contained AC (5%) and BN (remainder) plus CuS (5%).

## 2.2. Measurement of PCDDs, PCDFs, PCBs, and CBzs by GC/MS

In our earlier study, the concentrations of PCDDs and PCDFs in real and model samples were analyzed using high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS: HP-6890/Autospec Ultima by Agilent/Micromass) with two columns, SP-2331 and DB-17HT [9,17]. In this study, PCBs and CBzs were analyzed using HRGC/low-resolution MS (HP-6890/HP-5973) [9]. Sample pretreatment for the determination of chlorinated aromatic compounds was conducted according to Japanese Industrial Standards (JIS) K 0311 and 0312.

We placed 5 g of simplified model mixture into a quartz boat contained within a quartz tube (120 cm × 4 cm internal diameter), which was then placed in a preheated electronic furnace at 300 °C for 30 min under a flow of 10% oxygen/90% nitrogen delivered at 50 mL/min, to simulate the post-combustion zone of a thermal process. After heating, the concentrations of chlorinated aromatic compounds in the modeled fly-ash residue and in the gas phase collected in an impinger containing 100 mL of toluene were analyzed separately. For each heating experiment, analyses of the PCBs and CBzs were duplicated ( $n=2$ ). The concentrations of PCDDs and PCDFs in a modeled fly ash containing CuCl<sub>2</sub>·2H<sub>2</sub>O were previously measured three times ( $n=3$ ) to confirm reproducibility [9]. Concentrations of PCDFs, PCBs, and CBzs were of the same order as those from a modeled fly ash of similar composition reported by

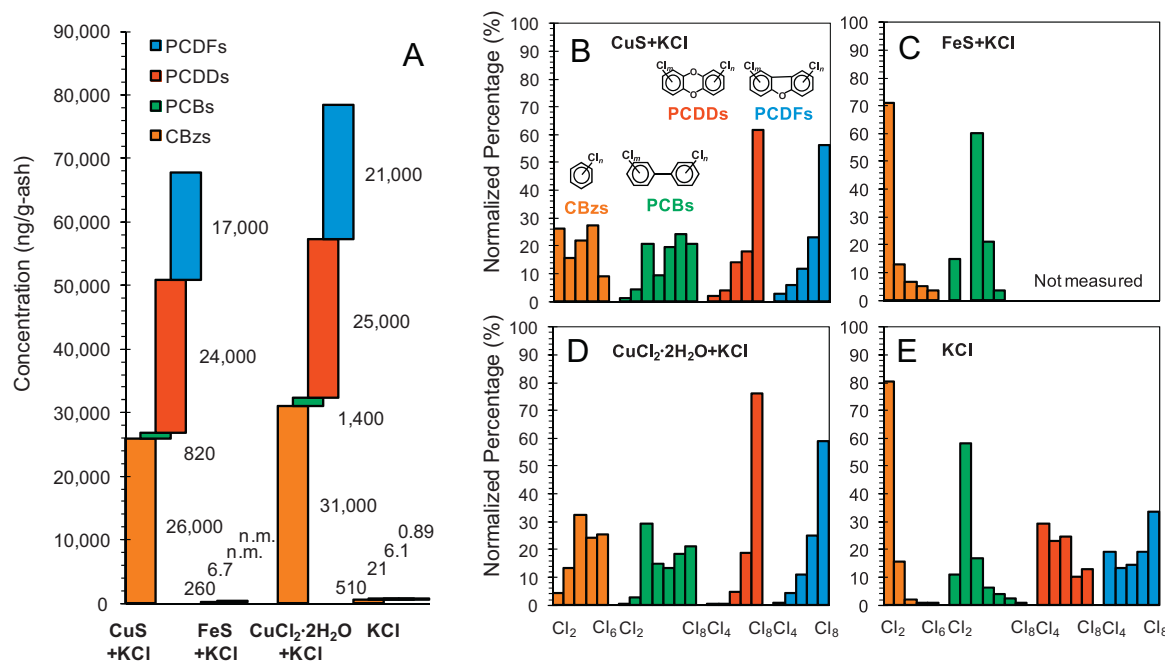
Stieglitz et al. [18], confirming the accuracy of our analytical procedures. Thereafter, concentrations of PCDDs and PCDFs in MSWI fly ash and modeled fly ash containing admixed metallic compounds, except for CuCl<sub>2</sub>·2H<sub>2</sub>O, were measured only once ( $n=1$ ).

