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Earth and Planetary Science Letters 253 (2007) 226–238
EPSL
www.elsevier.com/locate/epsl

Carbon isotopic compositions of organic matter across continental Cretaceous–Tertiary (K–T) boundary sections: Implications for paleoenvironment after the K–T impact event

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Received 17 July 2006; received in revised form 12 October 2006; accepted 16 October 2006
Available online 22 November 2006
Editor: R.W. Carlson

Abstract

To assess the environmental perturbation induced by the impact event that marks the Cretaceous–Tertiary (K–T) boundary, concentrations and isotopic compositions of bulk organic carbon were determined in sedimentary rocks that span the terrestrial K–T boundary at Dogie Creek, Montana, and Brownie Butte, Wyoming in the Western Interior of the United States. The boundary clays at both sites are not bounded by coals. Although coals consist mainly of organic matter derived from plant tissue, siliceous sedimentary rocks, such as shale and clay, may contain organic matter derived from microbiota as well as plants. Coals record δ^{13}C values of plant-derived organic matter, reflecting the δ^{13}C value of atmospheric CO_2, whereas siliceous sedimentary rocks record the δ^{13}C values of organic matter derived from plants and microbiota. The microbiota δ^{13}C value reflects not only the δ^{13}C value of atmospheric CO_2, but also biological productivity. Therefore, the siliceous rocks from these sites yields information that differs from that obtained previously from coal beds.

Across the freshwater K–T boundary at Brownie Butte, the δ^{13}C values decrease by 2.6‰ (from −26.15‰ below the boundary clay to −28.78‰ above the boundary clay), similar to the trend in carbonate at marine K–T sites. This means that the organic δ^{13}C values reflect the variation of δ^{13}C of atmospheric CO_2, which is in equilibrium with carbon isotopes at the ocean surface. Although a decrease in δ^{13}C values is observed across the K–T boundary at Dogie Creek (from −25.32‰ below the boundary clay to −26.11‰ above the boundary clay), the degree of δ^{13}C-decrease at Dogie Creek is smaller than that at Brownie Butte and that for marine carbonate.

About 2‰ decrease in δ^{13}C of atmospheric CO_2 was expected from the δ^{13}C variation of marine carbonate at the K–T boundary. This δ^{13}C-decrease of atmospheric CO_2 should affect the δ^{13}C values of organic matter derived from plant tissue. As such a decrease in δ^{13}C value was not observed at Dogie Creek, a process that compensates the δ^{13}C-decrease of atmospheric CO_2 should be involved. For example, the enhanced contribution of ^{13}C-enriched organic matter derived from algae in a high-productivity environment could be responsible. The δ^{13}C values of algal organic matter become higher than, and thus distinguishable from, those of plant organic matter in situations with high productivity, where dissolved HCO_3^- becomes an important carbon source, as well as dissolved CO_2. As the δ^{13}C-decrease of atmospheric CO_2 reflected a reduction of marine productivity, the compensation of the δ^{13}C decrease by the enhanced activity of the terrestrial microbiota means that the microbiota at freshwater environment recovered more rapidly than those in the marine environment.

A distinct positive δ^{13}C excursion of 2‰ in the K–T boundary clays is superimposed on the overall decreasing trend at Dogie Creek; this coincides with an increase in the content of organic carbon. We conclude that the K–T boundary clays include

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doi:10.1016/j.epsl.2006.10.028

^{13}C-enriched organic matter derived from highly productive algae. Such a high biological productivity was induced by phenomena resulting from the K–T impact, such as nitrogen fertilization and/or eutrophication induced by enhanced sulfide formation. The high productivity recorded in the K–T boundary clays means that the freshwater environments (in contrast to marine environments) recovered rapidly enough to almost immediately (within 10 yr) respond to the impact-related environmental perturbations.

Keywords: Continental Cretaceous–Tertiary boundary; Impact-induced environmental perturbation; Carbon isotope ratios; Freshwater biological productivity; Highly productivity algae

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1. Introduction

Previous measurements of δ^{13}C values of planktonic carbonate at marine Cretaceous–Tertiary (K–T) boundaries showed depletions of up to 2‰ compared to those below the boundary (e.g., [1–4]). The light isotope of carbon (^{12}C) is preferentially incorporated in organic matter during photosynthesis; thus, in aquatic environments, carbon dioxide (and, therefore, bicarbonate) becomes progressively depleted in ^{12}C with increasing organic carbon production. Therefore, a carbonate with a higher δ^{13}C value precipitates in an environment that has a higher rate of organic production. As a result, the negative δ^{13}C excursion at the K–T boundary has been interpreted as evidence for a reduction (or shutdown) of marine primary production [5]. Also, this isotopic anomaly at the K–T boundary has been linked to the disappearance of the vertical carbon isotope gradient (e.g., [6]), indicating that the supply of organic matter, which is oxidized at depth and incorporated in sediment as carbonate, from the

