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Novel evidence for natural formation of dioxins in ball clay

Yuichi Horii [a], Bert van Bavel [b], Kurunthachalam Kannan [a,*], Gert Petrick [c],
Kerstin Nachtigall [c], Nobuyoshi Yamashita [d,*]

[a] *Wadsworth Center, New York State Department of Health, and Department of Environmental Health Sciences, School of Public Health, State University of New York at Albany, Empire State Plaza, P.O. Box 509, Albany, NY 12201-0509, USA*
[b] *MTM Research Center, Department of Natural Sciences, Örebro University, 701 82 Örebro, Sweden*
[c] *Leibniz Institute of Marine Sciences at the University of Kiel, Dusternbrooker Weg 20, 24105 Kiel, Germany*
[d] *National Institute of Advanced Industrial Science and Technology, 16-1 Onogawa, Tsukuba, Ibaraki 305-8569, Japan*

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Abstract

Elevated concentrations of dioxins in ancient ball clay from the Mississippi Embayment suggest natural formation of dioxins in the environment. Evidence for such natural formation in ball clay derives from unique congener profiles in undisturbed ancient clay deposits and from the lack of other anthropogenic contaminants. Here we present novel evidence of natural formation of dioxins based on congener-specific carbon isotopic analysis of octachlorodibenzo-*p*-dioxin (OCDD) in ball clays from the USA and Japan. The analyses were performed using a combination of double-column high performance liquid chromatography clean-up and two-dimensional gas chromatography–isotope ratio mass spectrometry. Elevated concentrations of OCDD found in ball clays from the USA and Japan were isotopically distinguished from the anthropogenic source materials (fly ash and pentachlorophenol) and environmental samples (sediment and soil). The isotopic signatures and the occurrence of OCDD in ancient ball clays deposited in the Tertiary Era provide evidence for the *in situ* formation of dioxins.

Keywords: Stable carbon isotope; Octachlorodibenzo-*p*-dioxin; Kaolin; CSIA; Dioxin source; Pentachlorophenol; PCDD

1. Introduction

Since the 1980s, reports have suggested the natural formation of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) (hereafter referred to as dioxins) (Rappe et al., 1997; Silk et al., 1997; Bumb et al., 1980; Hoekstra et al., 1999; Gaus et al., 2001). Elevated concentrations and unique congener profiles of dioxins in sediment and soil from Mississippi, USA, were shown to arise from natural processes (Rappe et al., 1997). Later, several studies were conducted to elucidate the sources of high concentrations of dioxins, particularly PCDDs (>450 ng g^{-1} dry weight [dw], and >15 ng WHO-TEQ g^{-1} dw), in ball clays, which consist of kaolin, from the Southern-Central United States (Rappe et al., 1998, 2001; Ferrario et al., 2000; Ferrario and Byrne, 2002; Gadomski et al., 2004). An estimated 1.2 million metric tons of American ball clay were mined in 2006 for the ceramic industry (USGS, 2007). Ball clay in the United States is mainly mined in Tennessee, Texas, Kentucky, and Mississippi regions corresponding to the shores of the Mississippi Embayment. The ball clays are embedded in sediments laid down during the early to middle Eocene Epoch (approximately 40–45 Ma) (Ferrario et al., 2000). The presence of dioxins in such ancient clays presented an interesting scientific quandary. Dioxin profiles in ball clays are

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[*] Corresponding authors. Tel./fax: +81 29 861 8335 (N. Yamashita), tel.: +1 518 474 0015; fax: +1 518 473 2895 (K. Kannan).
E-mail addresses: kkannan@wadsworth.org (K. Kannan), nob.yamashita@aist.go.jp (N. Yamashita).

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characteristically dominated by the congener octachlorodibenzo-*p*-dioxin (OCDD) ($>$130 ng g^{-1} dw), and the concentrations of other congeners decrease with corresponding reduction in the level of chlorination. Furthermore, concentrations of PCDFs are very low or nondetectable, and 1, 2, 3, 7, 8, 9-hexachlorodibenzo-*p*-dioxin (HxCDD) predominate (relative to the other 2, 3, 7, 8-substituted HxCDD isomers). This pattern differs from the profile found for anthropogenic sources of contamination (Rappe et al., 2001). Chlorine isotope analysis of OCDD was carried out in ball clay recently (Holmstrand et al., 2006), and the chlorine isotope composition of OCDD suggested non-biologic origin of OCDD rather than an origin via biotic chlorination by perchlorooxidase enzymes. The chlorine isotope and black carbon results indicated abiotic and non-pyrogenic origin of dioxins in ball clay. High concentrations of dioxins were found not only in American ball clay, but also in kaolin clay from Germany and Spain (Rappe et al., 2001; Abad et al., 2002). Moreover, the PCDD isomer composition was fairly consistent among the ball clays from the various geographical regions in the world. Based on these findings, we hypothesize natural formation of dioxins in kaolin and *in situ* mineral-catalyzed synthesis.

Congener-specific carbon isotope analysis (CSIA-δ^{13}C) of complex mixtures by gas chromatography–isotope ratio mass spectrometry (GC–IRMS) is emerging as a powerful analytical tool to trace the origin and fate of anthropogenic organic pollutants (Abrajano, 1999). Several studies have reported the CSIA-δ^{13}C of organic pollutants such as polychlorinated biphenyls (PCBs) (Jarman et al., 1998; Drenzek et al., 2001; Horii et al., 2005), polychlorinated naphthalenes (Horii et al., 2005), brominated flame retardants (Vetter et al., 2007), and polycyclic aromatic hydrocarbons (PAHs) (O'Malley et al., 1994; McRae et al., 1999). Nevertheless, prior to our study, CSIA-δ^{13}C of dioxins has not been reported. The evidence for natural formation of dioxins in kaolin was based on a unique congener profile in undisturbed kaolin deposits, as well as a lack of other anthropogenic contaminants in kaolin deposits. However, to support the hypothesis of natural formation of dioxins, alternative approaches are required. Here, new evidence for the natural formation of dioxins is presented by comparison of CSIA-δ^{13}C of OCDD in kaolin with anthropogenic dioxin source materials (fly ash and pentachlorophenol [PCP]), and contaminated environmental samples (soil and sediment), as determined by a combination of double-column HPLC clean-up and two-dimensional (2D) GC–IRMS. In addition to congener-specific δ^{13}C values, bulk-δ^{13}C values and concentrations of OCDD were measured, to provide additional supporting evidence for our conclusions. This is the first study to analyze dioxins in Japanese ball clay (known as 'Gaerome' and 'Kibushi'), which resemble American ball clay in terms of their mineral constituents and origins. Many sedimentary kaolin deposits of the Pliocene Epoch (2–5 Ma) are distributed in Central Japan, and constitute the most productive kaolin-mining area in Japan (Sudo and Shimoda, 1978). The objectives of this study were to determine the carbon isotope signature of OCDD in samples from natural and anthropogenic sources, and to compare OCDD isotopic ratios in various samples containing high concentrations of OCDD. The carbon isotopic compositions in clay samples and in source materials of dioxins provide information regarding chemical pathway and natural formation of dioxins in kaolin.