## 2.3. In situ SR-XRD

The chemical forms in the simplified model mixture were determined using *in situ* powder X-ray diffraction using synchrotron radiation (SR-XRD). About 0.6 mg of a simplified model mixture was placed in a quartz capillary column (0.5-mm diameter) using a Pasteur pipette and sealed by a burner under atmospheric air. We placed the capillary under a Debye–Scherrer camera for measurement of SR-XRD using BL02B2 in SPring-8 (Hyogo, Japan). The diffraction X-ray pattern was detected using an imaging plate. The capillary was heated by nitrogen gas from room temperature to 450 °C, and we measured the SR-XRD pattern for which crystal information was identified using MDI Jade 6j software (Rigaku, Japan) containing an ICDD powder diffraction file.

## 2.4. In situ Cu K-edge XANES

Using *in situ* Cu K-edge XANES, we detected the chemical structure of Cu at the atomic level in the simplified model mixture. After the sample was ground using a mortar and agate mortar for 10 min respectively, 200 mg were pressed into a disk (13 mm in diameter). Cu K-edge XANES was performed using beamline BL01B1 in SPring-8 (Hyogo, Japan) as a sample disk was heated in the T-type *in situ* cell [11–13], which was constructed of a glass cell, a mantle heater, and a temperature controller. The cell consisted of a tubular part 4.0 cm in diameter, and the T measured 11.5 cm on each side. A sample disk was placed on a glass stand on a sample board and inserted in the cell. The X-rays passed through a window made of Kapton film. A water-cooled tube was coiled outside the Kapton film so that the thermal load did not affect the Kapton film. The temperature of the sample was increased gradually and linearly from room temperature to 450 °C. The 10% O<sub>2</sub> (90% N<sub>2</sub>) gas atmosphere was introduced from the inlet of the T-type

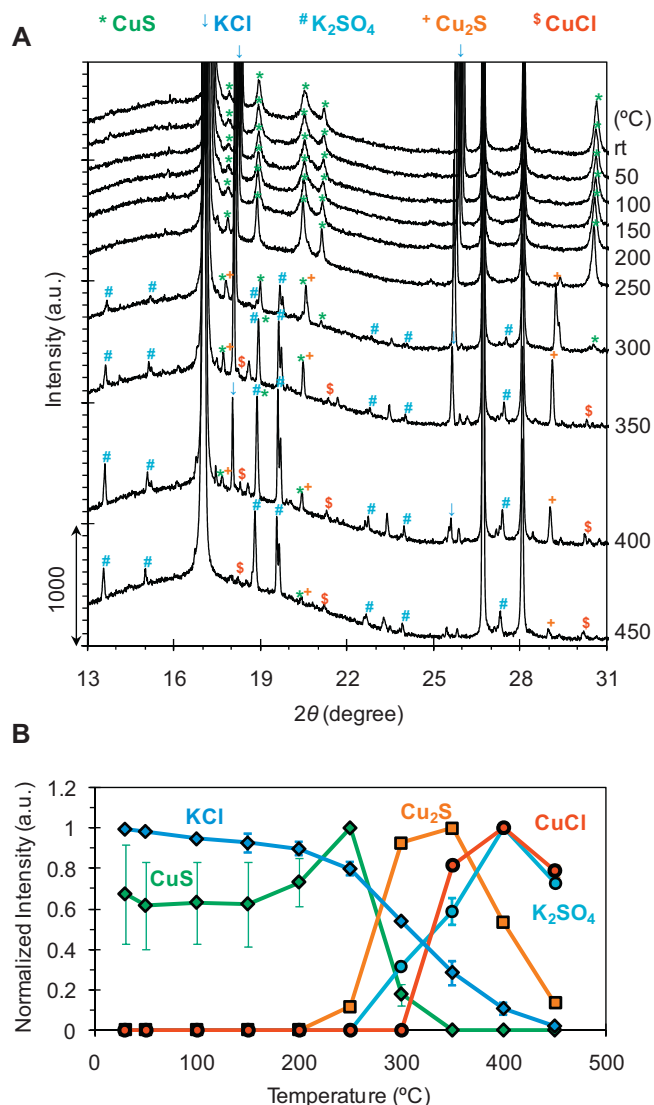


**Fig. 1.** Unexpected formation of organochlorine compounds via cupric sulfide (CuS). (A) Solid-phase concentrations of polychlorinated dibenzo-*p*-dioxins (PCDDs), furans (PCDFs), biphenyls (PCBs) and chlorobenzenes (CBzs) in four model samples heated to 300 °C. Normalized distribution patterns of PCDDs, PCDFs, PCBs, and CBzs in (B) CuS + KCl, (C) FeS + KCl, (D) CuCl<sub>2</sub>·2H<sub>2</sub>O + KCl [9], and (E) KCl [9]. Detailed information about model samples is described in the text under Section 2.