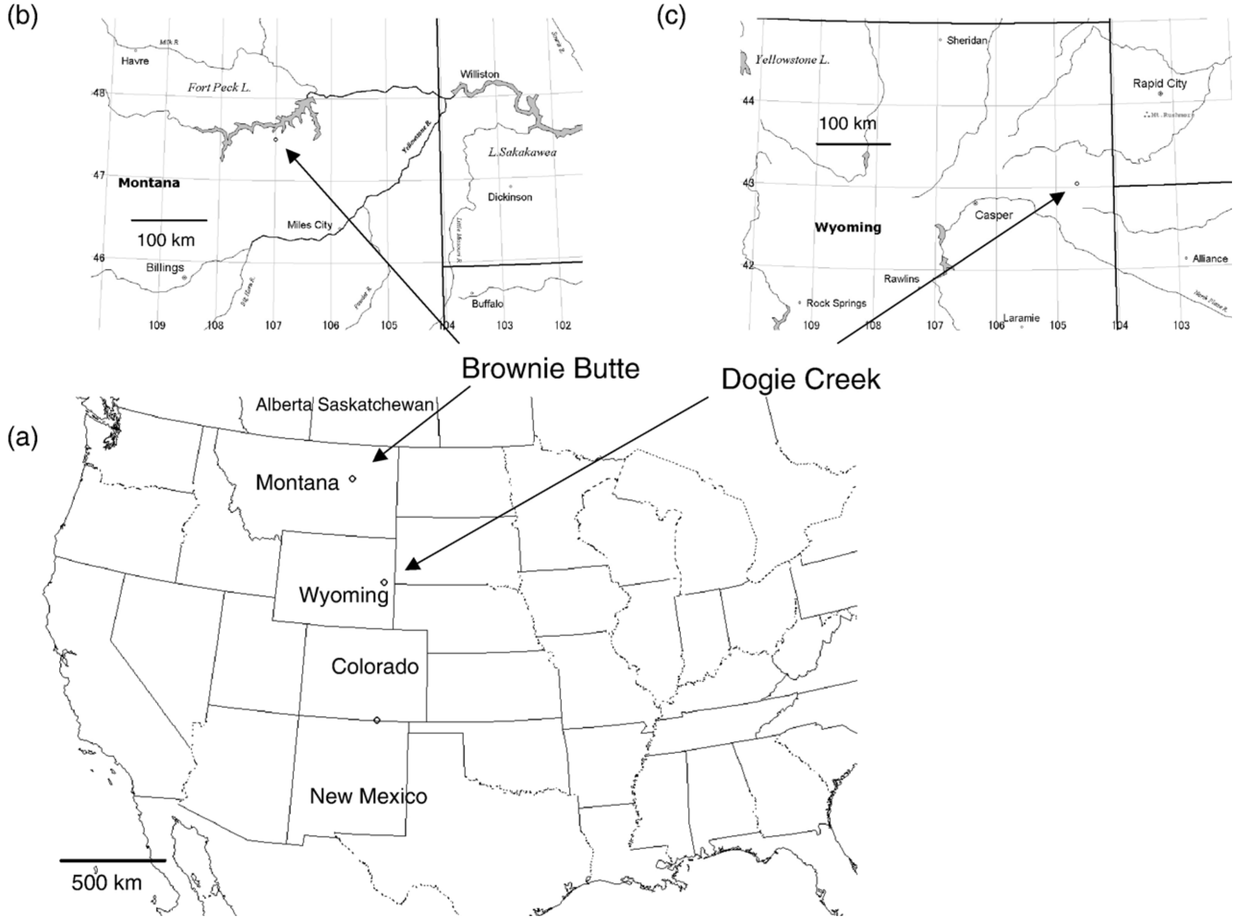

Fig. 1. (a) Map showing location of Brownie Butte site and Dogie Creek site. Enlarged map around (b) Brownie Butte site and (c) Dogie Creek site.

surface to the bottom was reduced in earliest Tertiary times [6]. Although the δ^{13}C anomaly has not been found at all sites [7], the widespread occurrence of the δ^{13}C decrease at the K–T boundary means that the reduction in marine primary productivity was an almost global phenomenon (e.g., [2]).

Negative δ^{13}C anomalies of organic carbon in the earliest Tertiary have also been reported for terrestrial K–T boundary sites (e.g., [8–13]), which should reflect a decrease of δ^{13}C of atmospheric CO_2 [13], resulting from the decrease of marine carbonate δ^{13}C values (e.g., [6]) and a very rapid (ca. one decade) equilibration between the ocean surface and the atmosphere (e.g., [14]). From the comparison of terrestrial organic δ^{13}C value as an index of marine productivity and palaeovegetation change, a more rapid recovery was proposed for the terrestrial biosphere than for the marine biosphere [11].

Brisman et al. [12] reported a positive excursion of δ^{13}C and a negative excursion of δ^{15}N at the K–T boundary sections at Starkville South, Colorado, and Raton Pass, New Mexico. These authors proposed global wildfires (e.g., [15–19]) as a cause of the C isotopic excursions. However, as the reported values of δ^{13}C in the boundary clays (i.e., −22.5‰ for Starkville South and −23.4‰ for Raton Pass) are higher than those of atmospheric carbon particulate material from biomass fires ($\delta^{13}C = -26.5 \pm 2.5$‰ [21]), incorporation of wildfire particulate cannot induce the positive shift of δ^{13}C observed at the K–T boundary. In addition, Belcher et al. [20] concluded that there was no evidence for wildfires across the North American continent related to the K–T event, based on the absence of charcoal in the K–T boundary layer. Therefore, the cause of these positive excursions of δ^{13}C at the K–T boundary clays remains an open question. As similar δ^{13}C excursions have not been recognized for K–T sections other than for the two sections reported by Brisman et al. [12], it is still important to analyze δ^{13}C values of organic matter at more sites. Such studies will help to understand if the positive excursions in the boundary clay occurred regionally or globally.

Here, we present new data for concentrations and carbon isotopic compositions of bulk organic matter for two continental K–T boundary suites (Dogie Creek, Wyoming, and Brownie Butte, Montana) in the Western Interior of the United States. The boundary clays at these sites are not associated with coal, in contrast to most other terrestrial sites where the boundary is interbedded or overlain by coal. The organic matter in coal consists mainly of organic matter derived from plant tissues, whereas the organic matter in siliceous sedimentary rocks, such as shale and clay, may include organic matter derived from microbiota as well as plant tissues. Therefore, the δ^{13}C values in siliceous sedimentary rocks provide information different from that obtained from coal δ^{13}C values. As suggested by Arens et al. [22], the δ^{13}C values of C3 plants are controlled primarily by variation in the isotopic composition of atmospheric CO_2, whereas the δ^{13}C values of organic matter derived from algae are controlled by productivity as well as variation in δ^{13}C of atmospheric CO_2. Therefore, we may obtain information on freshwater microbiota activity from the organic δ^{13}C values of siliceous rocks above the K–T boundary.

Gardner and Gilmour [13] already reported C isotope data for the Brownie Butte site. They treated the samples with an HF/HCl solution to dissolve carbonate and silicate, whereas we treated the samples with a solution of HCl or H_3PO_4 to dissolve only carbonate. Although the acids also dissolve labile organic matter as well as carbonate, an HF/HCl solution dissolves more labile organic matter than just an HCl solution. The comparison between $\delta^{13}C_{HCl}$ and $\delta^{13}C_{HF-HCl}$ may supply paleoclimate information, as suggested by [23].