2. Materials and methods

2.1. Samples and chemicals

The types of samples analyzed in this study were nine clays, five fly ashes, five pesticides, 11 soil and sediment samples, and eight standard solutions (Table 1). OCDD and octachlorodibenzofuran (OCDF) standards were purchased from four companies, namely, GL Sciences (Tokyo, Japan), Wellington Laboratories (Guelph, ON, Canada), Cambridge Isotope Laboratories (Andover, MA, USA) and AccuStandard (New Haven, CT, USA). Ball clays collected from mines located in Tennessee and Kentucky (Ferrario et al., 2007) and Spanish kaolin were kindly provided by Dr. Joseph Ferrario at the United States Environmental Protection Agency (USEPA) and Dr. Esteban Abad at IIQAB-CSIC, Barcelona, Spain, respectively. Two types of Japanese ball clays, Gaerome and Kibushi, which are used as raw materials in ceramic wares, floor and wall tiles, and pottery and Japanese bentonite (as a control) were obtained from clay industries. Gaerome is a plastic kaolin clay consisting of coarse quartz grains and occasional feldspar grains. Kibushi is a dark-colored, plastic kaolin clay stained by organic substances, and thus resembles the ball clay in the United States. Gaerome has a mineral composition similar to that of Kibushi; they consist mainly of platy, disordered kaolinite associated with minor amounts of tubular halloysite and quartz, and occasional illite and smectite. Sediment, soil, and fly ash samples containing high levels of dioxins were prepared as follows. Reference materials of river sediment (JSAC0432) and fly ash (JSAC0502) with certified concentrations of dioxins were purchased from The Japan Society for Analytical Chemistry (JSAC); OCDD concentrations in river sediment and fly ash were certified at 16.4 ng g^{-1} dry wt (dw), and 27.4 ng g^{-1} dw, respectively. Two fly ash samples, three sediment samples, and a soil sample from 7th to 11th rounds of the international intercalibration study for dioxins analysis (IIS) were used. In addition, two other fly ash samples produced by fluidized bed and stoker type incinerators in Japan were used in this study. Surface sediment and sediment core samples from Tokyo Bay, Japan, were collected from 2000 to 2004. Five PCP standards from different producers and lot numbers were obtained from Aldrich (St. Louis, MO, USA), Supelco (Bellefonte, PA, USA), RFR (Hope, RI, USA) and the USEPA (Washington, DC, USA).

Table 1
Concentrations of OCDD and stable carbon isotope data in sample matrices analyzed

Sample	Source or location	A $\delta^{13}C_{bulk}$ (‰)	B $\delta^{13}C_{OCDD}$ (‰)	Ratio A/B	OCDD conc. (ng g^{-1} dw)
Clay					
Bell Dark-Axner	Ball clay, USA	−24.9 ± 0.09	−26.2 ± 0.1	0.95	244
Amherst-Old Mine #4	Ball clay, USA	−25.4 ± 0.08	−25.9 ± 0.4	0.98	615
Jackson-Amherst	Ball clay, USA	−24.8 ± 0.04	−27.1 ± 0.2	0.92	659
Aligator-Old Mine #4	Ball clay, USA	−26.1 ± 0.01	−26.2 ± 0.1	1.00	237
Amherst-Thomas	Ball clay, USA	−24.8 ± 0.05	−25.7 ± 0.3	0.97	286
Spanish kaolin	Spain	−24.6 ± 0.4	nd	na	24
Bentonite	Japan	0.8 ± 0.09	na	na	nd
Gaerome	Ball clay, Japan	−26.5 ± 0.2	na	na	0.26
Kibushi	Ball clay, Japan	−27.6 ± 0.2	−23.5[d]	1.18	1.5
Fly ash					
Ash B, 8th round IIS[a]	IIS	−23.7 ± 0.6	−22.8 ± 0.3	1.04	381
Ash C, 10th round IIS	IIS	−31.6 ± 0.2	−24.0 ± 0.4	1.32	71
Fly ash, JSAC0502	JSAC[b]	−25.4 ± 0.07	−24.7 ± 0.3	1.03	33
Fly ash, stoker	Japan	−21.1 ± 0.6	−24.0 ± 0.5	0.88	3.4
Fly ash, fluidized bed	Japan	−22.0 ± 0.1	−23.1 ± 0.4	0.95	10
Pesticide					
PCP (AL), lot: 072697	Aldrich	−31.7 ± 0.1[c]	−32.4 ± 0.5	0.98	104 000
PCP (EPA), lot: 6204	US EPA	na	na	na	178
PCP (SU1), lot: 317–31	Supelco	na	na	na	172
PCP (RFR), lot: RCP-19	RFR, Corp.	na	na	na	308
PCP (SU2), lot: LA09081	Supelco	−30.9 ± 0.7[c]	−31.4 ± 0.1	0.98	17 100
Sediment and Soil					
Soil A, 9th round IIS	IIS	−22.5 ± 0.4	−30.1 ± 0.1	0.75	8.5
River sediment, JSAC0432	JSAC[b]	−25.7 ± 0.03	−30.1 ± 0.5	0.85	20
TB surface sediment1	Tokyo Bay, Japan	−19.7 ± 0.08	nd	na	1.2
TB surface sediment2	Tokyo Bay, Japan	−20.2 ± 0.8	−29.4[d]	0.69	2.4
TB surface sediment3	Tokyo Bay, Japan	−16.6 ± 1.3	nd	na	1.5
Sediment C, 7th round IIS	IIS	−26.4 ± 0.5	−32.0 ± 0.2	0.82	257
Sediment B, 8th round IIS	IIS	−23.3 ± 0.2	−28.6 ± 0.3	0.81	2.1
Sediment D, 11th round IIS	IIS	−22.4 ± 0.07	−27.1 ± 0.6	0.83	3.3
Sediment core, 8–12 cm	Tokyo Bay, Japan	−18.8 ± 0.1	−30.6 ± 0.6	0.61	2.3
Sediment core, 18–22 cm	Tokyo Bay, Japan	−19.2 ± 0.1	−30.9 ± 0.5	0.62	3.3
Sediment core, 28–32 cm	Tokyo Bay, Japan	−19.3 ± 0.04	−32.0 ± 0.4	0.60	5.6
Standard					
OCDD (GL), lot: 001	GL Science	na	−28.6 ± 0.2	na	na
OCDD (WL), lot: D0751201	Wellington	na	−29.9 ± 0.2	na	na
OCDD (CIL), lot: 729−91	CIL	na	−28.7 ± 0.1	na	na
OCDD (AS), lot: 970325R-AC	AccuStandard	na	−30.7 ± 0.3	na	na
OCDF (GL), lot: F810415	GL Science	na	−25.8 ± 0.2[e]	na	na
OCDF (WL), lot: F1350404	Wellington	na	−25.8 ± 0.2[e]	na	na
OCDF (CIL), lot: 21985–49	CIL	na	−24.1 ± 0.4[e]	na	na
OCDF (AS), lot: 990224-LB-AC	AccuStandard	na	−24.6 ± 0.1[e]	na	na