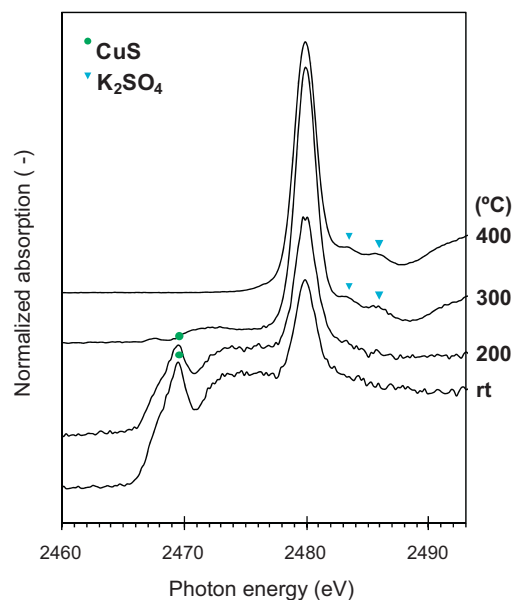
cell at 50 mL/min and exhausted from the outlet. The energy area from 8730 to 9820 eV was measured in 2.5 min using quick scan mode. XANES spectra of a sample disk were collected in transmission mode with a Si(1 1 1) monochromator. The energies were first adjusted using the reference copper foil. The spectra of reference materials,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{CuCl}_2$ ,  $\text{CuCl}$ ,  $\text{Cu}_2(\text{OH})_3\text{Cl}$ ,  $\text{CuO}$ ,  $\text{Cu}_2\text{O}$ , and  $\text{Cu}$ , were measured to compare their spectral shapes and to identify major species; an XANES spectrum can be used as a fingerprint that reflects the local environment of copper. Species can be distinguished using the linear combination fit technique, in which spectra of known reference species are fitted to the spectrum of the unknown sample. We conducted a linear combination fit of the XANES spectrum to determine the major species using REX 2000 ver 2.5.5 software (Rigaku, Japan). The residual value,  $R \text{ value} = \frac{\sum(\text{XANES}_{\text{measd}} - \text{XANES}_{\text{calcd}})^2}{\sum(\text{XANES}_{\text{measd}})^2}$ , was used to evaluate the linear combination fit for the experimental spectra.

### 2.5. Cl and S K-edge NEXAFS

The Cl and S forms present after the simplified model mixture was heated were determined by measuring the Cl and S K-edge NEXAFS, respectively. A sample was ground using a mortar for 10 min. The sample powder was then inserted on a quartz boat



**Fig. 2.** (A) *In situ* SR-XRD was performed and (B) normalized intensities of KCl, CuS,  $\text{Cu}_2\text{S}$ , CuCl, and  $\text{K}_2\text{SO}_4$  were calculated using tiny diffraction peaks.



**Fig. 3.** S K-edge NEXAFS spectra at room temperature (rt), 200 °C, 300 °C and 400 °C.  $\text{CuS}$  standard compound was measured in this study. We referred to  $\text{K}_2\text{SO}_4$  from Takahashi et al. [28].