2. Samples

The K–T boundary unit in the Western Interior of North America consists of two layers: a lower kaolinitic (melt ejecta) layer and an upper smectitic (fireball) layer. The melt ejecta layer is believed to be an altered distal impact ejecta deposit (e.g., [24]). In contrast, the fireball layer

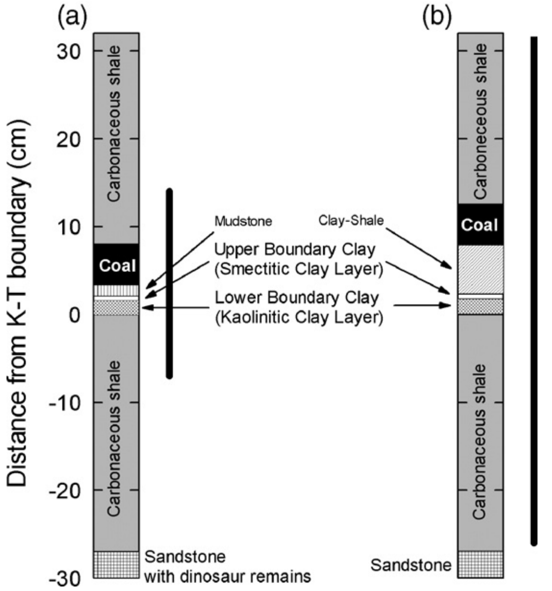

Fig. 2. Schematic columnar section through the Cretaceous–Tertiary boundary claystone at (a) Brownie Butte (after Fastovsky et al. [32]) and (b) Dogie Creek (after Bohor et al. [26]). Solid bars on the right of the columnar section represent the interval analyzed in this study.

contains shocked minerals [25,26], high-nickel magnesioferrite crystals (e.g., [26]), and high amount of iridium (e.g., [27]), suggesting that this layer originated from a cloud of vaporized bolide and entrained target material.

At some K–T boundary sites, including Sugarite, Madrid East, and Carmel, Raton Basin, Colorado and New Mexico, the lower and upper boundary layers were deposited in a coal swamp. They are interbedded with or overlain by coal or impure coal [28]. At other sites at Raton Basin, such as Raton Pass, Clear Creek North, and Berwind Canyon, these units were deposited just prior to the inception of a coal-forming event. They occur above carbonaceous shale that formed in fluvial and pond environments and below the coal bed that formed in a coal swamp [28]. At the K–T boundary sections in Wyoming and Montana, USA, and in Alberta and Saskatchewan, Canada, the boundary units were deposited before the onset of a coal-forming event (e.g., [27,29]). The samples analyzed in this study were from this area (Fig. 1).

2.1. Brownie Butte, Montana

The latest Cretaceous in eastern Montana is represented by the Hell Creek formation, a 100 m thick sequence of sandstone, mudstone, and shale, deposited by a meandering fluvial system. The earliest Tertiary sedimentary rocks in this region are mainly ponded water deposits, assigned to the Tullock Formation. In eastern Montana, the K/T transition was concomitant with extensive flooding of the landscape, indicated by coal deposition and by the ponding [30,31]. A thin claystone layer at the base of the lowest lignite in the Tullock

Table 1

Concentration and isotopic composition of carbon in residues treated with 2 M HCl for the Cretaceous–Tertiary boundary rocks from Brownie Butte and Dogie Creek

Distance from KTB				2 M HCl (10 h)			
Sample	Bottom (cm)	Top (cm)	Description	C in residue (wt.%)	$\delta^{13}C$ (‰)	Loss (%)	$C_{2M\text{–}HCl\ resistant}$ (wt.%)
Brownie Butte							
BB-11	12	14	Gray shale	0.316±0.008	−25.02±0.11	4.5	0.33±0.01
BB-10	10	12	Gray shale	0.379±0.010	−25.60±0.13	5.1	0.40±0.01
BB-9	8	11	Carbonaceous shale	7.858±0.199	−25.89±0.11	11.1	8.84±0.22
BB-8	6	8	Lignite	40.920±1.193	−26.17±0.11	20.6	51.51±1.50
BB-7	4	6	Lignite	45.856±1.026	−27.84±0.10	23.1	59.63±1.33
BB-6	2	4	Mudstone+Lignite	15.425±0.338	−28.78±0.11	16.0	18.36±0.40
BB-14	1.8	2	Smectitic claystone	3.010±0.122	−27.95±0.11	20.4	3.78±0.15
BB-13	0	1.8	Kaolinitic claystone	0.346±0.009	−25.67±0.10	6.2	0.37±0.01
BB-5	0	1.8	Kaolinitic claystone	0.392±0.023	−25.95±0.12	6.3	0.42±0.02
BB-4	−2	0	Carbonaceous shale	2.978±0.115	−26.15±0.10	8.9	3.27±0.13
BB-3	−4	−2	Carbonaceous shale	2.979±0.105	−25.79±0.12	6.2	3.18±0.11
BB-2	−6	−4	Carbonaceous shale	3.025±0.107	−25.71±0.10	10.1	3.37±0.12
BB-1	−7	−6	Carbonaceous shale	3.038±0.107	−25.63±0.18	7.5	3.28±0.12
Dogie Creek							
LC-86-Q	30	32	Carbonaceous shale	0.697±0.025	−26.11±0.14	4.9	0.73±0.03
LC-86-P	20	22	Carbonaceous shale	2.300±0.057	−27.81±0.16	6.9	2.47±0.06
LC-86-O	16	18	Carbonaceous shale	2.170±0.147	−27.01±0.28	7.4	2.34±0.16
LC-86-N	10	13	Lignite	27.586±0.725	−26.80±0.10	19.4	34.23±0.90
LC-86-M	6	8	Clay-shale	5.185±0.387	−25.73±0.09	11.1	5.83±0.44
LC-86-L	4	6	Clay–shale	0.842±0.022	−26.26±0.11	4.3	0.88±0.02
LC-86-K	2	4	Clay–shale	0.801±0.018	−26.11±0.10	3.8	0.83±0.02
Fireball Layer	1.8	2	Smectitic claystone	3.698±0.202	−25.66±0.10	10.4	4.13±0.23
Melt Ejecta Layer	0	1.8	Kaolinitic claystone	2.766±0.133	−23.47±0.13	14.8	3.25±0.16
LC-86-H	−2	0	Carbonaceous shale	0.394±0.009	−25.32±0.10	4.0	0.41±0.01
LC-86-G	−4	−2	Carbonaceous shale	0.434±0.015	−25.23±0.09	4.4	0.45±0.02
LC-86-F	−6	−4	Carbonaceous shale	0.454±0.010	−25.21±0.12	4.1	0.47±0.01
LC-86-E	−10	−8	Carbonaceous shale	0.478±0.011	−25.11±0.09	4.8	0.50±0.01
LC-86-D	−14	−12	Carbonaceous shale	0.453±0.012	−25.02±0.10	4.4	0.47±0.01
LC-86-C	−18	−16	Carbonaceous shale	0.454±0.010	−24.99±0.09	3.7	0.47±0.01
LC-86-B	−22	−20	Carbonaceous shale	0.372±0.010	−24.82±0.11	4.7	0.39±0.01
LC-86-A	−26	−24	Carbonaceous shale	0.353±0.014	−24.73±0.11	4.5	0.37±0.01