na: not available and nd: limit of detection.

[a] International intercalibration study for PCDDs and PCDFs analysis; IIS.

[b] The Japan Society for Analytical Chemistry; JSAC.

[c] Bulk-δ^{13}C values of PCP were represented in δ^{13}C value of PCP measured by 2DGC–IRMS.

[d] Result from single analysis.

[e] δ^{13}C value of OCDF.

2.2. Analysis of OCDD concentration

The sample extraction and clean-up procedure for OCDD were based on the method described earlier (Taniyasu et al., 2003; Hanari et al., 2004; Horii et al., 2004; Wyrzykowska et al., 2006; Jiang et al., 2007), with minor modifications. Briefly, dried sample (sediment, soil, and fly ash) was extracted using a mixture of acetone and *n*-hexane (1:1, v/v) and toluene in an accelerated solvent extractor (ASE-200, DIONEX Co.) (Horii et al., 2004). The extracts were concentrated to 2 ml and first pre-cleaned by passing through a multi layer silica gel packed into a glass column in descending order as follows: silica gel (1 g), 2% (w/w) KOH–silica gel (3 g), silica gel (1 g), 44% (w/w) H_2SO_4–silica gel (4.5 g), 22% (w/w) H_2SO_4–silica gel (6 g), silica gel (1 g), 10% (w/w) $AgNO_3$–silica gel (6 g) and anhydrous sodium sulfate (1 cm) loaded on the top. The column was pre-washed with 200 ml of *n*-hexane, and target compounds were eluted with 200 ml of *n*-hexane. The analytes were then cleaned-up and fractionated using 10 g of activated basic alumina column chromatography. The analytes were eluted with 160 ml of 50% dichloromethane (DCM) in *n*-hexane (F3, dioxins) after passing 25 ml of *n*-hexane (F1) and 30 ml of 5% DCM in *n*-hexane (F2). The target chemicals were further isolated using double-column HPLC, porous, activated graphite carbon column (Hypercarb; Thermoelectron Co., San Jose, CA, USA) and pyrenyl silica column (PYE; Nacalai Tesque, Tokyo, Japan) (Taniyasu et al., 2003; Hanari et al., 2004; Horii et al., 2004). The aliquot (F3) from alumina column was manually injected into Hypercarb-HPLC which was eluted forward using 5% DCM in *n*-hexane (12 ml), 50% toluene in *n*-hexane (33 ml) and back flushed using toluene (37.5 ml) by heating the column at 50 °C. Due to the need for separation of OCDD and OCDF, the toluene fraction (F3.3) was further sub-fractionated using the PYE-HPLC column. The analytes from the PYE-HPLC column were eluted with 10% DCM in *n*-hexane (27 ml) followed by DCM (48 ml). The OCDD fraction (F3.3.2) from 57 to 64 min was collected in a glass concentration tube separately. Each sub-fraction (F3.3.2) was micro-concentrated to 100 µl under a gentle stream of nitrogen, and 2 µl aliquot was taken for measuring concentrations of OCDD using high-resolution gas chromatography and high-resolution mass spectrometry (HRGC–HRMS). The remaining extract was concentrated to 10–50 µl depending on OCDD concentration, and was used for CSIA-δ^{13}C of OCDD. PCP samples (5–24 mg) were diluted in a mixture of *n*-hexane and toluene (4:1, v/v) were loaded on a multi layer silica gel column, and then followed the same sample clean-up procedure as described above.

The concentrations of OCDD were determined by using a HP6890 interfaced with a micromass AutoSpec-Ultima mass spectrometer operated in the electron impact (38 eV and 500 µA current) selected ion monitoring (SIM) mode at a resolution $R > 10000$ MU (10% valley). The GC was equipped with DB-17 capillary column (0.25 µm film thickness; 30 m length × 0.25 mm i.d., J&W Scientific, Folsom, CA, USA). The details of analysis and validation of OCDD concentrations are given in previous publications (Hanari et al., 2004; Wyrzykowska et al., 2006). Coefficient of variation for OCDD concentrations measured in this study and the JSAC certified values were less than 5%.

2.3. CSIA-δ^{13}C and bulk-δ^{13}C analysis

CSIA-δ^{13}C of OCDD was carried out using 2DGC equipped with Finnigan MAT252 IRMS with a combustion furnace (Horii et al., 2005). The 2DGC system was built into a Trace GC 2000 (Thermo Electron Co.) equipped with a moving capillary stream switching (MCSS) (CE Instruments, Mainz-Kastel, Germany) (Duinker et al., 1988; Schulz et al., 1989). The MCSS technique cuts >98% of effluents from the first column, and transfers almost all of the target compounds into the second column. The cut functions were programmed according to the retention time of target congeners traced on a monitor detector (flame ionization detector; FID in this study) connected to a dome shape glass tube. First and second column flow rates were kept at 1.5–2 ml min^{-1}. OCDD was separated from interferences by a less polar capillary column, DB-5 (30 m × 0.25 mm i.d. × 0.25 µm; J&W Scientific), cut by MCSS and separated again on another column (Rtx-200, 15 m × 0.32 mm i.d. × 0.25 µm; Restek Corp., Bellefonte, PA). The column oven temperature was programmed from 70 (1 min) to 200 °C at a rate of 20 °C min^{-1}, and to 280 °C at 5 °C min^{-1}, which was held for 10 min, then finally to 300 °C (5 min) at 20 °C min^{-1} for OCDD analysis, and from 70 (1 min) to 200 °C at a rate of 20 °C min^{-1}, and then to 280 °C (5 min) at 5 °C min^{-1} for PCP analysis. Usually 2 µl aliquot was injected manually in a splitless mode at 280 °C. OCDD was identified based on the retention time comparing with an authentic standard. Oxidation and reduction reaction temperatures were held at 940 and 600 °C, respectively. Reoxidation of the combustion furnace catalysts was performed once a day by oxygen backflow for 20 min.