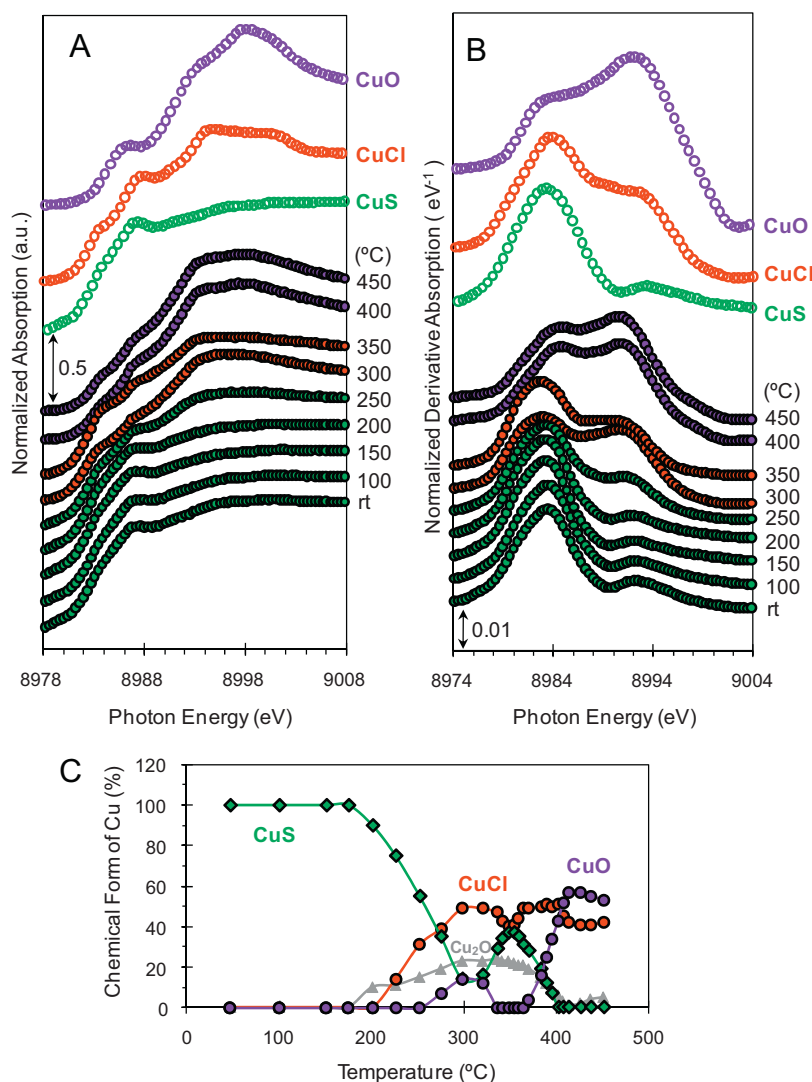
into a quartz tube (120 cm  $\times$  4.0 cm in diameter) filled with 10%  $\text{O}_2$  (90%  $\text{N}_2$ ) at 50 mL/min and heated for 30 min in an electric furnace preheated to 200, 300, and 400 °C. After the heating procedure, the sample powder was sealed as quickly as possible, the measurement of Cl and S K-edge NEXAFS was performed using a BL-11B at the Photon Factory (Tsukuba, Japan). The *in situ* cell could not be used in the Photon Factory because of physical restrictions of the device. Powdered samples were mounted on carbon tape, and their NEXAFS spectra were collected in total fluorescence yield (TFY) mode in a vacuum.

The X-ray absorption spectra of Cl and S in different inorganic and organic reference compounds were collected to assist in the identification of the chemical state of Cl and S in the sample after heating (Cl described in detail, Refs. [12–14]). The references for copper and sulfur compounds were  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{CuCl}_2$ ,  $\text{CuCl}$  and  $\text{Cu}_2(\text{OH})_3\text{Cl}$ , and  $\text{CuS}$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{Na}_2\text{S}_2\text{O}_3$  and  $\text{Na}_2\text{SO}_3$ , respectively, with polyvinyl chloride as an aliphatic organic carbon connected to Cl, and their NEXAFS spectra were measured in total electron yield (TEY) mode in a vacuum. We selected Cl references 1,3,5-, 1,2,4,5-, and pentachlorobenzene and 2,3-, 2,4-, 2,6-, 3,4-, 2,3,6- and 2,3,4,6-chlorophenol connected to aromatic carbon. Cl K-edge NEXAFS spectra of chlorobenzenes and chlorophenols were measured under atmospheric pressure by the conversion electron yield (CEY) method at BL-9A at the Photon Factory. All Cl-NEXAFS spectra were calibrated against the intense absorption feature of solid KCl at 2822.8 eV. The absorption peaks of Cl combined with aliphatic and aromatic carbon and copper were below 2820.2 and  $2821.1 \pm 0.1$  eV, and above 2822.0 eV, respectively. Copper chlorides have pre-edge features (about 2817 eV). Therefore, Cl bound to inorganic, aromatic or aliphatic carbon can be distinguished by the features of a Cl XANES spectrum [4]. Reflected in these spectral features, analyses were performed by a linear combination fit using reference materials of chlorine using REX 2000.