Table 2
Concentration and isotopic composition of carbon in residues treated with 0.4 M H_3PO_4 for the Cretaceous–Tertiary boundary rocks from Dogie Creek

Distance from KTB			0.4 M H_3PO_4 (18 h)			
Sample	Bottom (cm)	Top (cm)	C in residue (wt.%)	$\delta^{13}C$ (‰)	Loss (%)	$C_{0.4M\ H3PO4}$ (%)
Dogie Creek						
LC-86-Q	30	32	0.705±0.017	−25.75±0.15	2.1	0.72±0.02
LC-86-P	20	22	2.238±0.084	−27.68±0.15	3.9	2.33±0.09
LC-86-O	16	18	2.139±0.050	−26.93±0.15	3.7	2.22±0.05
LC-86-N	10	13	26.286±1.148	−26.65±0.14	7.1	28.29±1.23
LC-86-M	6	8	4.956±0.296	−25.56±0.16	5.6	5.25±0.31
LC-86-L	4	6	0.863±0.023	−25.96±0.16	2.1	0.88±0.02
LC-86-K	2	4	0.804±0.018	−25.89±0.17	1.7	0.82±0.02
Fireball Layer	1.8	2	3.445±0.095	−25.38±0.16	4.1	3.59±0.10
Melt Ejecta Layer	0	1.8	2.962±0.120	−23.22±0.18	11.1	3.33±0.13
LC-86-H	−2	0	0.385±0.011	−25.05±0.09	1.1	0.39±0.01
LC-86-G	−4	−2	0.420±0.012	−25.02±0.10	2.0	0.43±0.01
LC-86-F	−6	−4	0.444±0.012	−25.04±0.10	1.7	0.45±0.01
LC-86-E	−10	−8	0.475±0.013	−25.14±0.14	2.0	0.48±0.01
LC-86-D	−14	−12	0.460±0.013	−25.07±0.09	2.3	0.47±0.01
LC-86-C	−18	−16	0.457±0.013	−25.03±0.09	1.7	0.46±0.01
LC-86-B	−22	−20	0.390±0.014	−24.79±0.10	2.9	0.40±0.01
LC-86-A	−26	−24	0.370±0.017	−24.80±0.10	2.4	0.38±0.02

Formation near Brownie Butte in Garfield County, east-central Montana was discovered [25]. This claystone (1 to 1.5 cm thick) contains 1 ppb iridium [25]. Based on palynological observations [25], such as the disappearance of the Cretaceous marker pollens *Proteacidites* and *Aquilapollenites*, and the abrupt increase in the fern to angiosperm ratio across the claystone layer [25], the K–T boundary occurs on the base of the claystone layer. The claystone is immediately overlain by a 1.5 cm-thick megaflora-bearing mudstone, which is overlain by a shaly lignite [32]. A series of 13 samples from 7 cm below the boundary to 14 cm above was analyzed (Fig. 2a).

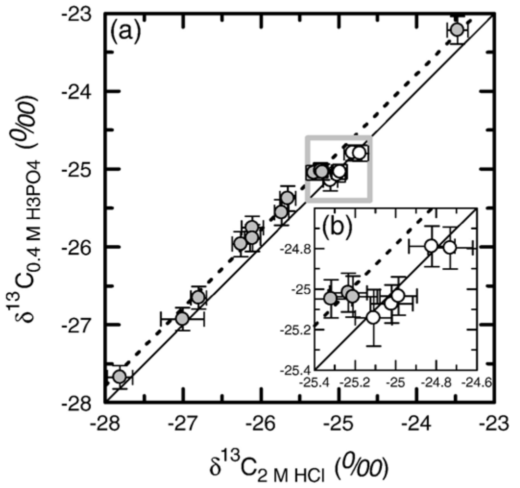

Fig. 3. (a) Comparison of $\delta^{13}C$ values of organic matter in a residue after 2 M HCl and 0.4 M H_3PO_4 treatments for Dogie Creek samples and (b) enlarged diagram of gray square in (a). Open and gray circles represent data for samples located at lower level (LC-86-A to -E) and upper level (LC-86-F to -Q), respectively. Solid line represents 1:1 relationship. Dotted line represents the regression line for the gray-circle data, assuming that the $\delta^{13}C$ difference between 2 M HCl- and 0.4 M H_3PO_4-resistant organic matters are constant for the upper-level samples.

2.2. Dogie Creek, Wyoming

The boundary clay at Dogie Creek in Wyoming was discovered in the uppermost part of the Lance Formation, 4–7 cm beneath the lowermost lignite in the Paleocene Fort Union Formation and approximately 1 m above a fragmented dinosaur bone [26]. The boundary clay consist of a basal kaolinitic claystone layer 0–3 cm thick containing hollow goyazite spherules, overlain by a 2–3 mm smectitic layer containing shock-metamorphosed minerals, such as shocked quartz grains showing planar deformation features, and an iridium anomaly of 20.8 ppb [26]. The boundary clay lies above a carbonaceous shale and is overlain by 4–7 cm of clay–shale containing numerous plant fragment impressions. This clay–shale is overlain by 3–4 cm of lignite. A series of 17 samples form 26 cm below the boundary to 26 cm above was analyzed (Fig. 2b). Detailed palynological data for the same samples are given by Bohor et al. [26], but a short summary follows here. Numerous specimens of the characteristic Cretaceous pollen genera *Aquilapollenites*