Bulk carbon isotope ratio analysis was carried out using an elemental analyzer (EA1110 CHNS) equipped with Finnigan ConFlo III and Delta plus IRMS. Well-milled sample (1–100 mg) was packed in a tin cup, and was combusted to release CO_2 and N_2 in oxidation and reduction reactors at 1000 and 650 °C, respectively (Carman and Fry, 2002). Isotope ratios of carbon are reported in parts per thousand, per mil (‰), and all values reported are relative to the international standard by conventional delta notation (δ^{13}C). For CSIA-δ^{13}C of OCDD, the CO_2 reference gas from our laboratory was calibrated by isotopic ratio reference gas from Oztech Co (Dallas, TX, USA) (SHOKO-944C), $\delta^{13}C = -40.84$‰ versus the Pee Dee Belemnite (PDB). Accuracy of the bulk isotope ratio analysis for carbon was verified using IAEA-NBS 22 ($\delta^{13}C = -29.7$‰) from the National Institute of Standards and Technology (Gaithersburg, MD, USA).

2.4. Quality assurance/quality control

The stability of the 2DGC–IRMS system and background contamination were checked daily. OCDD standard (AccuStandard, product no.: D-801N, lot no.: 970325R-AC) was analyzed at the beginning and at the end of sample measurements to check stability of the instrument. Uncertainties in measurements are shown by standard deviation from multiple injections. The standard deviation of repeated measurements of samples was 0.30‰ (average of $\delta^{13}C_{OCDD}$: −30.64‰, $n = 46$). The δ^{13}C of the control sample did not vary throughout the experiment. Recovery test was performed by spiking 10 µg of OCDD standard into sodium sulfate prior to extraction and procedural blanks were routinely analyzed. The recovery rate of OCDD through the whole analytical procedure was 76% ($n = 3$), and $\delta^{13}C_{OCDD}$ was

$-30.60 \pm 0.33‰$, which is very close to the average value of quality control standard measured daily. The shift in $\delta^{13}C$ value, isotopic fractionation during whole analytical procedure, was lower than 0.4‰, and this value is negligible considering the general analytical error of CSIA for organic compounds. As a quality control check for bulk carbon isotopic analysis, approximately 0.3 mg of peptone was analyzed at the beginning and at the end of sample analysis and after every three samples run on the instrument. The standard deviation of repeated measurements of bulk carbon was 0.31‰ for bulk-$\delta^{13}C$ ($n = 34$).

3. Results and discussion

3.1. Precision and accuracy of CSIA-$\delta^{13}C_{OCDD}$

Samples containing different concentrations of OCDD, ranging from 9.8 to 98 ng (3.1–31 ng of carbon), were analyzed in triplicate to test the efficiency of combustion of carbon to CO_2 and the $\delta^{13}C$ values under the system conditions specified above. Peak areas were linear ($r^2 > 0.9987$) and $\delta^{13}C$ values were stable at quantities above 24 ng of OCDD with a standard deviation that ranged from 0.06‰ to 0.42‰ (Fig. 1). However, below 20 ng of OCDD, $\delta^{13}C$ values of OCDD shifted upwards with corresponding standard deviation increasing to 0.83‰ when measuring 9.8 ng of OCDD. Therefore, in this study, CSIA-$\delta^{13}C$ of OCDD was reported as below the limit of obtaining precise data if the peak area was not above the threshold amount (0.4 V s); correspondingly, the limit of detection of OCDD was approximately 20 ng.

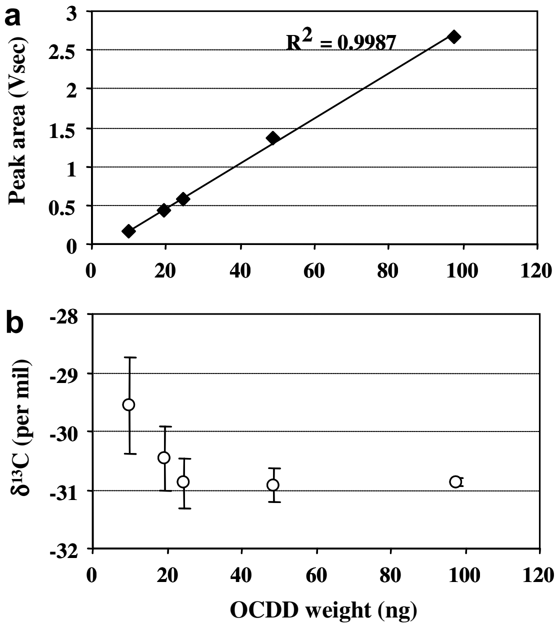

Fig. 1. Accuracy and precision of CSIA-$\delta^{13}C$ of OCDD at different concentration ranges (from 9.8 to 98 ng). Samples containing different concentrations of OCDD were analyzed in triplicate. Peak areas were linear ($r^2 > 0.9987$) (a) and $\delta^{13}C$ values were stable at quantities above 24 ng of OCDD (b).