## 3. Results and discussion

### 3.1. Thermochemical concentrations of PCDDs, PCDFs, PCBs, and CBzs by a sulfide of copper

In general, a Cu–S bonding compound was thought to be a weak promoter of chlorination of carbon [19–22]. A model



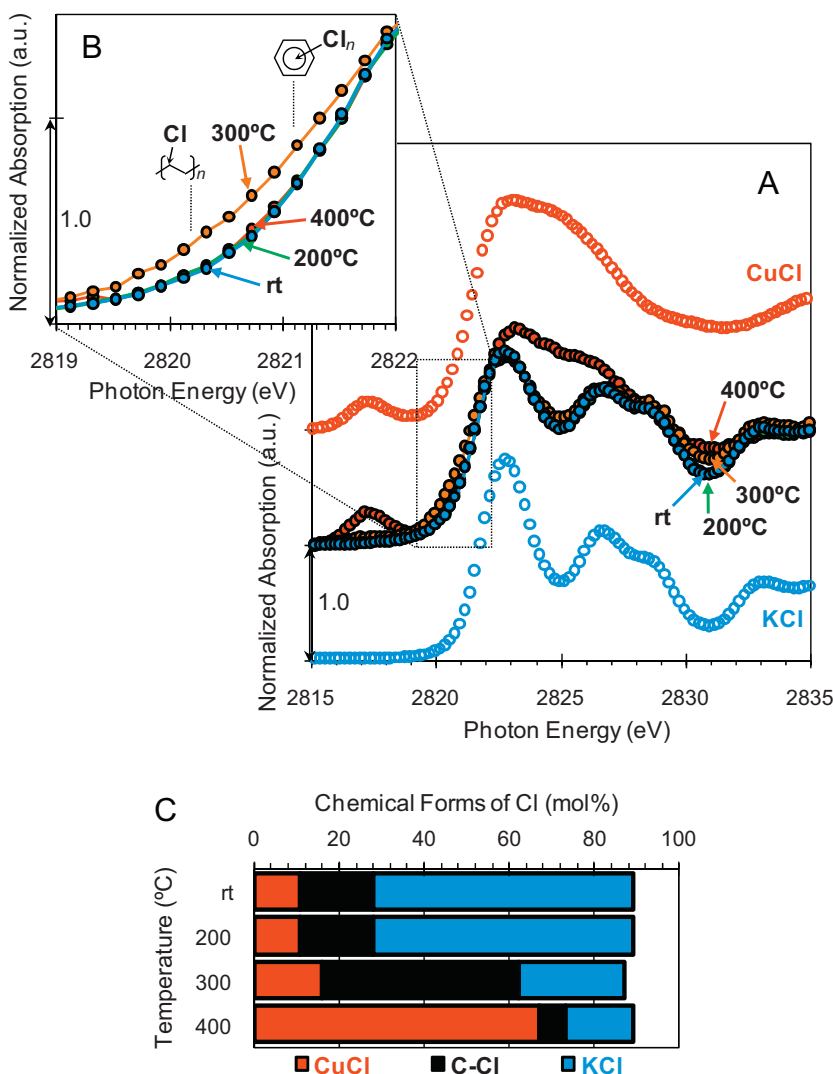
**Fig. 4.** (A) *In situ* Cu K-edge XANES spectra and (B) derivative XANES spectra. (C) The composition of the Cu chemical form was computed by comparing reference spectra such as CuS, CuCl, and CuO.