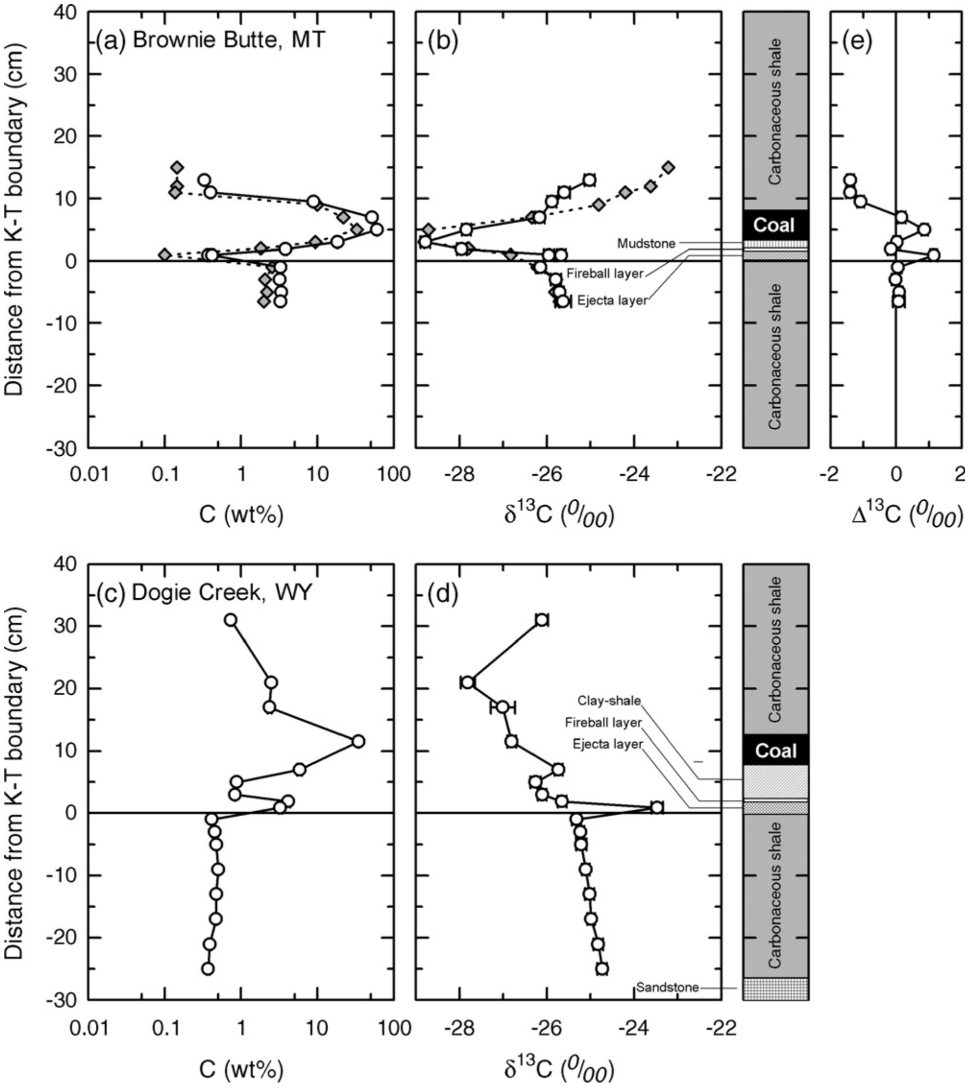

Fig. 4. Chemostratigraphic profiles for (a) organic concentrations and (b) δ^{13}C values of bulk organic carbon for the Brownie Butte samples and for (c) organic concentrations and (d) δ^{13}C values of bulk organic carbon for the Dogie Creek samples. Open circles and gray diamonds represent data obtained in this study and those obtained by Gardner and Gilmour [13], respectively. (e) δ^{13}C difference between data of this study and Gardner and Gilmour [13], which can be used as a temperature proxy [23]. The decrease in the difference above the K–T boundary suggests warming after the K–T impact event.

and *Proteacidites* are present in all samples below the kaolinitic claystone layer. Except for rare specimens of *Proteacidites* sp. found in samples 14–16 and 28–30 cm above the kaolinitic claystone layer, the uppermost Cretaceous assemblage is absent from samples above the smectitic claystone layer. The palynomorph assemblage of the lower boundary clay layer consists almost entirely of fern spores (93%), among which *Cyathidites diaphana* is the dominant species. The upper boundary clay layer yielded abundant palynomorphs, but only a few species are well represented; the abundance of fern spores is 63.5%. The lignite 10–13 cm above the bottom of the lower boundary clay layer yields a rich and varied assemblage of palynomorphs dominated by angiosperm pollen of many species, in which fern spores are a minor component. On the basis of the palynological evidence, the K–T boundary occurs at the base of the kaolinitic claystone layer, which yielded the fern spores but no pollen of unequivocally Cretaceous age.

3. Experimental methods

3.1. Acid treatment

About 3 to 4 g of the sedimentary rocks were powdered in an agate mortar. A few hundred mg of the powdered sample were treated with 2 M HCl for 10 h (for Brownie Butte and Dogie Creek samples) or 0.4 M H_3PO_4 for 18 h (Dogie Creek samples) in order to eliminate carbonate in the samples. Following acid leaching, the residues were centrifuged for 30 min and the supernatant was removed. The residues were washed with de-ionized water and were dried at 60 °C for about 3 d. Then, the residues were homogenized with a mortar and were kept in a desiccator before mass spectrometry.

3.2. Mass spectrometry

Concentrations and isotopic compositions of carbon were measured in the acid-resistant residues using a helium-gas continuous flow isotope ratio mass spectrometer (CF-IR-MS; Micromass Optima; [33,34]) at the stable isotope lab of the Department of Geological Sciences (formerly at the Institute of Geochemistry), University of Vienna. The δ^{13}C values, compared with those of the reference gas, were converted to those of V-PDB (Vienna-Pee Dee Belemnite) scale based on comparison with the analytical results for two standards (USGS-24: graphite, -15.994 ± 0.105‰; IAEA-CO-9: $BaCO_3$, -47.119 ± 0.149‰[35]) and determined with a reproducibility of $\pm \sim 0.1$‰ (1σ). The standard materials were also used for the calibration of measured carbon concentrations, determined at a precision of 3 rel%.

4. Results

The δ^{13}C values (relative to V-PDB) and carbon concentrations of the 2 M HCl-treated residues are listed in Table 1 for the Brownie Butte and Dogie Creek samples and those of the 0.4 M H_3PO_4-treated residues are listed in Table 2 for the Dogie Creek samples.