The double-column clean-up technique resulted in excellent separation and removal of interferences from OCDD. The FID chromatograms obtained from each clean-up step using a monitor detector of 2DGC–IRMS system are shown in Fig. 2. The OCDD fraction of the alumina column contained several PCDD/Fs, non-*ortho* PCBs and other organic compounds apart from OCDD itself (Fig. 2a) (Horii et al., 2004); therefore, several peaks were found in the vicinity of OCDD on the DB-5 column (Fig. 2b). Most of these neighboring peaks were removed from the extract by performing subsequent double-column HPLC fractionation (Fig. 2c). OCDD and OCDF can be fully separated by PYE-HPLC fractionation. Although there were concerns regarding passing samples through

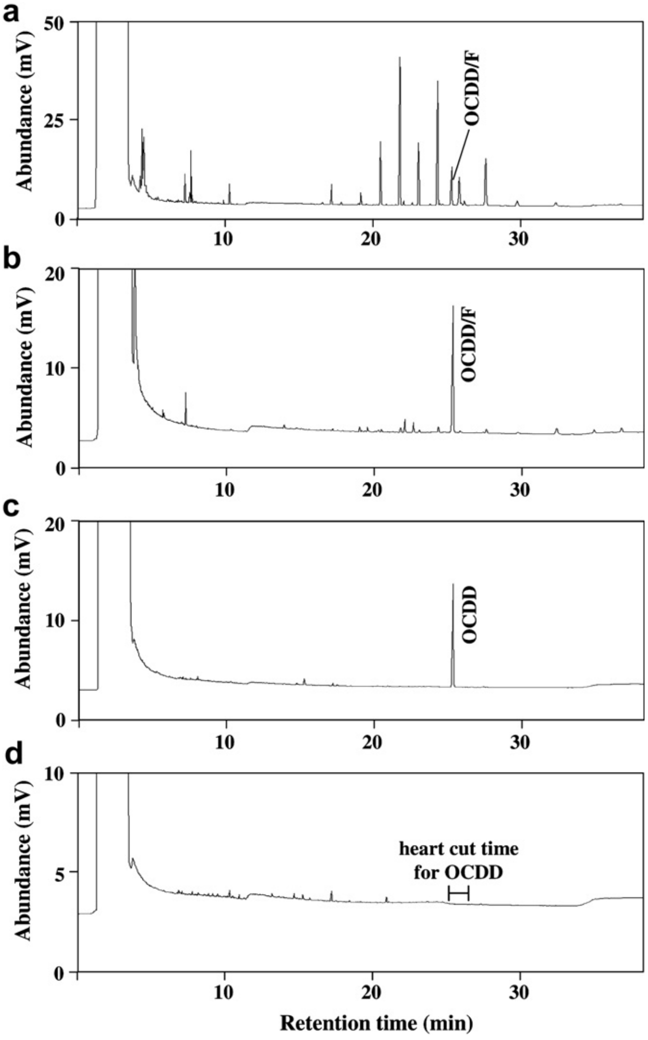

Fig. 2. FID chromatograms of OCDD (monitor detector of 2DGC–IRMS, in this study) from each clean-up step for American ball clay, and whole procedural blank. The OCDD fraction of alumina column clean-up contained several dioxins and other organic compounds (a). Most of the neighboring peaks with OCDD/F were removed from the OCDD fraction after Hypercarb-HPCL clean-up (b). OCDD and OCDF can be fully separated by PYE-HPLC fractionation (c). Procedural blank of OCDD in the final extract were below the detection limit, and the baseline of chromatogram was stable near the OCDD elution time (d).

multiple clean-up steps, as increase in sample contact time may lead to high procedural blank levels of OCDD and the use of large volume of organic solvents, it is evident from Fig. 2d, that the baseline of chromatogram of the final fraction (F3.2.2) of procedural blank was stable at the OCDD elution time and there were no interferences. The 2DGC–IRMS enabled significant improvement in the resolution and sensitivity of OCDD. This high sensitivity and selectivity were attained because in a 2DGC–IRMS by MCSS, only target compound (OCDD), is selected based on the precise retention time identified on the monitor detector (FID), and this target compound is selectively transferred to the oxidation furnace by pure helium flow via a second more polar column, in addition to multiple clean-up steps of sample extract. The background signal of m/z 44 was significantly reduced to <10 mV even at high temperatures (300 °C) due to the elimination of column bleeding or solvent peak from the first column. Thus, blank level of OCDD in final solution (<few hundreds of pg of OCDD as calculated by HRGC–HRMS) was significantly lower than the detection limit of IRMS (20 ng of OCDD). Characterization of carbon isotope signature of OCDD in kaolin and several other matrices analyzed here were subjected to this highly sensitive and selective quantification method.

3.2. Occurrence of OCDD in kaolin and anthropogenic sources

Concentrations of OCDD in kaolin (American and Japanese ball clays, and Spanish kaolin) and bentonite (a control material), typical source materials (fly ash and PCP), and contaminated environmental samples (sediment and soil) were determined (Tables 1 and 2). The concentrations of OCDD in American ball clay varied from 237 to 659 ng g^{-1} dw, with an average value of 400 ng g^{-1} dw. This average value was greater than the average concentration in fly ash from waste incinerators (3.4–381 ng g^{-1} dw) or in contaminated environmental samples (1.2–257 ng g^{-1} dw). The OCDD concentration in Spanish kaolin was relatively high at 24 ng g^{-1} dw. Elevated concentrations of OCDD in American ball clay and Spanish kaolin found in this study confirm the previous results (Ferrario et al., 2000; Rappe et al., 2001; Holmstrand et al., 2006). We found high OCDD levels in Japanese clays (Gaerome [$n = 1$] and Kibushi [$n = 1$]) at concentrations of 0.26 and 1.5 ng g^{-1} dw, respectively, while Japanese bentonite (control, $n = 1$) did not contain detectable concentrations (<0.05 ng g^{-1} dw) of OCDD. The average concentration of OCDD in Japanese ball clays (0.76 ng g^{-1} dw fell between that of US kaolin (0.19 ng g^{-1} dw) and German kaolin (3.2 ng g^{-1} dw) (Rappe et al., 2001). PCP, an agrochemical that is now banned (Masunaga et al., 2001), contained OCDD at concentration ranging from 170 to 104 000 ng g^{-1}. The dioxin concentration in PCP can vary depending on the production period and/or reaction conditions.

Table 2
Concentrations of OCDD in ball clay and anthropogenic source materials

Sample	Source/source type	OCDD conc. (ng g^{-1} dw)
American ball clay	Clay/N	408
Spanish kaolin	Clay/N	24
Japanese ball clay	Clay/N	0.76
Bentonite (control)	Clay/N	nd (<0.05)
American kaolin, Georgia[a]	Clay/N	0.19
German kaolin[a]	Clay/N	3.2
Marine sediment[b]	Queensland, Australia/N	0.57
Fly ash	Incineration/A	100
Pentachlorophenol	Pesticide/A	24400
Marine sediment	Tokyo Bay/A	3.5

OCDD concentrations (ng g^{-1} dw) are presented as the average for each sample matrix, along with their source and source type, natural (N) or anthropogenic (A).

[a] Rappe et al. (2001).

[b] Gaus et al. (2001).