mixture of CuS+KCl, in which cupric sulfide (CuS, 0.2% Cu) combined with inorganic chloride (KCl, 10% Cl), activated carbon preheated at 500 °C under an N<sub>2</sub> gas stream to eliminate any organochlorine compounds (AC, 3%), and silicon dioxide (SiO<sub>2</sub>, rest) in solid phase, was ground in mortar for ca. 10 min and heated at the 300 °C for ca. 30 min under a 50-mL/min 10% O<sub>2</sub> (N<sub>2</sub> balance) gas stream. Surprisingly, our results show that the highest concentrations of PCDDs (24,000 ng/g-ash sum of Cl<sub>4</sub>–Cl<sub>8</sub>), PCDFs (17,000 sum of Cl<sub>4</sub>–Cl<sub>8</sub>), PCBs (820 sum of Cl<sub>2</sub>–Cl<sub>8</sub>), and CBzs (26,000 sum of Cl<sub>2</sub>–Cl<sub>6</sub>) in the heated CuS+KCl were comparable to concentrations in other heated model mixtures (CuCl<sub>2</sub>·2H<sub>2</sub>O+KCl) using the most well studied and most active metal catalyst (CuCl<sub>2</sub>·2H<sub>2</sub>O [9], 0.2% Cu), KCl (10% Cl), AC (3%), and SiO<sub>2</sub> (rest) as shown in Fig. 1A. In contrast, heated ferrous sulfide (FeS, 0.2% Fe) under the same KCl–AC–SiO<sub>2</sub> matrix (FeS+KCl) did not promote organochlorine compounds such as PCBs and CBzs. Furthermore, the distribution patterns of highly chlorinated compounds (CBzs, PCBs, PCDDs and PCDFs) in CuS+KCl; Fig. 1B) were remarkably similar to that of CuCl<sub>2</sub>·2H<sub>2</sub>O+KCl (Fig. 1D), unlike the patterns of low chlorination in FeS+KCl and the heated KCl–AC–SiO<sub>2</sub> matrix denoted by KCl [9] (Fig. 1C and 1E, respectively). FeS+KCl showed lower concentrations of CBzs and PCBs than KCl as shown in Fig. 1A, which implied that FeS acts as inhibitor [30] and is not a chemical form promoting

the chlorination. And elemental copper was reported to show weak potential to generate organochlorine compounds [33]. So, chlorination of carbon by S-bonding copper (CuS) might be combination effects of Cu and S. These results imply the similarity of the thermochemical formation paths of organochlorine compounds in solid phase between cupric sulfide and cupric chloride.

### 3.2. X-ray spectroscopic evidences

Why did CuS strongly promote the solid-phase formation of toxic organochlorine compounds and appear to use a formation path similar to that of cupric chloride? Using a simplified model mixture (CuS+KCl+AC+a base material), we performed detailed experiments to answer this question, specifically utilizing *in situ* Cu K-edge X-ray absorption near edge structure (XANES), *in situ* synchrotron-radiation X-ray diffraction (SR-XRD), and Cl and S K-edge near-edge X-ray absorption fine structure (NEXAFS) at beam-line BL01B1, BL02B2 (SPring-8, Hyogo) and BL-11B/9A (Photon Factory, Tsukuba), respectively. The changes in chemical crystal states during temperature increases were detected and analyzed using tiny diffraction peaks in SR-XRD (Fig. 2A). Although CuS and KCl existed in stable condition up to 250 °C, CuS dramatically decreased by ca. 80% from 250 to 300 °C, and KCl also continuously



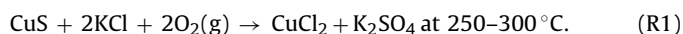
**Fig. 5.** (A) Cl K-edge NEXAFS spectra provided direct knowledge about the chlorination of carbon. (B) A close-up figure showing spectrum evidence of chlorine bonded with aliphatic and aromatic carbon at 300 °C. This is supported by (C) a linear combination fitting with reference Cl compounds.

decreased at temperatures greater than 250 °C (Fig. 2B). Instead, CuCl, K<sub>2</sub>SO<sub>4</sub>, and Cu<sub>2</sub>S appeared at ca. 250 °C. Cu<sub>2</sub>S remained over a short temperature range (300–350 °C). When we analyzed the sulfur element by S K-edge NEXAFS, the thermochemical change of CuS to K<sub>2</sub>SO<sub>4</sub> was also detected (see Fig. 3). Fig. 2B shows that changing trends in CuCl and K<sub>2</sub>SO<sub>4</sub> were synchronized and that the two chemicals maintained their crystal structures at temperatures greater than 350 °C. By analyzing the *in situ* Cu K-edge spectra of XANES (Fig. 4A) and its derivative spectra (Fig. 4B), we confirmed similar temperature profiles of the existence ratio of copper compounds including copper oxides (Cu<sub>2</sub>O and CuO), which were not detected by the other techniques (Fig. 4C). CuS, CuCl, and Cu<sub>2</sub>O decreased, increased, and increased their ratios, respectively, from ca. 200 °C (100%, 0%, and 0%, respectively) to 300 °C (15%, 50%, and 20%, respectively). Furthermore, when CuS and Cu<sub>2</sub>O began to decrease and finally vanished from 380 to 400 °C, the ratio of CuO jumped by 60% instantly, then the CuCl ratio stabilized. These *in situ* results indicate that 300 °C was the turning point of chlorination for carbon derived from the CuS+KCl system. At hot-spot temperatures less than and greater than 300 °C, the Cl K-edge NEXAFS spectra provided strong evidence of the chlorination of carbon (Fig. 5A). We discovered a bulging structure from 2819 to 2822 eV only at 300 °C (Fig. 5B), which was caused by chlorine bonding with