4.1. Comparison of data for residues treated with HCl and H_3PO_4

Showers and Angle [36] analyzed isotopic composition of organic matter in the Amazon continental shelf sediments. They noted an isotopic difference between samples treated with 0.4 M H_3PO_4 and 1 M HCl, and reported that the samples treated with 1 M HCl had a systematically lower δ^{13}C value by 0.3‰ than those treated with 0.4 M H_3PO_4. They considered this phenomenon the result of the loss of the isotopically heavier more labile organic matter during washing the HCl leached samples with deionized water to remove HCl. Isotopic differences between 0.4 M H_3PO_4- and 2 M HCl-treated residues (0.22 ± 0.08‰) are observed for the samples located above sample LC-86-F, whereas no difference was observed below that level (Fig. 3). As the concentrations of the 0.4 M H_3PO_4-resistant carbon are similar to those of 2 M HCl-resistant carbon ($C_{0.4\ \mathrm{M}\ \mathrm{H3PO4}}/C_{2\mathrm{M}\ \mathrm{HCl}} = 0.944 \pm 0.056$; average for the samples located above the sample LC-86-F), both acids should dissolve labile organic matter with a slightly different isotopic composition. Moreover, the isotopic differences between HCl- and H_3PO_4-treated residues are not constant for all the samples, as stated above. Therefore, we will not discuss differences of δ^{13}C of less than 0.3‰, because such uncertainties are derived from the behavior of labile organic matter during chemical procedures, even though the accuracies of the δ^{13}C values in this study are better than 0.3‰. As organic matter after the HCl-treatment is slightly more abundant than that after the H_3PO_4 treatment, we conclude that the H_3PO_4-treatment alters organic concentrations and, therefore, δ^{13}C values of these samples are more severely affected than those treated by HCl. Therefore,

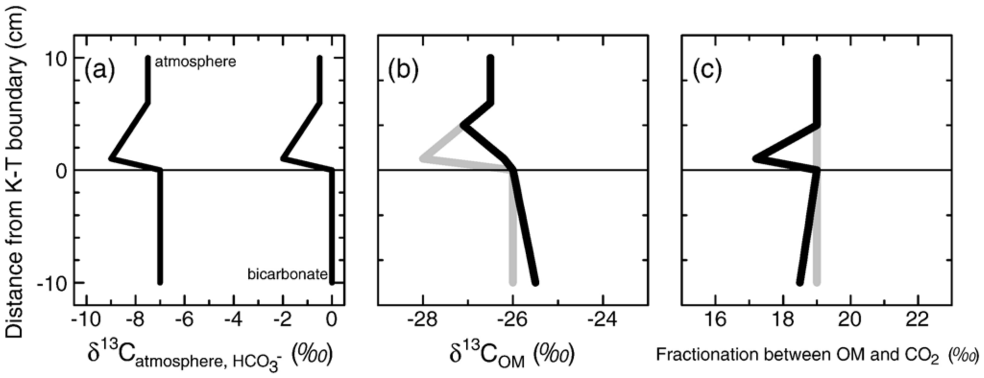

Fig. 5. Schematic diagram of isotopic variation across the Cretaceous–Tertiary boundary for (a) atmospheric CO_2 and dissolved inorganic carbon in sea water and (b) terrestrial organic matter (OM). The isotopic composition of organic matter represented as gray and solid lines results from isotopic fractionation between atmospheric CO_2 and organic matter represented as gray and solid lines, respectively, in (c).

we use only data for HCl-treated residues for the comparison between the two sites and applied only the HCl treatment to the Brownie Butte samples.

4.2. Chemostratigraphic profiles of concentration and isotopic composition of organic carbon

The concentrations and the δ^{13}C values of organic carbon are shown as chemo-stratigraphic profiles for the Brownie Butte (Fig. 4a and b) and Dogie Creek (Fig. 4c and d) section. Data for Brownie Butte are compared with those obtained by [13].

4.2.1. Concentration of organic carbon

At Brownie Butte, uppermost Cretaceous organic C concentrations are typically 3 wt.%, but decrease markedly to 0.4 wt.% at the lower boundary layer (melt ejecta layer) (Fig. 4a). The organic C concentration increases in the upper boundary layer (fireball layer) to 3.8 wt.% before rising sharply to 60 wt.% in the lowermost Tertiary coal layer. The concentration gradually decreases above the coal layer until a drop to 0.3 wt.% at ~13 cm above the K–T boundary. As shown in Fig. 4a, a similar trend for the organic C concentration was also reported by [13], although their concentrations are generally lower than those reported here. Gardner and Gilmour [13] removed carbonates and silicates from their samples using HCl and HF–HCl solutions, whereas we removed only carbonates from the samples. It is likely that their treatments removed more organic matter than our treatments, because some organics strongly associate with silicate surfaces [37].

A constant organic C concentration for the upper Cretaceous is also observed at Dogie Creek (Fig. 4c), although their typical concentrations (0.4 wt.%) are lower than those at Brownie Butte (3 wt.%). These similar carbon concentrations imply that parameters, such as organic carbon flux to the water, oxygen concentrations of the bottom water, and sedimentation rate, were constant over the interval, as suggested by [38]. The organic C concentration increased markedly in the lower boundary clay layer at Dogie Creek, whereas a decrease in the lower boundary clays is observed at Brownie Butte (this study and [13]) and other sites, such as Berwind Canyon [13], Starkville South, and Raton Pass [12]. Above the upper boundary clay, the organic concentrations at Dogie Creek decrease relative to those of the boundary clays, but are still higher than those of the latest Cretaceous (typically, 0.4 wt.%). The organic concentrations increase again after the minimum around 5 cm above from the boundary until the coal layer from 8 cm to 13 cm above the K–T boundary. Above the coal layer, the organic concentrations at Dogie Creek decreased gradually.

4.2.2. Isotopic compositions of bulk organic carbon

At Brownie Butte, we find that δ^{13}C decreases of 2‰ from −26‰ at the lower boundary clay to −28‰ at the upper boundary clay (Fig. 4b), followed by a minimum just above the K–T boundary clays, and that, at 7 cm above the K–T boundary, δ^{13}C values return to the same as those in the uppermost Cretaceous, similar to observations by [13].