The concentration of OCDD in Kibushi was similar to that found in surface sediments from Tokyo Bay, Japan (1.2–2.4 ng g^{-1} dw), and was 1.5–4-fold lower than the OCDD concentrations in sediment core from Tokyo Bay collected at a depth of 8–32 cm (2.3–5.6 ng g^{-1} dw). Tokyo Bay is known to be highly contaminated with dioxin-like compounds (Yamashita et al., 2000). Furthermore, the concentrations of OCDD in Japanese ball clays were similar to concentrations in marine sediment from Queensland, Australia (Gaus et al., 2001), in which dioxin profiles resembled those reported for soil and sediment from Mississippi and kaolin from Germany (Rappe et al., 1997,2001). This is the first study to report high concentrations of OCDD in Japanese ball clays. These results suggest the existence of significant amount of OCDD in the strata in the Tertiary Era.

3.3. Characterization of $\delta^{13}C_{OCDD}$ in kaolin and anthropogenic sources

Carbon isotope signatures of OCDD in natural (kaolin) and anthropogenic source materials (fly ash and PCP), and environmental samples (soil and sediment) were determined. The δ^{13}C values in the samples and OCDD/F standards ($n = 30$) varied widely, from −32.4‰ (PCP) to −22.8‰ (fly ash) (Fig. 3 and Table 1). The $\delta^{13}C_{OCDD}$ values in the matrices were -25.8 ± 1.1‰ for clay, -30.1 ± 1.6‰ for soil and sediment, -23.7 ± 0.8‰ for fly ash, -31.9 ± 0.7 for PCP, and -29.5 ± 1.0‰ for OCDD standard. The δ^{13}C values of OCDF standards were -25.1 ± 0.8‰, i.e., there was approximately 4‰ depletion of ^{13}C, relative to δ^{13}C values of OCDD standards. OCDD and OCDF are synthesized by similar processes, viz., chlorination of dibenzo-*p*-dioxin or dibenzofuran by chlorine gas in the presence of iron catalyst. This similarity suggests that the difference in isotopic composition observed between OCDD and OCDF standards derive from the carbon sources of the raw materials. In this

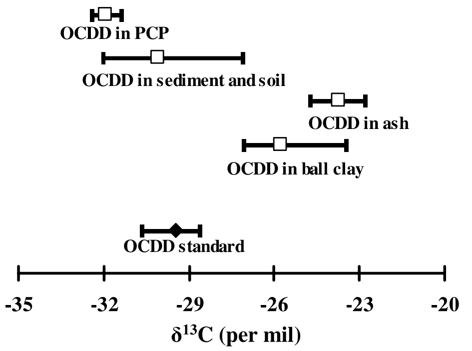

Fig. 3. Mean and range of δ^{13}C values of OCDD in ball clay and anthropogenic source materials, along with OCDD standards. The $\delta^{13}C_{OCDD}$ values in each matrix were −25.8 ± 1.1‰ for clay ($n = 6$), −30.1 ± 1.6‰ for soil and sediment ($n = 9$), −23.7 ± 0.8‰ for fly ash ($n = 5$), −31.9 ± 0.7 for PCP ($n = 2$), and −29.5 ± 1.0‰ for OCDD standard ($n = 4$).

study, the greatest ^{13}C depletion was determined for PCP. In contrast, enrichment of ^{13}C was found for fly ash. There exists approximately 10‰ difference in δ^{13}C between the two major dioxin sources. The exhaust gas from waste incineration processes and several banned agrochemicals such as PCP and 2,4,6-trichlorophenyl-4′-nitrophenyl ether (CNP) have been the most prominent sources of dioxins in the environment in Japan (Masunaga et al., 2003). PCP was extensively used as a rice herbicide during the 1960s and the early 1970s. A total of 170000 tons of the PCP active ingredient was sprayed in rice fields in Japan during that time. It is noteworthy that δ^{13}C values of OCDD in PCP and fly ash showed discriminant isotope signatures. This indicates that $\delta^{13}C_{OCDD}$ represents a powerful diagnostic tool by which to identify the sources of dioxins in the environment. Further, the magnitude of contributions from different sources to dioxin contamination in samples can be determined, by mass balance calculations (O'Malley et al., 1994), if the isotope signatures of the sources retain their integrity during transport.

The δ^{13}C values of OCDD in all ball clays analyzed here were similar, ranging from −27.1‰ to −23.5‰. The average $\delta^{13}C_{OCDD}$ in ball clay was 2‰ depleted relative to the value for fly ash, and 6‰ enriched relative to the value for PCP. This suggests that OCDD in ball clay originated from a different carbon source, or via a different precursor, and/or from a different chemical pathway. The δ^{13}C values of OCDD in ball clays fell within the range reported for marine crude oil (−30‰ to 20‰) (Park and Dunning, 1961), and were similar to values reported for terrestrial plants, especially C3 plants (Calvin cycle, −26‰) (Farquhar et al., 1982). Further, δ^{13}C values of OCDD in ball clays fell within the ranges reported for other organohalogen compounds such as PCBs (−34.4‰ to 22.0‰) (Horii et al., 2005), PCNs (−26.3‰ to −21.7‰), and organochlorine pesticides including Toxaphene (−31.8‰ to −22.4‰) (Drenzek et al., 2002; Vetter et al., 2006), although these organohalogens had a wide range of δ^{13}C values. It is possible that naturally formed OCDD is distinguished from anthropogenic OCDD on the basis of carbon isotope composition. Further studies are needed to elucidate the δ^{13}C profiles of other anthropogenic sources of dioxins such as CNP, and those from steel and chloralkali industries.

3.4. $\delta^{13}C_{bulk}$ versus $\delta^{13}C_{OCDD}$

Stable carbon isotopic composition is useful to identify and quantify transformation reactions, and to examine the reaction mechanisms and source apportionment. The δ^{13}C value of OCDD congener relative to the bulk δ^{13}C value can be used to trace the origin of carbon in OCDD, and to elucidate the mechanisms of dioxin formation. The correlation analysis of δ^{13}C between bulk carbon and OCDD ($\delta^{13}C_{bulk}$ versus $\delta^{13}C_{OCDD}$ profiles) in the samples analyzed in this study is presented (Fig. 4). The $\delta^{13}C_{bulk}$ to $\delta^{13}C_{OCDD}$ ratios in the samples can be classified into two groups. When the $\delta^{13}C_{bulk}$ to $\delta^{13}C_{OCDD}$ ratio is around 1, then the carbon source of OCDD can be suggested to be related to the carbon in the sample matrices. As can be seen in Fig. 4, for PCP, fly ash, and ball clay samples, there was a similarity in δ^{13}C values between the bulk sample and OCDD congener. For these samples, it is most likely that OCDD is produced within the sample matrix (*in situ*). In the further analysis, this group is termed Group A (below). The samples that deviate from the diagonal line of $\delta^{13}C_{bulk}$ versus $\delta^{13}C_{OCDD}$ ratio of 1 are classified as Group B, in which OCDD in the sample is considered to have originated from a different carbon. This