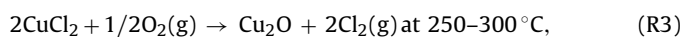
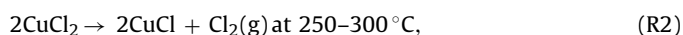
aliphatic and aromatic carbons (2820.4 eV for polyvinylchloride and 2821.1 ± 0.1 eV for aromatics, respectively [12–14]). Analysis of spectra (Fig. 5C) at 300 °C shows the maximum ratio of ca. 50% chlorine connected to carbon. Decreasing KCl (200–400 °C) and increasing CuCl (300–400 °C) match other spectroscopy analyses.

### 3.3. Formation mechanism of organochlorine compounds in solid phase

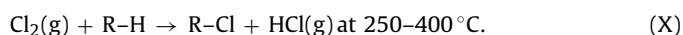
A scheme of thermochemical chlorination of carbon by solid-phase cupric sulfide, including the total quantitative measurement and spectroscopic characterization, is shown in Fig. 6. At nearly 300 °C, CuS and KCl interchanged their S and Cl in the solid phase:

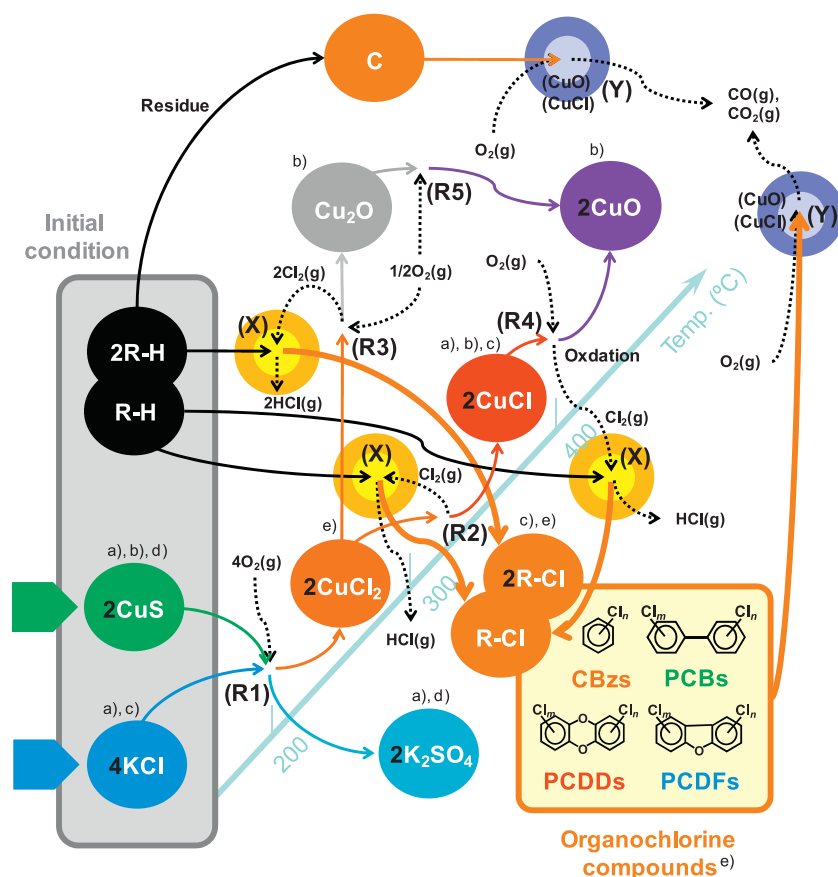


Immediately, intermediate CuCl<sub>2</sub> released Cl<sub>2</sub> (g) via two paths,



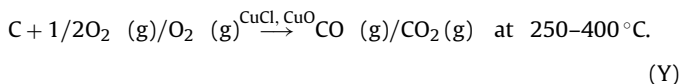
then direct chlorination of carbon (R-Cl) [12] progressed, i.e.