At Dogie Creek, a distinct positive δ^{13}C spike of 2‰ in the lower boundary clay is superimposed on the overall decreasing trend. A similar positive δ^{13}C-excursion in the lower boundary clay was observed in K–T sections at Raton Pass and Starkville South at Raton basin [12]. Except for the positive δ^{13}C excursion in the lower boundary clay, the δ^{13}C values decrease continuously through the K–T boundary with a minimum at ~19 cm above the K–T boundary at Dogie Creek, whereas the δ^{13}C values decrease markedly at the K–T boundary clay at Brownie Butte.

5. Discussion

5.1. Difference between $\delta^{13}C_{HCl}$ and $\delta^{13}C_{HF-HCl}$

As noted above, there is a difference between δ^{13}C values obtained by demineralization using HCl (this study) and HF–HCl [13] (Fig. 4e). Krishnamurthy et al. [23] proposed $\Delta^{13}C = \delta^{13}C_{HCl} - \delta^{13}C_{HF-HCl}$ as a climate proxy. They found a correlation between Δ^{13}C and δD of organic matter, which was interpreted as a temperature proxy (e.g., [39,40]), in which colder climates lead to higher Δ^{13}C values. The 2‰ decrease in Δ^{13}C above the K–T boundary (Fig. 4e) suggests warming after the K–T impact event, although its extent is difficult to quantify. A warming after the K–T impact was expected from green–house effect of CO_2 released from the sedimentary target at Chicxulub (e.g., [41–44]).

5.2. Organic δ^{13}C variation across the K–T boundary

Based on literature data, Arens et al. [22] showed that the δ^{13}C values of C3 plants are controlled primarily by variation in the isotopic composition of atmospheric CO_2. The δ^{13}C value of plant tissue does not vary with atmospheric CO_2 concentration [22,45]. In addition, it takes only about a decade for the carbon isotopic equilibration between the surface ocean and the atmosphere (e.g., [14]). Therefore, it is reasonable to conclude that the decrease of organic δ^{13}C reflects changes in the δ^{13}C values of atmospheric CO_2 (e.g., [13]), resulting from the equilibration between the ^{13}C-depleted surface ocean and the atmosphere. The minimum of $\delta^{13}C$ values at Brownie Butte occurs just above the K–T boundary (Fig. 4b and gray line in Fig. 5b), which is similar to the sudden decrease of marine carbonate $\delta^{13}C$ values (e.g., [1–4,6]). This means that the isotopic fractionation between organic matter and atmospheric CO_2 during the organic matter production at Brownie Butte was almost constant across the time represented by the analyzed sequence (gray line in Fig. 5c).

The organic $\delta^{13}C$ values at Dogie Creek decrease continuously across the K–T boundary (Fig. 4d and solid line in Fig. 5b). Therefore, some mechanism that partially compensated the effect of the sudden atmospheric $\delta^{13}C$-decrease (i.e., a mechanism that increases $\delta^{13}C$ values in organic matter) has to be involved during sedimentation at Dogie Creek (solid line in Fig. 5c). Two plausible mechanisms (diagenesis after sedimentation or mixing between land-derived plant and algal organic matters) can be tested against our results as a cause of the compensation of the sudden $\delta^{13}C$ decrease.

5.2.1. Diagenesis after sedimentation?

The isotopic composition of organic matter can be altered during its decomposition (e.g., [46,47]). Selective loss of specific fractions of the total organic carbon can produce diagenetic shifts in $\delta^{13}C$ [48], because different classes of organic compounds have different $\delta^{13}C$ values (e.g., [49]). Organic compounds with a low $\delta^{13}C$ value, such as lignin, decompose more slowly than those with a high $\delta^{13}C$ value, such as cellulose [41], leading to a relatively more rapid loss of ^{13}C compared to ^{12}C during decomposition and to a depletion of ^{13}C in the remaining substrate (e.g., [50]). In contrast, ^{12}C is preferentially used for respiration by decomposers (e.g., [51]), leading to high $\delta^{13}C$ values in the remaining substrate (e.g., [52,53]). Although isotopic composition of soil organic matter reflects the competition between chemically preferential decomposition (^{13}C-depletion in the remaining organic matter) and biological isotopic fractionation (^{13}C-enrichment in the remaining organic matter), the effect of chemically preferential decomposition is significant only during the early stages [54]. Therefore, enhanced decomposition of organic matter can cause a ^{13}C-enrichment at relatively low organic concentrations [51–53]. Enhanced decomposition after the K–T impact, relative to that before the event, would have led to increasing $\delta^{13}C$ values, which might compensate the sudden atmospheric $\delta^{13}C$ decrease. However, the ^{13}C-enrichment must be related to the high organic carbon concentrations compared to those below and above the layer (Fig. 4c), which contradicts the enhanced decomposition model. Therefore, this process cannot explain the observed $\delta^{13}C$ shift above the Dogie Creek K–T boundary.

5.2.2. Mixing between land-derived plant and algal organic matter

The $\delta^{13}C$ values of freshwater algal organic matter are typically indistinguishable from those of C3 organic matter from the surrounding watershed (e.g., [55]). However, $\delta^{13}C$ values of algal organic matter can be higher than, and thus be distinguishable from, those of plant organic matter in situations with a high productivity [56–58] or with an alkaline pH (e.g., [59]), where dissolved HCO_3^- ($\delta^{13}C = 1‰$) becomes an important carbon source, as well as dissolved CO_2 ($\delta^{13}C = -7‰$). Therefore, an increased contribution of organic matter from algae with $\delta^{13}C$ values higher than that of land-plants can increase the bulk organic $\delta^{13}C$ value. This $\delta^{13}C$ increase can partially compensate the sudden decrease in atmospheric $\delta^{13}C$ (Fig. 5a). The enhanced contribution of algal organic matter with a $\delta^{13}C$ value higher than that of plant-derived organic matter results from stimulated algal activity. This results in a high production of organic matter, which is indicated from the higher concentration of organic matter above the K–T boundary compared to below the K–T boundary. As the $\delta^{13}C$-decrease of atmospheric CO_2 reflects biological productivity in marine microbiota, the compensation of the $\delta^{13}C$-decrease by the terrestrial microbiota means a more rapid recovery of microbiota in freshwater environments after the K–T impact event, compared to a slower recovery of biota in the marine environment (on a timescale of a few hundred thousand years; [3,60]).