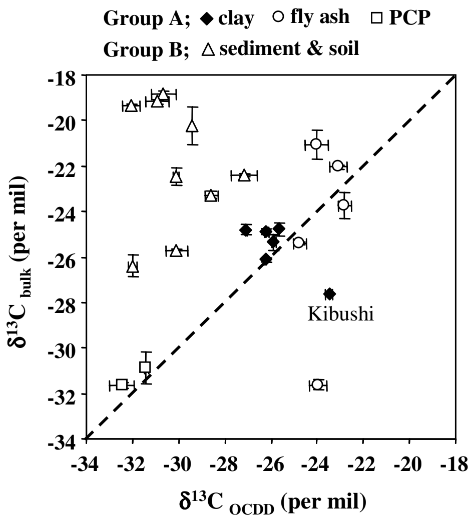

Fig. 4. $\delta^{13}C_{bulk}$ versus $\delta^{13}C_{OCDD}$ plot of natural and anthropogenic sources of dioxins. X and Y axes are $\delta^{13}C_{OCDD}$ (per mil) and $\delta^{13}C_{bulk}$ (per mil), respectively. The samples can be classified into two groups; Group A consists of samples with carbon in OCDD derived from sample matrices themselves, and this includes PCP, fly ash, and ball clay (i.e., OCDD produced *in situ*). Values for samples in this group fell close to the diagonal; the scales of x and y axes are represented by the same range (−34‰ to 18‰). The correlation coefficient between $\delta^{13}C_{bulk}$ and $\delta^{13}C_{OCDD}$ in Group A was $r^2 = 0.39$ ($p < 0.05$). Group B consists of samples with carbon in OCDD derived from multiple sources; this group includes the soil and sediment samples (i.e., OCDD produced *ex situ*).

group includes all of the soil and sediment samples. Based on the differing $\delta^{13}C$ ratios of bulk carbon and OCDD, we infer that for Group B samples, the OCDD most likely originates from different carbon sources other than the sample matrix (*ex situ*).

Group A. For fly ash samples, $\delta^{13}C_{OCDD}$ values were in a narrow range at $-23.7 \pm 0.8‰$, whereas $\delta^{13}C_{bulk}$ values varied widely from $-31.6‰$ to $-21.1‰$. The carbon sources of OCDD in fly ash are several different types of waste materials (e.g., municipal, industrial, and/or hazardous wastes). This can explain the wide range of bulk $\delta^{13}C$ values in fly ash samples. The $\delta^{13}C_{OCDD}$ values in fly ash samples differed by 0.6–7.7‰ from the bulk $\delta^{13}C$ values. The fly ash sample showing the lowest $\delta^{13}C_{bulk}$ value originated from a hazardous waste incinerator operating at high temperatures, while the other fly ash samples originated from municipal solid waste incinerators operating at lower temperatures. O'Malley et al. (1994) reported that $\delta^{13}C$ values for PAHs having a combustion origin (such as flue gases) ranged from $-26.5‰$ to $-23‰$ (O'Malley et al., 1994). That range is similar to the range found for OCDD in fly ash in our study. Coal combustion at low temperature yielded $\delta^{13}C$ values of PAHs similar to those of bulk coal, whereas $\delta^{13}C$ was depleted by 2–7‰ for high-temperature coal combustion (McRae et al., 1999). Carbon isotopic ratios of OCDD can vary according to the type of incinerator employed and the temperature, as is the case with different congener compositions of PCDDs in fly ash. Carbon isotopic compositions of bulk PCP product and OCDD present in PCP were similar; $\delta^{13}C_{PCP}$ values were $-31.3 \pm 0.5‰$, and corresponding $\delta^{13}C_{OCDD}$ values were $-31.9 \pm 0.7‰$. PCDD impurities in PCP were primarily highly chlorinated congeners, especially OCDD (Masunaga et al., 2001). A common process in the production of PCP is the chlorination of phenol. In this procedure, OCDD can be produced by the coupling of two PCP molecules. Carbon itself does not participate in the dechlorination. Thus, dechlorination does not alter the carbon isotope signature in PCP and OCDD present as an impurity in PCP.

As shown in Fig. 4, stable carbon isotopic compositions of bulk material and of OCDD in American ball clays showed similar profiles, with the plotted values clustered along the diagonal. The $\delta^{13}C_{bulk}$–$\delta^{13}C_{OCDD}$ profile of Japanese ball clay (Kibushi) was distinguished from those of American ball clays. Further studies are needed to assess the differences in carbon isotopic profiles between American and Japanese ball clays. For samples in Group A, the $\delta^{13}C_{bulk}$–$\delta^{13}C_{OCDD}$ ratios were 1.00 ± 0.09, 1.04 ± 0.17, and 0.98 ± 0.01 for ball clay, fly ash, and PCP, respectively. There was a significant correlation between bulk carbon ($\delta^{13}C_{bulk}$) and OCDD ($\delta^{13}C_{OCDD}$) in the samples ($p < 0.05$). This suggests that the relationship between carbon sources of the bulk material and OCDD present in the sample is direct and depends on a number of parameters, whereas the amount of bulk carbon is absolutely greater (>10000 times greater, in the case of American ball clay) than that of OCDD in the samples. Overall, the isotopic data provided here strongly support the hypothesis of natural formation of dioxins in ball clays.

Group B. $\delta^{13}C$ values of OCDD in sediments and soil varied widely ($-32.0‰$ to $-27.1‰$) and these values represented 4–9‰ depletion of ^{13}C relative to the bulk $\delta^{13}C$ values (Fig. 4). All of the $\delta^{13}C_{bulk}$–$\delta^{13}C_{OCDD}$ plotted values for sediment and soil samples were positioned in the upper left of quadrant of the plot (Fig. 4), unlike the samples from Group A. The ratios of $\delta^{13}C_{bulk}$–$\delta^{13}C_{OCDD}$ for samples in Group B ranged from 0.60 to 0.85. It is noteworthy that sediments contaminated with anthropogenic dioxin sources and clays containing naturally formed OCDD can be distinguished in the $\delta^{13}C_{bulk}$–$\delta^{13}C_{OCDD}$ plot. Incineration and agrochemicals are the most prominent dioxin sources in Japan. In environmental samples, contributions to dioxin contamination that result from incineration and agrochemicals can now be estimated by use of $\delta^{13}C_{OCDD}$ values. It is clear that the $\delta^{13}C_{OCDD}$ in soil and sediment samples did not originate from the bulk carbon of the sample, but are related to an agrochemical source (PCP) rather than an incineration (fly ash) source. The $\delta^{13}C_{OCDD}$ value ($-29.4‰$) in surface sediment sampled from an industrial area in Tokyo Bay has enriched ^{13}C relative to the sediment core sample. The carbon isotopic composition in this sediment indicates slightly higher contribution of combustion source of dioxins.