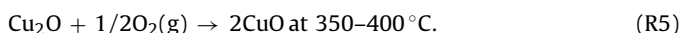
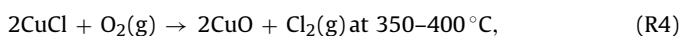


**Fig. 6.** Thermochemical solid-phase interaction scheme triggered by cupric sulfide. Reactions in solid and gas phases show solid and dotted arrows, respectively. Each chemical compound was detected and identified by (a) SR-XRD, (b) Cu K-edge XANES, (c) Cl K-edge NEXAFS, (d) S K-edge NEXAFS, and (e) GC/MS analyses. Eqs. (R1)–(R5), (X) and (Y) mean thermochemical reactions described in text. In particular, Eqs. (X) and (Y) indicate chlorination and gasification of carbon by target circles with warm and cold colors, respectively.

Although Eq. (X) shows cupric chloride acted as chlorine source by reduction in Eq. (R2) or oxidation in Eq. (R3), oxychlorination cycle to generate R–Cl compounds also was thought to occur catalyzed by  $\text{CuCl}_2$  [11,31]. However, the present study did not directly detect this catalytic behavior of copper.  $\text{CuCl}$  was studied as a spill-over catalyst to form a surface oxygen complex [12,23] as a dioxin-like carbon framework, then gasification of some active edge of carbon matrix [12] occurred:



At nearly  $400^\circ\text{C}$ , some  $\text{CuCl}$  and  $\text{Cu}_2\text{O}$  were oxidized to  $\text{CuO}$  by  $\text{O}_2(\text{g})$ :



Although chlorination in Eq. (X) via Eq. (R4) partially reacted, carbon gasification strongly catalyzed by  $\text{CuO}$  [12,24] mainly occurred at temperatures greater than ca.  $400^\circ\text{C}$  in Eq. (Y). The dioxin-like framework of carbon was destroyed by gasification from  $300$  to  $400^\circ\text{C}$  (Fig. 4C). In addition, temperatures between  $300$  and  $400^\circ\text{C}$  were reported as showing the maximum concentrations of organochlorine compounds such as dioxins [25]. Therefore, from the balanced chlorination in Eq. (X) and gasification in Eq. (Y) of the carbon matrix, we determined that the thermochemical formation of toxic organochlorine compounds in solid phase functioned by utilization of  $\text{CuS}$  as a starting material.

#### 4. Conclusion

In conclusion, we discuss the environmental implications of this study. Generally, most fly ash contains chlorine in inorganic form, such as  $\text{KCl}$  and  $\text{NaCl}$  [14,26]. However, only inorganic chlorines do not promote the formation of organochlorine compounds in solid phase [14,27]. From a global viewpoint, the homologue distributions of PCDDs and PCDFs in natural, clean environmental samples recorded patterns similar to those from anthropogenic thermal facilities [6,9]. In addition, the distribution patterns of PCDDs, PCBs, and CBzs derived from heated  $\text{CuS} + \text{KCl}$  were similar to the patterns of ash produced by municipal solid-waste incineration by clustering [9]. Except for well-known metal promoters such as  $\text{Cu}\text{--}\text{Cl}$  [9–12,14],  $\text{Cu}\text{--}\text{O}$  [9,10,15], and  $\text{Fe}\text{--}\text{Cl}$  [9,10,13,14] compounds, our results imply that a fraction of cupric sulfide promoted the solid-phase thermochemical formation of a large proportion of organochlorine compounds that used inactive inorganic chloride as chlorine storage. Chemical bonding of  $\text{Cu}$  and  $\text{S}$  indirectly influenced chlorination of carbon, by interchanging of sulfur in S-bonding copper and chlorine in inorganic chloride as shown in Eq. (R1). Further, these organochlorine compounds are a partial source of environmental pollution. Identifying this causative factor provides an opportunity to correctly estimate environmental pollution in depth. In the future, we will attempt to test other trace promoters and more complex real systems; the study of the environmental and anthropogenic thermochemical solid phase may yet provide much useful scientific data. According to these results, not only eliminating the inflow of copper to thermal facilities but also chemically inhibiting copper at the atomic level [32] might

decrease the creation of organochlorine compounds by thermal processes.

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