Based on the Ar–Ar dating of sanidine single crystals in coal layers [61] and the stratigraphic distance of the coal layers, the early Tertiary sedimentation rate for Hell Creek, Montana, was estimated at 7 cm/ka. This is identical to the sedimentation rate estimated for York Canyon, New Mexico [8]. Using this estimate for Brownie Butte, the time represented by the recovery of the $\delta^{13}C$ values can be estimated at about a thousand years. Therefore, algal organic matter was the likely cause of high organic $\delta^{13}C$ values not only at Dogie Creek, but also at Brownie Butte. This agrees with Gardner and Gilmour [13], who reported that the contribution of hydrocarbons derived from algae and bacteria is higher above the K–T boundary than that below the K–T boundary.

5.2.3. $\delta^{13}C$ positive excursion at the K–T boundary clay

A distinct positive $\delta^{13}C$ excursion of 2‰ in the K–T boundary clay is superimposed on the overall decreasing trend at Dogie Creek. A similar extent of the positive excursions of δ^{13}C was also reported for Starkville South and Raton Pass [12]. As mentioned above, Brisman et al. [12] proposed incorporation of wildfire particulate as a cause of these positive excursions in the K–T boundary clay. However, such process cannot induce positive δ^{13}C-excursions, because the δ^{13}C values of the boundary clay are higher than those expected for atmospheric carbon particulate from biomass fires.

Organic matter in carbonaceous chondrites (inferred as the composition for the K–T impactor [62,63]) generally have higher δ^{13}C values (−13 to −21‰ relative to V-PDB (e.g., [64]) than terrestrial organic matter. Organic matter from high trophic organisms (consumers), the supply of which was most likely enhanced by the die-off after the K–T impact event, has higher δ^{13}C values than those of their diet (primary producers) (e.g., [64,65]). Enhanced supply of such organic materials can cause increase of δ^{13}C values in the sedimentary rocks; however, this cannot explain a high δ^{13}C value in the K–T boundary clays, judging from their δ^{15}N values. Both materials show δ^{15}N values higher than those of plant-derived organic matter (e.g., [64] for extraterrestrial material, [66] for consumers); however, a negative excursion of the δ^{15}N values correlate with a positive excursion of the δ^{13}C values at the K–T boundary at Starkville South and Raton Pass [12].

As mentioned above, respiration by decomposers (e.g., [51]) causes a ^{13}C-enrichment in the remaining organic matter. This process alters the δ^{15}N values of organic matter; however, it causes a ^{15}N-enrichment in the remaining organic matter [67–69]. Therefore, it cannot cause the negative excursion of δ^{15}N simultaneous with δ^{13}C positive excursion observed at the K–T boundary clays [12]. After several days, the δ^{13}C value of the evolved CO_2 during respiration under absence of sunlight becomes lower than that of total organic matter (e.g., [70]). This also leads to a ^{13}C- and ^{15}N-enrichment in the leaf organic matter, similar to those induced by decomposer respiration. Although the shutdown of sunlight (and, therefore, photosynthesis) proposed for the K–T impact event [71] might induce “dark” respiration for a few years, this process also cannot explain the positive excursion of δ^{13}C observed in the K–T boundary clays.

The positive δ^{13}C-excursion can be explained by the enhanced contribution of algal organic matter before a decrease of the δ^{13}C value of atmospheric CO_2. Although δ^{13}C of algal organic matter can be distinguished from that of plant organic matter in a high productivity environment, such high productivity can be expected after the K–T impact, which might cause nitrogen fertilization [72,73] and eutrophication induced by enhanced sulfide formation [38,74]. Nitrogen fertilization should cause ^{15}N-depletion in plant tissues (e.g., [75,76]); therefore, this process can explain the negative δ^{15}N-excursion observed at Starkville South and Raton Pass [12]. The inverse correlation between δ^{13}C and δ^{15}N values of organic matter can be also induced by eutrophication (e.g., [77–79]). Our data alone do not allow us to determine which of the two processes (i.e., nitrogen fertilization and eutrophication) was responsible for the δ^{13}C positive excursion in the K–T impact clays. As both processes should have finished within about a decade after the K–T impact event [80], the microbiota must have recovered enough within a decade to respond to the impact-induced environmental perturbation.

6. Summary and conclusions

Carbon concentrations and isotopic compositions of bulk organic matter in sedimentary rocks across the terrestrial K–T boundary sequences at Brownie Butte, Montana, and Dogie Creek, Wyoming, in the Western Interior of the United States, show that there is a δ^{13}C minimum above the K–T boundary at both Brownie Butte and Dogie Creek. The organic δ^{13}C values at Dogie Creek decrease continuously across the K–T boundary, whereas the δ^{13}C values at Brownie Butte decrease suddenly at the K–T boundary. The sudden δ^{13}C decrease at Brownie Butte reflects changes in the δ^{13}C values of atmospheric CO_2, resulting from the equilibration between the ^{13}C-depleted surface ocean and atmosphere. The effect of atmospheric δ^{13}C decrease was partially compensated by an enhanced contribution of ^{13}C-enriched algal organic matter at Dogie Creek. As ^{13}C-enriched algal organic matter is produced only in a high productivity environment, the enhanced contribution of ^{13}C-enriched algal organic matter occurred after the recovery of terrestrial microbiota. The enhanced contribution of ^{13}C-enriched organic matter occurred before the δ^{13}C-recovery of atmospheric CO_2, which reflected the recovery of marine microbiota; therefore, the terrestrial microbiota recovered before the recovery of marine microbiota.

A positive δ^{13}C excursion of 2‰ in the K–T boundary clay is superimposed on the continuous decrease at the Dogie Creek section. This excursion can be explained also by the enhanced contribution of high-productivity ^{13}C-enriched algal organic matter. If the high productivity resulted from nitrogen fertilization [72,73] and/or eutrophication induced by an enhanced sulfide formation [38,74] (both processes were predicted to have taken place within 10 yr after the K–T impact event (e.g., [75])), the δ^{13}C excursion means the freshwater microbiota recovered enough within a decade to respond to the impact-induced environmental perturbation.

Acknowledgments

We would like to thank Richard W. Carlson and two anonymous reviewers for their constructive reviews and suggestions. This work was supported by the Austrian Science Foundation, FWF project Y-58-GEO and P17194-N10 (to C.K.).

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