3.5. Natural formation of dioxins

The possibility of natural formation of dioxins in kaolin (ball clay) has been discussed for over a decade, and several hypotheses have been put forward. These include: (i) pyrolytic organic compounds from vegetation fire (or volcano), (ii) existence of chloroperoxidase enzymes in clay, (iii) mineral-promoted synthesis, and (iv) percolation of anthropogenic dioxins from surface soils to deeper layers (Gaus et al., 2002). Our results suggest that the percolation of anthropogenic dioxins from surface soils to kaolin present in deep layers is extremely low, given that profiles of $\delta^{13}C_{OCDD}$ in ball clays are distinct from those of anthropogenic sources (as shown in Fig. 3). Vertical profiles of PCDD concentrations in ball clay cores taken from Tennessee and Kentucky, USA, have been studied (Gadomski et al., 2004); the vertical gradient of PCDD concentrations did not generally increase toward the surface. Further, the dominance of OCDD and the very low or non-detectable concentrations of PCDF in sediment cores suggest that formation due to vegetation fires is unlikely. This, taken in combination with the $\delta^{13}C_{bulk}$–$\delta^{13}C_{OCDD}$ plots given in Fig. 4, allows us to reject the first of four hypotheses. Holmstrand et al. (2006) reported bulk radiocarbon, chlorine isotopic composition of OCDD, and black carbon (BC) in a ball clay core with high levels of OCDD. Linear regression between BC content and PCDD concentrations revealed poor correlations. The chlorine isotope compositions of OCDD were $-0.2‰$, higher than the postulated range for biotic chlorination by chloroperoxidase enzymes ranging from −12‰ to −11‰, and fell within the known range for abiotic organochlorines (−6‰ to +3‰). Taken together, the absence of PCDFs, the lack of a close association between BC and PCDDs, and the chlorine isotope composition suggested that ball clay OCDD is not derived from either vegetation fires (i) or biotic chlorination (ii). Our results provide strong evidence for abiotic natural formation due to surface-promoted reactions associated with clay minerals. High temperatures and pressures in deep layers coupled with presence of carbonaceous precursors (e.g., lignin) and minerals (e.g., Fe) may promote the formation of dioxins. Nevertheless, the reason for the formation of OCDD exclusively needs further investigation.

Based on the carbon isotopic compositions of bulk material and OCDD in ball clay samples, our results also indicate *in situ* promoted reactions of OCDD. The carbon source of OCDD is the carbon present in the clay itself. Moreover, the discovery of relatively high concentrations of OCDD in Japanese ball clays strengthens the hypothesis of natural formation and strongly suggests *in situ* formation of dioxins. Note, however, that sedimentation conditions such as temperature, pressure, and pH may have some effect on the formation mechanism.

Clay minerals display many surface charge activities such as ion exchange, adsorption, imbibition, and catalysis. For example, clay catalyst is used in the production of polychlorobenzenes at 100 °C (Balogh and Laszlo, 1993). This suggests the formation of dioxins and PCBs in municipal incinerators. Particles of fly ash having a seat like structure are comparable to that in clay. Oxidative coupling is an important natural and environmental process, and these reactions are promoted by the presence of minerals such as Fe, Al, and Mn oxides and hydroxides, and clays. Xenobiotic compounds, such as phenol, chlorinated phenols, and other hydroxylated aromatic compounds, can undergo oxidative coupling reactions by radical formation and/or self- or cross-coupling (Schoonen and Strongin, 2005). Generally, temperature, and pressure in a stratum increase according to increasing sedimentation depth. Normal geothermal and geopressure gradient are 0.03 °C m^{-1} and 9.8 kPa m^{-1}, respectively. The strata of ball clay in the United States and Japan were laid down >2 Ma and can reach high pressures, and temperatures depending on sediment depth. These conditions in kaolin resemble the process of OCDD synthesis as described above. Moreover, the conditions are very similar to the preparation of technical PCB mixture. PCBs are obtained by chlorination of biphenyls in the presence of iron chloride or iron turnings as catalysts, and the reaction temperature is kept above the melting point of biphenyl, but below 150 °C. Depending on the desired chlorine content, this process can take 12–36 h (Sułkowski et al., 2003). OCDD in kaolin can be formed by chlorination of backbone chemicals (dibenzo-*p*-dioxin or phenol) associated with the clay catalyst and long-term contact with gaseous chlorine. The long reaction times and the specific sediment conditions contribute to the elevated proportions of OCDD and reduced amounts of low chlorinated dioxins in ball clays.

In this study, high concentrations of OCDD were found in ball clays deposited in Tertiary Era (>2 Ma) in the United States and Japan, and the OCDD was isotopically distinguishable from anthropogenic sources based on $\delta^{13}C_{bulk}$–$\delta^{13}C_{OCDD}$ values. Based on the average concentration of OCDD measured, OCDD inventory in American ball clay production was estimated at 490 kg in 2006. For Japanese ball clays (Gaerome and Kibushi) with production in 2005 at 214 000 and 156 000 metric tons, respectively (Ministry of Economy, Trade and Industry, Japan, 2005), the total OCDD inventory from both of these productions was estimated at 290 g. In the production of ceramics, dioxins present in kaolin can be destroyed or volatilized at high temperatures that typically exceed 1000 °C in kilns (Ferrario and Byrne, 2002). As proposed by Rappe et al. (2001), high levels of dioxins with the specific 'natural' formation pattern are not limited to the Mississippi Embayment, and dioxins are ubiquitous in kaolin. The $\delta^{13}C_{bulk}$–$\delta^{13}C_{OCDD}$ ratios in soil and sediment samples from various locations worldwide confirmed that the origin of OCDD is from agrochemical sources (PCP). Identification of sources of persistent organic pollutants (POPs) in the environment by $\delta^{13}C$ can be accomplished by this powerful diagnostic tool.

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